

## **Practical Wastewater Treatment**

# Practical Wastewater Treatment

Second Edition

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*Lilburn, Georgia*

Global Environmental Operations Inc.

## Preface

The first edition of this book was developed from a course I taught for the American Institute of Chemical Engineers. It was a first attempt to introduce industrial wastewater treatment theory, practices, and issues into the Chemical Engineering community as a stand-alone discipline. It ultimately led to the first edition of this book.

There is a natural separation between industry and academia, and consequently the academics teach the basics of engineering, but more and more the separation between the way the subject material is taught and the way it is practiced is growing. Historically, much of the wastewater treatment field has been the provenance of the civil engineering community because of its association with sanitary engineering. Much of the time I spent in consulting, designing, and supervising the construction of municipal wastewater treatment plants was profoundly formulaic, and a largely mechanical exercise requiring little imagination and presenting few new challenges. The treatment of industrial wastes was far more interesting because the wastes varied so greatly, and their treatment required imagination and research.

My introduction to industrial wastewater treatment came through a Philadelphia-based consulting company, and then subsequent work assignments for companies specializing in industrial wastewater treatment, and ultimately into the chemical industry. At one point, along the way, I realized that I was much more at home with the chemical engineers than with the civil engineers, and I still am.

This book was developed to give the student and the experienced practitioner some information and balance with regard to industrial practices and goals, and to describe how the water industry works, and what is important in it. I have tried to cover a wide range of topics to dump the more than 40 years of my experience into this brief volume to help the reader investigate the topics, and point out useful tools for further study and mastery of the subjects. I do not try to solve problems for the reader, but have provided a few problems on topics of interest.

Mistakes in this volume are mine alone. In compiling this work, I have amassed a wide list of reference materials, and have attempted to download a copy of the references for my own use, and to make them available to others. The Internet is full of both permanent and temporary information. Some of the information I have provided through links will undoubtedly be obsolete by the time this book is published or has a few years of age on it. So, if in researching the topics in the book, one finds that a key topic or paper is missing, contact me, and I will send you a copy of the individual paper, or the entire set of references for your digital library.

*Dave Russell, PE*  
(dlr@mindspring.com)

# 1

## Composition, Chemistry, and Regulatory Framework

*Much water goeth by the mill  
That the miller knoweth not of.*

John Heywood (1497–1580)

### 1.1 Water Composition

Water is composed of two parts hydrogen and one part oxygen. It is not the materials of the water but the contaminants in it that make it important. If we look at a chemical reaction, we would be extremely satisfied with a reaction yield of 99% purity, as many reactions are in the 70–90% range. However, for water, even a 1% level of impurity is unacceptable. The levels of contaminants that we often consider insignificant in many products and foods can prevent us from using water. Impurities in water at the 1% level are equivalent to 10 000 ppm or  $\text{mg l}^{-1}$ . At that level, even things like sodium chloride, table salt, in the water will render it undrinkable or harmful if consumed. In other instances, even a few milligrams of the right compound can render the water unpalatable or unusable for many aquatic purposes.

From another standpoint, the challenges that are presented to a wastewater treatment plant can be formidable. From a process standpoint, the reaction yields we look for produce a treated effluent with contamination levels of less than  $10 \text{ mg l}^{-1}$ , and in a number of instances under  $2 \text{ mg l}^{-1}$  of particular contaminants. That is pretty good for a waste stream which may start out at  $500 \text{ mg l}^{-1}$  or more – it represents a 99.6% removal efficiency.

The usability of the water depends upon the compounds either dissolved in it or suspended in it. Contaminants can be organic or inorganic, solids or liquids. The usability of the water also depends upon the purpose of the use. For example, water used for cooling does not necessarily need to be of the same quality (purity) as that used for drinking or food preparation. Fecal and bacterial contamination of cooling water is often unavoidable in cooling towers, and

tower water is treated with chemicals to reduce corrosion and inhibit excessive bacterial growth. In all cases, this water quality is not suitable for food preparation, nor for drinking. The sterility, turbidity, and dissolved constituents in the water are important quality control issues, but not all three are necessary for a specific use.

Water can also be too pure for a specific use. As an example, there are a number of locations worldwide that have their drinking water from thermal desalination sources. At one specific facility in the Middle East, the water is slightly above 43 °C, which is a bit uncomfortable for drinking, but because it is from a thermal desalination plant, it is *distilled*. Hence the water is aggressive because it is so low in carbonates and minerals that it has the effect of leaching the calcium from the asbestos-cement piping, thus weakening it. Similarly, distilled water will corrode iron and steel piping, and drinking distilled water can also cause health problems such as diuresis, and a change in the electrolyte concentration in the body<sup>1</sup>.

## 1.2 Water Characteristics and Physical Properties

Water ( $\text{H}_2\text{O}$ ) is dense, weighing in at 999.972 kg m<sup>-3</sup>, boiling at 99.98 °C (212.96 °F), and melting at 0.0 °C. It is the standard for viscosity, at 1 centipoise (cp) at 20 °C, and has a vapor pressure which is temperature-dependent, from 611 Pa (0.180 in. of Hg) at 0 °C to 101 901.3548 Pa at 100 °C. The formula for vapor pressure of water in that range is

$$P_w = 10^{A-B/(C+T)}$$

where A = 8.07131, B = 1730.63, and C = 233.426 and the temperature T is in Celsius between 0 °C and 100 °C.  $P_w$  is in pascals; for reference, 1 atmosphere is 101 325 Pa, or 764.2602 mm of Hg, and 1 mm of Hg is equal to 133.333 Pa.

Pure water is an excellent insulator, but water is seldom, if ever, pure, and contains small quantities of dissolved salts and many materials. The known maximum resistivity of pure water is 182 KΩ m<sup>-1</sup> at 25 °C, (or  $5.4945 \times 10^{-6}$  S m<sup>-1</sup> or 0.054945 μS cm<sup>-1</sup>).<sup>2</sup> Very small levels of contaminants, sometimes in the parts per trillion (ppt) range ( $10^{-12}$  g l<sup>-1</sup>), can cause large increases in its conductivity. The conductivity of water is dependent not only on the quantity of contaminant, but on the type of contaminant. If the contaminant has an interaction with the water, and a secondary and/or tertiary ionization constant, it is much harder to relate conductivity to concentration.

When water has salts (ionic material) in it, it can become an excellent conductor. The electrical conductivity of water can be used to estimate the dissolved

**Table 1.1** Approximate conductivity of various chemicals in water where the substance is the principal contaminant.

Salt	Conductivity equivalent	TDS/conductivity
Sodium chloride	1.00 ppm TDS = $2.04 \mu\text{S cm}^{-1}$	0.49
Sodium sulfate	1.00 ppm TDS = $1.49 \mu\text{S cm}^{-1}$	0.67
Calcium sulfate	1.00 ppm TDS = $1.36 \mu\text{S cm}^{-1}$	0.74
Sodium bicarbonate	1.00 ppm TDS = $1.06 \mu\text{S cm}^{-1}$	0.91

solids concentration in water if that value is less than about  $1500 \text{ mg l}^{-1}$ . Above that point, the conductivity to dissolved solids curve flattens out and becomes unreliable. Most conductivity meters use a formula of:

$$\text{Total dissolved solids, TDS (mg/l)} = C \times 1000 \times \text{conductivity in microsiemens/cm}$$

Depending upon the water source and components, the value of C can vary anywhere from 0.51 to 0.83.<sup>3</sup> At higher levels of dissolved solids, the coefficient changes. Table 1.1 illustrates the difference in conductivity of certain soluble materials in water. It should be noted that the conductivity is a function of the molecular structure of the solid or gas, and in some cases, substances that have second ionization constants or which react with water have substantially different values for conductivity which will not follow the formula shown above. Multiple ions in solution will have a nonlinear relationship to the values given in the table.

Conductivity can also be used to measure the amount of calcium carbonate in water, if that is the principal dissolved salt. Calcium carbonate and its forms are referred to as hardness, and represent the ability of the water to leave  $\text{CaCO}_3$  deposits in piping, on heat exchangers, cooling towers, and so on. We will cover hardness in later chapters.

If an electric current is passed through water, it will generate hydrogen and oxygen in the ratio of 2:1 by volume. If there are salts such as sodium chloride in the water, a quantity of chlorine gas ( $\text{Cl}_2$ ) will be generated along with the hydrogen and oxygen. If large concentrations of high purity salt are dissolved in the water, and the positive and negative electrodes are separated by a membrane, the electric current becomes the basis for an electrolytic cell used in the chemical industry for the generation of chlorine gas and caustic soda ( $\text{NaOH}$ ). With water having a conductivity less than  $1200 \mu\text{S}$ , the voltage requirements increase as the salt concentration becomes proportionally less.

### 1.2.1 Solubility of Gases in Water

The most important dissolved gas is oxygen, and the second most important gas is nitrogen, because it comprises approximately 79% of our atmosphere, and is a potential source of nutrients for certain aquatic plants.

The solubility of various gases in water is given in many tables found in chemical and analytical handbooks, and on many commercial websites, including [www.engineeringtoolbox.com](http://www.engineeringtoolbox.com), and in handbooks and analytical reference materials.<sup>4</sup>

Table 1.2 is a listing of the solubility of oxygen in water at temperatures between 0 °C and 30 °C, for various values of salts in the water. Table 1.2 shows the solubility of selected gases in water.

L.E. Geventman published a research paper on the solubility of selected gases in water.<sup>5</sup> Geventman's paper states that the solubility of the selected gases can be calculated by the following formula:

$$\ln X_1 = A + B/T^* + C \ln T^*$$

where  $T^* = T/100\text{ K}$ , and  $X_1$  is the solubility of the gas. A, B, and C are determined experimentally from chemical data. His paper provides a list of the coefficients. All values refer to a partial pressure of the gas of 101.325 kPa (1 atm).

The concentration of oxygen in water at any temperature is given by the following equation found in *Standard Methods*:<sup>6</sup>

$$\begin{aligned} \ln O_2 = & -139.34411 + (1.575701 \times 10^5 / T^2) - (6.642308 \times 10^7 / T^2) \\ & + (1.243800 \times 10^{10} / T^3) - (8.621949 \times 10^{11} / T^4) \\ & - \text{Chl}((3.1929 \times 10^2) - (1.9428 \times 10 / T) + (3.8673 \times 10^3 / T^2)) \end{aligned}$$

where Chl is the chlorinity measured in grams/kilogram and is defined as chlorinity = salinity/1.80655, and salinity is approximately equal to total solids in water after carbonates have been converted to oxides and after all bromide and iodide have been replaced by chloride.

Figure 1.1 illustrates the solubility of oxygen in water at varying temperatures and values of chlorinity of zero and 1000 mg l<sup>-1</sup>.

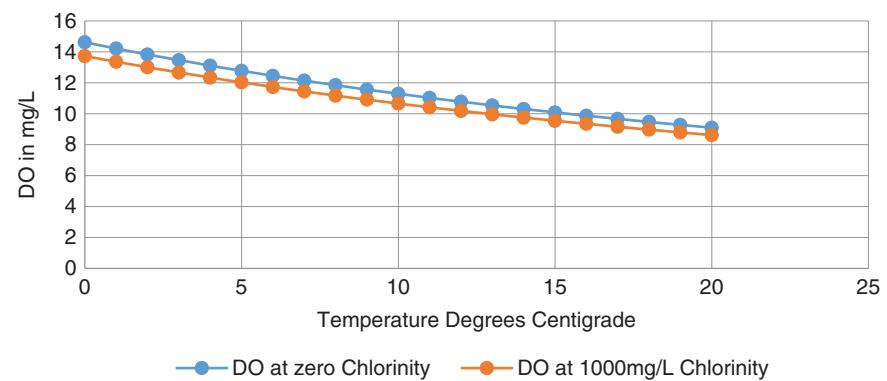
#### 1.2.1.1 Nitrogen

Nitrogen is soluble in water, but in the gaseous or N<sub>2</sub> form is essentially inert. Principal forms of nitrogen in water are ammonia, nitrate, and nitrite. The only time one has to worry about the solubility of nitrogen is in its ionized forms, as ammonia nitrite, or nitrate (to be discussed later) or when one is designing a pressure flotation system.

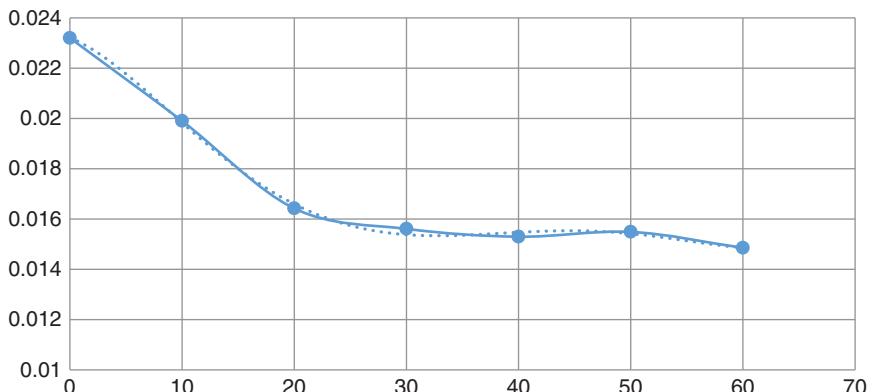
Figure 1.2 illustrates the solubility of nitrogen gas (N<sub>2</sub>) in water at temperatures between 0 °C and 60 °C.

**Table 1.2** Solubility of oxygen in mg l<sup>-1</sup> in water exposed to water-saturated air at atmospheric pressure (101.3 kPa).

Temperature	Chlorinity					
	0	5	10	15	20	25
0	14.621	13.728	12.888	12.097	11.355	10.657
1	14.216	13.356	12.545	11.783	11.066	10.392
2	13.829	13.000	12.218	11.483	10.790	10.139
3	13.460	12.660	11.906	11.195	10.526	9.897
4	13.107	12.335	11.607	10.920	10.273	9.664
5	12.770	12.024	11.320	10.656	10.031	9.441
6	12.447	11.727	11.046	10.404	9.799	9.228
7	12.139	11.442	10.783	10.162	9.576	9.023
8	11.843	11.169	10.531	9.930	9.362	8.826
9	11.559	10.907	10.290	9.707	9.156	8.636
10	11.288	10.656	10.058	9.493	8.959	8.454
11	11.027	10.415	9.835	9.287	8.769	8.279
12	10.777	10.183	9.621	9.089	8.586	8.111
13	10.537	9.961	9.416	8.899	8.411	7.949
14	10.306	9.747	9.218	8.716	8.242	7.792
15	10.084	9.541	9.027	8.540	8.079	7.642
16	9.870	9.344	8.844	8.370	7.922	7.496
17	9.665	9.153	8.667	8.207	7.770	7.356
18	9.467	8.969	8.497	8.049	7.624	7.221
19	9.276	8.792	8.333	7.896	7.483	7.090
20	9.092	8.621	8.174	7.749	7.346	6.964
21	8.915	8.456	8.021	7.607	7.214	6.842
22	8.743	8.297	7.873	7.470	7.087	6.723
23	8.578	8.143	7.730	7.337	6.963	6.609
24	8.418	7.994	7.591	7.208	6.844	6.498
25	8.263	7.850	7.457	7.083	6.728	6.390
26	8.113	7.711	7.327	6.962	6.615	6.285
27	7.968	7.575	7.201	6.845	6.506	6.184
28	7.827	7.444	7.079	6.731	6.400	6.085
29	7.691	7.317	6.961	6.621	6.297	5.990
30	7.559	7.194	6.845	6.513	6.197	5.896



**Figure 1.1** Solubility of oxygen in water at varying temperatures, and values of chlorinity of zero and 1000 mg L<sup>-1</sup>.



**Figure 1.2** Solubility of nitrogen gas (N<sub>2</sub>) in water at temperatures between 0 °C and 60 °C (liters per kg of water).

Other common gases soluble in water are shown in Table 1.3 in terms of millimols. This enables calculation of the volume of the listed gases as a function of pressure. There is an example below.

### 1.2.2 Henry's Law

Henry's law gives us some idea of the solubility of other gases. In 1803, William Henry stated: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

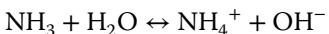
$$P = K'_C$$

**Table 1.3** Molar Henry's law constants for aqueous solutions at 25 °C.

Gas	Constant (Pa (mol dm <sup>-3</sup> ) <sup>-1</sup> )	Constant (atm (mol dm <sup>-3</sup> ) <sup>-1</sup> )
He	$282.7 \times 10^6$	2865.0
O <sub>2</sub>	$74.68 \times 10^6$	756.7
N <sub>2</sub>	$155 \times 10^6$	1600.0
H <sub>2</sub>	$121.2 \times 10^6$	1228.0
CO <sub>2</sub>	$2.937 \times 10^6$	29.76
NH <sub>3</sub>	$5.69 \times 10^6$	56.9

where  $P$  is the partial pressure of the gas,  $C$  is its molar concentration, and  $K'_{\text{C}}$  is the Henry's law constant. This is universally true for almost all liquids. However, as the concentrations and partial pressures increase, deviations from Henry's law become noticeable. This behavior is very similar to the behavior of gases, which deviate from the ideal gas law as pressures increase and temperatures decrease. Solutions that obey Henry's law are sometimes called ideal dilute solutions. Values of the Henry's law constants for many gases in many different organic compounds and gases have been measured. The inverse of the Henry's law constant, multiplied by the partial pressure of the gas above the solution, is the molar solubility of the gas.

Henry's law does not hold for gases that react with water and which have secondary and tertiary ionization constants. Some of those gases include hydrogen sulfide, chlorine, and carbon dioxide. The reactions of these gases are often pH-dependent, and the free molar form of the gas is directly related to the inverse of the pH at which it is most soluble. For example, ammonia tends to form NH<sub>3</sub>OH in water, which is ammonium hydroxide, and is a strongly ionized base. As the pH of the water increases, the equilibrium reaction of:



shifts leftward, releasing more free ammonia into the solution. At a value of pH 12, the reaction is essentially complete and there is essentially no ionic ammonia left in aqueous solution. This relationship is shown in Figure 1.3.

The value of the Henry's law constant is temperature-dependent. The value generally increases with increasing temperature. As a consequence, the solubility of gases generally decreases with increasing temperature. One example of this can be seen when water is heated on a stove. The gas bubbles appearing on the sides of the pan well below the boiling point of water are bubbles of air, which evolve due to the lowered solubility from hot water. The addition of boiled or distilled water to a fish tank will cause the fish to die of suffocation unless the water has been allowed to re-aerate before addition.

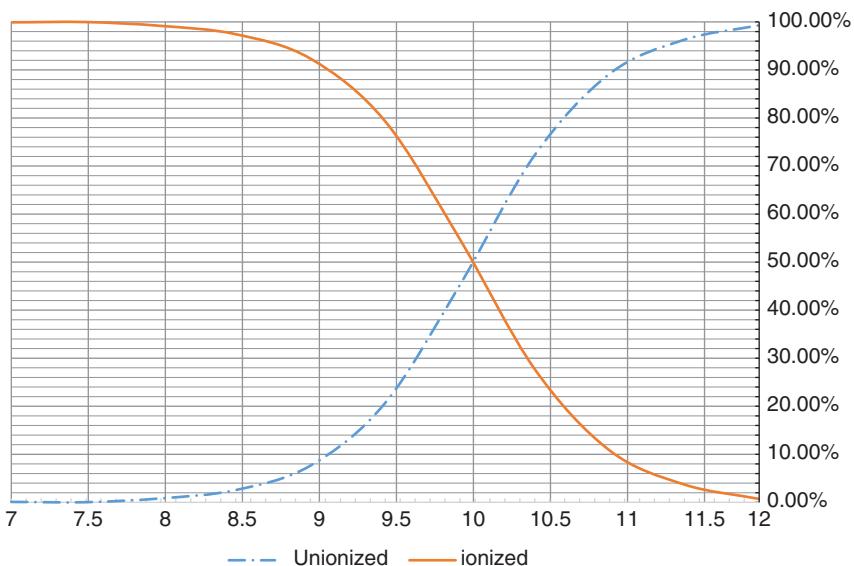


Figure 1.3 Ionized vs. free ammonia (%) at various pH levels at 0 °C.

A very complete listing of many Henry's law constants can be found at <http://www.henrys-law.org/henry.pdf>. The US Environmental Protection Agency (USEPA) has "Guidance for Reporting on the Environmental Fate and Transport of the Stressors of Concern in Problem Formulations," which has a section on calculation of Henry's law coefficients: [http://www.epa.gov/pesticides/science/efed/policy\\_guidance/team\\_authors/endangered\\_species\\_reregistration\\_workgroup/esa\\_reporting\\_fate.htm](http://www.epa.gov/pesticides/science/efed/policy_guidance/team_authors/endangered_species_reregistration_workgroup/esa_reporting_fate.htm).

The US Geological Survey lists many Henry's law coefficients for organic compounds starting on page 16 of their Survey Professional Paper: *Transport, Behavior and Fate of Volatile Organic Compounds in Streams*. This can be found at <http://www.books.google.com/books?id=uVLwAAAAMAAJ&pg=RA5-PA16&lpg=RA5-PA16&dq=allintext:+Calculating+Henry%27s+Law+Coefficients&source=bl&ots=Dshx6nVwhi&sig=DNbPSdFW4rXGdLYznU0MdRQNm5w&hl=en&sa=X&ei=ZS9RVMfXFYSYgwTKsoCoAg&ved=0CFQQ6AEwCQ#v=onepage&q=allintext%3A%20Calculating%20Henry's%20Law%20Coefficients&f=false>. And, there is a Henry's gas law calculator on the Internet at [http://www.webqc.org/henry\\_gas\\_law.html](http://www.webqc.org/henry_gas_law.html).

A computer program for calculating Henry's law coefficients can be found at <http://www.srcinc.com/what-we-do/environmental/tools-and-models.html>. The program is called the EPI Suite, which was developed for the USEPA, and it can also be found at <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>. The program is used for predicting chemical values of spilled substances, but is not limited to those applications.

If you have one value for a Henry's coefficient at a given set of conditions ( $\text{m}^3 \text{ atm/mol}$ ) it can be transformed to another set of conditions by the equation:

$$H_{TS} = H_R \times \exp[-H_{V,TS}/\{R_c(1/T_S - 1/T_R)\}]$$

where  $H_{TS}$  is the coefficient at temperature  $T_S$ , and  $T_R$  is the reference temperature in degrees kelvin. The term  $H_{V,TS}$  is the enthalpy of vaporization at  $T_S$  in units of cal/mol, and  $R_c$  is the gas constant, which has a value of  $1.9872 \text{ cal (mol K)}^{-1}$ . The enthalpy can be obtained either from steam tables for water or chemical engineering tables for other fluids, or by using an alternative procedure for estimating the enthalpy of vaporization from the USEPA website: <http://www.epa.gov/athens/learn2model/part-two/onsite/esthenry.html>. Henry's coefficients may not really be considered as constants, but will vary with temperature and pressure.<sup>7</sup>

The study of Henry's law gained renewed interest in the environmental field when the remediation of benzene, toluene, ethylbenzene, xylene, and MTBE from leaking underground gasoline storage tanks became a US government funded program through a tax-supported trust fund. The study of Henry's law led to various remediation options, including vacuum stripping of volatile organics that were trapped in the soil above the water table.

Henry's law is useful in a number of ways, as illustrated below.

**Example 1.1 Oxygen in Water** Oxygen at 1 atm would have a molar solubility of  $(1/756.7) \text{ mol dm}^{-3}$ , or  $1.32 \text{ mmol dm}^{-3}$ . The following examples will help in understanding this concept.

The amount of oxygen dissolved in air-saturated water under normal atmospheric conditions at  $25^\circ\text{C}$  can be calculated as follows:

Normal atmospheric condition is  $20.948 \text{ mol\%}$  oxygen, which makes the partial pressure of oxygen  $0.20948 \text{ atm}$  or  $20.67 \text{ kPa}$ . Using Henry's law, the concentration of oxygen is  $0.20948 \text{ atm}/(756.7 \text{ atm (mol dm}^{-3})^{-1})$ , which is  $0.2768 \text{ mmol dm}^{-3}$ ; given the weight of  $32 \text{ g mol}^{-1}$ , that comes out to be  $0.0000088576 \text{ g dm}^{-3}$  or about  $8.85 \text{ mg l}^{-1}$ , which is to be compared with the value of  $8.263 \text{ mg l}^{-1}$  from Table 1.2.

**Example 1.2 Dissolved Air Flotation Systems** If we want to run a dissolved air flotation (DAF) system at 50 psig (pounds per square inch gauge, or  $115.23 \text{ ft}$  of water pressure or  $3.4473785 \text{ bar}$ ) for the pressure for flotation, how much nitrogen and oxygen will be produced when we release the pressure back to atmospheric?

The density of water is about  $1 \text{ kg dm}^{-3}$  or  $1000 \text{ kg m}^{-3}$ . The basic pressure on the water from the DAF system (50 psig) is approximately equal to a column of water  $34.474 \text{ m}$  high. A column of water  $34.47 \text{ m}$  high would exert a pressure of  $344.737 \text{ kg dm}^{-2}$  on its base, which converts to  $344.73748 \text{ kPa}$  pressure. The total system pressure is atmospheric pressure plus compression

or  $101.325 \text{ kPa} + 344.7375 \text{ kPa}$  or a total of  $446.0625 \text{ kPa}$ . (This is equivalent to  $446.0625/101.325 = 4.4023 \text{ atm}$ .) The pressure change of  $3.4023 \text{ atm}$  ( $4.4023 \text{ atm total} - 1 \text{ atm} = 3.4023 \text{ atm}$ ) will produce a concentration change of  $3.4023/1600 = 0.0021264375 \text{ mol dm}^{-3}$ . (The pressure change of  $344.738 \text{ kPa}$  will cause a concentration change of  $2.12644 \text{ mmol dm}^{-3}$ .) For each gallon of water the amount of nitrogen generated is  $3.785 \times 2.12644 \text{ mmol} = 8.418 \text{ mmol}$  of nitrogen per gallon, or about  $189 \text{ ml}$  of nitrogen per cubic foot.<sup>8</sup>

For oxygen, the change is about  $4.496 \text{ mmol dm}^{-3}$  or about  $89.2 \text{ ml}$  of  $\text{O}_2$  per cubic foot. (Note that the proportionality is approximately equal to the ratio of the Henry's constants for each of the gases.) The total volume for flotation is about  $89.2 + 189 = 278.2 \text{ ml}$  of gas per cubic foot.

**Example 1.3 Benzene Concentration** In a remediation situation, the client has spilled gasoline. You use a calibrated portable ionization detector and determine that the concentration of benzene in the soil gas is 20 ppm. What is the concentration of benzene in the groundwater?

First, let's look at the Henry's law coefficient for benzene. A good source of data is the USEPA Superfund Guidance section.<sup>9</sup> The tabular values for that reference list the following parameters:

CAS No.	Name	Sol. ( $\text{mg l}^{-1}$ )	$K_c (\text{atm}\cdot\text{M}^3 \text{ mol}^{-1})$	$K_c' (\text{dimensionless})$
71-43-2	Benzene	1.75E+03	5.55E-03	2.28E-01

where  $K_c'$  is a dimensionless value for the Henry's law coefficient.

Assuming that the soil vapor and the water are in equilibrium, what is the concentration in the water? The mol. wt of benzene is  $78.114 \text{ g mol}^{-1}$ .

20 ppm in air is a volume measurement; in order to get  $\text{mg m}^{-3}$  we need to multiply the gram molecular weight by the concentration and divide it by 23.235 (which is the volume of a mole (22.41 l) at  $0^\circ\text{C}$  corrected for the temperature of the ground which is approximately  $10^\circ\text{C}$ ). So concentration C in  $\text{mg m}^{-3} = 20 \times 78.114/23.235 = 67.238 \text{ mg m}^{-3}$  in air. The molar concentration is then  $67.238/78.114 = 0.8608 \text{ mmol m}^{-3}$  or  $0.0008608 \text{ mol m}^{-3}$ . Then  $C = 0.00555/0.0008608$  or  $0.00645 \text{ mol m}^{-3}$  or  $0.503 \text{ g m}^{-3} = 0.503 \text{ mg l}^{-1}$ .

### 1.3 Solution Chemistry: Salts and Ions in Water

Water is the universal solvent. Everything dissolves in water to a greater or lesser extent. Depending upon the various elements and their combinations, organic and inorganic compounds are more or less soluble in water. Chemists use the *solubility product* as an indication of the solubility of a substance. In a

later chapter we will discuss the practical uses of solubility product manipulation for the purposes of wastewater and drinking water treatment.

The solubility product is calculated by the following:

$$K_{sp} = [\text{Cation}^+][\text{Anion}^-]$$

If we call the substance AC, the formula is then

$$K_{sp(AC)} = [C][A]$$

Or if the substance is  $A_2C_3$  then

$$K_{sp} = [C^+]^2[A^-]^3$$

where the substances in brackets are the molar concentrations.

But if one wants to calculate the solubility of the compound AC in water, make the substitution  $[A] = [C]$  and that would give you either  $[A]^2$  or  $[C]^2$  and the concentration of the compound would be  $[A] = [C] = \sqrt{K_{sp}}$  or the square root of the solubility product. If the compound is more complex and has the general formula of  $A_2C_3$ , then

$$K_{sp} = [C]^2[A]^3$$

The appropriate substitution to get the solubility of the compound would be:

$$[2C]^2[3A]^3 = K_{sp}$$

where C or A represent moles of ion in solution, and we get 1.5 mole of A for every mole of C at equilibrium.

These equations assume that the substance does not react with water to form a weak acid or a weak base. It is also useful to note that the solubility product can be used to manipulate the solubility of specific compounds in water. If one adds or subtracts selected ions from the water, the solubility will be increased or decreased until equilibrium is restored.

**Example 1.4 Copper Chloride** Copper (cuprous) chloride ( $CuCl$ ) has a  $K_{sp} = 1.2 \times 10^{-6}$ . If one had a saturated solution of  $CuCl$ , at equilibrium, the concentration of copper would be equal to the quantity of chloride in solution or  $[Cu] = \sqrt{1.2 \times 10^{-6}} = 1.0954 \times 10^{-3} \text{ mol l}^{-1} = 0.06961 \text{ g l}^{-1}$ , or  $69.1 \text{ mg l}^{-1}$ .

If we need to get copper in the solution down to  $1 \text{ mg l}^{-1}$  or less, that can be done by adding chloride:  $1 \text{ mg l}^{-1} = 0.000015737 \text{ mol l}^{-1} = 1.5737 \times 10^{-5} \text{ mol l}^{-1}$ . Back-calculating to the  $K_{sp}$ :  $1.2 \times 10^{-6} / 1.5737 \times 10^{-5} = 0.07626 \text{ mol l}^{-1}$  of chloride in solution to reduce the Cu concentration to  $1 \text{ mg l}^{-1}$  or less.  $0.07626 \text{ mol l}^{-1}$  of chloride required is  $35.453 \times 0.07626 = 2.703 \text{ g l}^{-1}$ .

A list of metals and their solubility products will be presented in a later chapter on precipitation.

Hydroxide precipitation is also to be covered later, but it represents an exception to the general principles of solubility. Some metals form hydroxyl precipitates, which have optimum pH precipitation ranges. Outside those ranges, the solubility of the metal is higher. An example is aluminum hydroxide  $\text{Al(OH)}_3$ , which has an optimum precipitation range at approximately  $\text{pH} = 5.5$ .<sup>10</sup>

## 1.4 Disassociation Constants for Weak Acid and Bases

Strong acids and bases fully disassociate in water.  $\text{HCl}$ ,  $\text{NaOH}$ ,  $\text{HNO}_3$ , and others completely disassociate in water to form acids and bases. Weak acids or bases partially disassociate, and the equation used to describe that disassociation is similar to the one used for solubility. It is called an *ionization constant*, and if the compound is an acid, it would generally be expressed as



where  $\text{H}^+$  represents the cation (generally hydrogen) and A is the acid portion of the compound, for example,  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ .

For bases, the base would be written



where M is generally a metal and  $\text{OH}^-$  is the hydroxyl ion from water, for example,  $\text{NaOH}$  or  $\text{Ca}(\text{OH})_2$ .

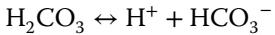
The equilibrium constant is written slightly differently from the solubility product:

$$K_{\text{eq}} = \frac{(\text{H})(\text{A})}{(\text{HA})} \text{ for the HA acid and a similar formulation}$$

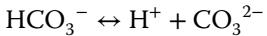
for the MOH base.

As a convention, the square brackets are used to express solids in solution, and the round brackets are used for weak acids and bases.

Take for an example:



and



The first and second ionization constants are:

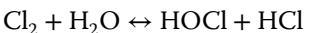
$$K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} \text{ and } K_2 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)}$$

So for  $\text{H}_2\text{CO}_3$ , which is obtained when  $\text{CO}_2$  is bubbled through water,  $K_1 = 4.45 \times 10^{-7}$ , and  $K_2 = 4.65 \times 10^{-11}$ .

The equations can be simplified and combined so that for  $\text{CO}_2$  bubbled through water the overall reaction may be combined into  $K_1 \times K_2 = (\text{H}^+)^2 (\text{CO}_3^{2-}) / (\text{H}_2\text{CO}_3)$  which gives a combined value of  $K_{1-2}$  of  $2.06925 \times 10^{-17}$ .

Another way of expressing the disassociation constant is similar to the way in which we express the acidity or alkalinity of a liquid, or pH. For water, pH is defined as the negative logarithm (to the base 10) of the concentration of ions in the water, or  $\text{pH} = -\log_{10}(\text{H}^+)$  or  $-\log_{10}(1/(\text{H}^+))$ . Since  $K_{\text{water}} = (\text{H}^+) \times (\text{OH}^-) = 10^{-14}$ , the pH of a neutral solution is approximately 7 at 25 °C.<sup>11</sup> For a 0.1 M concentration of hydrochloric acid, pH = 1.0, and for a 0.1 M concentration of sodium hydroxide, pH = 14. Chemists often express the values of the ionization constant of acids and bases in terms of p notation, and for compounds with multiple ionization constants, the ionization constants are listed in order as  $K_1$ ,  $K_2$ , etc. for the specific compound.

For example, consider the reactions of chlorine with water.

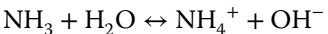


which further resolves into



The HCl completely ionizes into  $\text{H}_3\text{O}^+$  +  $\text{Cl}^-$ .

Ammonia is another substance that partially dissociates in water. The reaction is:



The equilibrium reaction is:

$$K = (\text{NH}_4^+) (\text{OH}^-) / (\text{NH}_3) = 1.65 \times 10^{-5}$$

A few disassociation constants are listed in Table 1.4. A more complete list of disassociation constants for weak acids and bases in water can be found at: [http://chemwiki.ucdavis.edu/Reference/Reference\\_Tables/Equilibrium\\_Constants/E1%3A\\_Acid\\_Dissoociation\\_Constants\\_at\\_25%20%C2%B0C](http://chemwiki.ucdavis.edu/Reference/Reference_Tables/Equilibrium_Constants/E1%3A_Acid_Dissoociation_Constants_at_25%20%C2%B0C), and their page E2 contains data for bases. Another source is: <http://www.csudh.edu/oliver/chemdata/data-ka.htm>.

**Question:** Where or how is this knowledge useful?

**Answer:** Given a waste with emulsified oils and suspended solids, one can remove most of the oil by breaking the emulsion with salts of iron or aluminum and sulfuric acid. Reduce the pH to about 2 with  $\text{H}_2\text{SO}_4$ , and then attack the oily wastewater with aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) until the emulsion breaks. When that occurs the oil will float to the surface and can be skimmed off. To reduce the dissolved solids in the system, add a small amount of a suspension of milk of lime ( $\text{Ca}(\text{OH})_2$ ) to the mix. The lime will react with and neutralize the acid, raising the pH and precipitating the

**Table 1.4** Aqueous disassociation constants.

Name	Formula	First disassocation constant ( $K_a$ )	Second disassocation constant		
			pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	$1.75 \times 10^{-5}$	4.765		
Boric acid	H <sub>3</sub> BO <sub>3</sub>	$5.4 \times 10^{-10}$	9.27	>14	
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	$4.5 \times 10^{-7}$	6.35	10.33	
Hydrogen sulfide	H <sub>2</sub> S	$8.9 \times 10^{-8}$	7.05	19	
Hypochlorous acid	HClO	$4.0 \times 10^{-8}$	7.40		
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	$6.9 \times 10^{-3}$	2.16	7.21	12.32
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	Strong	Strong	1.99	
Ammonia	NH <sub>3</sub>	$1.8 \times 10^{-5}$	4.75		
Magnesium hydroxide	Mg(OH) <sub>2</sub>	$2.6 \times 10^{-3}$	2.56		
<i>Bases</i>					
Ammonia	NH <sub>3</sub>	$1.8 \times 10^{-5}$	4.75		
Calcium hydroxide	Ca(OH) <sub>2</sub>	$3.72 \times 10^{-3}$	2.43		
Ethylamine	C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub>	$4.5 \times 10^{-4}$	3.35		
Magnesium hydroxide	Mg(OH) <sub>2</sub>	$2.6 \times 10^{-3}$	2.58		
Sodium hydroxide	NaOH		0.2		

aluminum as Al(OH)<sub>3</sub>, and will react with and precipitate the calcium as a sulfate (CaSO<sub>4</sub>), and both will fall out of the system. The remaining water will have a slight yellow color and will be almost free of suspended solids. At near-neutral pH, the aluminum concentration will be in the low mg/l range and the calcium sulfate will be soluble at between 1200 and 1600 mg l<sup>-1</sup>. At that point, most of the other remaining cations will be precipitated to within most regulatory limits for discharge to a wastewater treatment plant.

**Example 1.5** Chromium exists in two forms, Cr<sup>3+</sup> and Cr<sup>6+</sup>. The Cr<sup>3+</sup> form is much less toxic than the Cr<sup>6+</sup> form.<sup>12</sup> The higher valence form is sometimes used in cooling towers and industrial applications because it is a passivator (protects metals from corrosion) and a powerful disinfectant, but it is lethal to bacterial and many aquatic organisms. Hexavalent chromium is also used in chromium plating of metallic parts. The wastes can be highly toxic. In order to remove chromium from the water, it is best reduced in valence from the 6+ to the 3+ form with sulfur dioxide (SO<sub>2</sub>) at low pH, or sodium bisulfite (NaHSO<sub>3</sub>) or sodium meta-bisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) or H<sub>2</sub>S, or ferric sulfate. The solubility product for the hydroxide is  $6.3 \times 10^{-31}$ . At a pH of

about 7.5, the solubility of  $\text{Cr}^{3+}$  in water is approximately  $0.18 \text{ mg l}^{-1}$ , as will be shown later. However, if nickel is also present in the water, as is a common occurrence, sulfide is added to the water, the reaction will proceed to  $\text{Cr}_2\text{S}_3$ , and with precipitation and simple filtration the chromium concentration remaining in solution is between 2 and 7 ppb ( $\mu\text{g l}^{-1}$ ).<sup>13</sup>

### 1.4.1 Common Minerals Dissolved in Freshwater and Seawater

There are a variety of compounds dissolved in water. The most abundant is sodium chloride, which represents about 3.5% by weight, and it is followed by salts of calcium and magnesium chloride and various sulfates. Table 1.5 shows the approximate concentrations of the principal dissolved elements in freshwater, and Table 1.6 shows the approximate concentrations of dissolved minerals in seawater.

Calcium and magnesium salts are the most abundant in freshwater, and the interactions between carbon dioxide and limestone (calcium carbonate and magnesium carbonate formations) also play a significant role in water and water treatment. In some areas, and depending upon the geological formations, some groundwaters may contain high enough concentrations of certain

**Table 1.5** Solubility of common minerals in freshwater.

	1	2	3	4	5	6	7	8	9	10	11	12
Calcium	0.8	0.65	40.7	1.68	14	22	241	400	144	6.5	3.11	4540
Magnesium	1.2	0.14	7.2	0.24	13	17	7200	1350	55	1.1	0.7	160
Sodium	9.4	0.56	1.4	0.16	8	14	83 600	10 500	~27	~37	3.03	2740
Potassium	–	0.11	1.2	0.31	–	0.5	4070	380	~2	~3	1.09	32.1
Bicarbonate	4	–	114	5.4	104	129	251	28	622	77	20	55
Sulfate	7.6	2.2	36	1.3	4.7	1.3	16 400	185	60	15	1.0	1
Chloride	17	0.57	1.1	0.06	8.5	33	140 000	19 000	53	17	0.5	12 600
Silica	0.3	–	3.7	0.7	24	30	48	3	22	103	16.4	8.5
TDS	38	4.7	207	10	120	180	254 000	35 000	670	222	36	20 338
pH	5.5	–	–	6.9	7.7	7.0	7.4	–	–	6.7	6.2	6.5

Key to analyses: (1) rainwater from Menlo Park, California; (2) average rainwater from sites in North Carolina and Virginia; (3) composition of the Rhine River as it leaves the Alps; (4) stream draining igneous rocks in the Washington Cascades; (5) Jump-Off Joe Creek, southwestern Oregon, wet season, November 1990; (6) Jump-Off Joe Creek, southwestern Oregon, dry season, September, 1991; (7) Great Salt Lake, Utah; (8) average seawater; (9) groundwater from limestone of the Supai Formation, Grand Canyon; (10) groundwater from volcanic rocks, New Mexico; (11) groundwater from a spring, Sierra Nevada Mountains: short residence time; (12) groundwater from metamorphic rocks in Canada: long residence time.

Source: <http://www.watencyclopedia.com/En-Ge/Fresh-Water-Natural-Composition-of.html#ixzz3Nxvp1Kpk>.

**Table 1.6** Some of the most common elements dissolved in seawater.

Element	Concentration in mg l <sup>-1</sup>	Element	Concentration in mg l <sup>-1</sup>	Element	Concentration in mg l <sup>-1</sup>
Oxygen	$8.57 \times 10^5$	Potassium	380	Argon	0.6
Hydrogen	$1.08 \times 10^5$	Bromine	65	Nitrogen	0.5
Chlorine	$1.9 \times 10^4$	Carbon	28	Lithium	0.18
Sodium	$1.05 \times 10^4$	Strontium	8.1	Rubidium	0.12
Magnesium	$1.35 \times 10^3$	Boron	4.6	Phosphorus	0.07
Sulfur	$8.85 \times 10^2$	Silicon	3	Iodine	0.06
Calcium	$4.0 \times 10^2$	Fluorine	1.3	Barium	0.03

Source: *Handbook of Chemistry and Physics*, 66th ed., CRC Press.

cations, including arsenic and radium, to make drinking the groundwater harmful to health.<sup>14</sup>

The solubility of materials in water is largely determined by the types of ion forms.

## 1.5 Sources of Water

### 1.5.1 Groundwater

Groundwater serves the majority of the smaller inland communities in the United States and elsewhere in the world. It is a source of drinking water, agricultural water, industrial water, and just about anything else. Groundwater is characterized by natural minerals in moderate to low concentrations.

Flow regimens in groundwater are linear, and flow through porous media is analogous to heat transfer through a solid medium. The overall equations used to calculate flow regimens are the Darcy equations, and they are laminar flow equations. The one noticeable exception is flow through fractured rock and some limestone. The limestone may develop solution cavities; the fractured rock (including granite and other highly crystalline rocks) are often of low porosity, and the movement of water takes place primarily in the cracks.

Groundwater quality is highly variable as it depends upon the rocks and minerals with which it is in contact. In some areas, calcium, magnesium, and iron salts comprise the greatest contaminant. In other areas, sulfates and dissolved salts of toxic metals such as arsenic and cadmium can be found in the groundwater, sometimes rendering it non-potable. Where the underlying rock formations are limestone-rich ( $\text{CaCO}_3$ ) or have magnesium carbonate ( $\text{MgCO}_3$ ), and even iron ( $\text{Fe}^{2+}$ ) in them, the waters are often considered to be “hard waters.” The waters may contain varying amounts of dissolved minerals which can cause

discoloration or deposits in heat exchangers, sinks, on cooling towers, and in boilers and hot water heaters. These deposits, with time, act as an insulator and reduce the thermal transfer efficiency of the heat exchangers and hot water heaters, and also cause unsightly deposits.

### 1.5.2 Groundwater Quality

The quality of the groundwater in a particular area is dependent upon a number of factors, including the following general factors.

1. First and foremost, the quality of the water is dependent upon the formation and characteristics of the aquifer and its geology.
2. The geology includes aquifer chemistry, pore and grain size, fractures, organic materials in the soil, clays, and soil structure and profile.
3. The movement and age of the water in the aquifer. The older the water, the more likely it is to be in chemical equilibrium with the rocks in the aquifer.
4. The source and quality of the water that enters the aquifer. Often the source of groundwater is rainwater. In order to get to the aquifer, the water must pass through the soil, and it will pick up some of the minerals in the soil. Note that in recent years the presence of sulfur dioxide in the atmosphere has created acid rain, as very weak sulfuric acid in the rainwater. This acid tends to dissolve more of the minerals in the rocks of the aquifer, resulting in higher mineral content in the waters.
5. The number and kinds of aquifers and aquiclude. There are often multiple aquifers, which may or may not be hydraulically connected, and it is not uncommon to have a shallow aquifer that is contaminated from surface sources, and a deeper aquifer that is pristine, with an aquiclude separating the aquifers.
6. Mixing of groundwaters with other sources. This is entirely dependent upon hydraulic gradients in the ground. In most instances, the groundwater moves very slowly, in terms of a few meters per year, and the flow regimen is laminar. Mixing will occur very, very slowly, and given the tens or perhaps thousands of years of age of the groundwater, diffusion of contaminants and dissolution of rocks is an important parameter.
7. Anthropogenic factors such as surficial contamination or infiltration from various sources. Runoff from roadways and sidewalks contains lead, rubber, and oils. Sanitary sewers leak, while asphalt parking areas contribute to groundwater contamination through the leaching of the asphalt solvents during precipitation. Storm and sanitary sewers and septic tanks contribute their share of contaminants, and agricultural application of pesticides and fertilizers are potential and actual huge sources of groundwater contamination. Industrial discharges and waste disposals, and residential and industrial landfills can be a potent source of contamination.

### 1.5.3 Other Principal Contaminants in Groundwater

The largest single group of organic contaminants soluble in water is found in petroleum. It is even more remarkable that the contamination is so widespread when petroleum has been around as a fuel only since 1859 when the first commercial well struck oil in Pennsylvania. Initially, the fire marshalls and insurance companies mandated that gasoline tanks and certain types of chemical tanks be placed underground to reduce fire and release hazards. In the late 1980s the US started a program to identify, register, and test underground storage tanks (USTs). Leaking tanks were to be removed or replaced, and leaks and spills from leaking tanks were remediated.

When the UST regulation, testing, replacement, cleanup and remediation program began in the US, there were over 2.1 million tanks which were suspected to be leaking petroleum into the groundwater. In New York and New Jersey alone (USEPA Region 2), the Federal and State actions closed over 1.5 million (old and leaking) substandard tanks, cleaned up more than 300 000 petroleum leaks, and reduced the number of new releases from these regulated tanks from a high of over 66 000 in 1990 to roughly 7000 in 2008. EPA Region 2 still has approximately 50 246 federally regulated USTs and 37 579 leaking underground storage tanks (LUSTs), but cleanups have been initiated at 36 569 of the LUST sites and 30 432 cleanups have been completed.<sup>15</sup> When a leak occurs into the soil from a LUST, approximately 75% of the leak is retained in the soil, about 24% can be found floating on the soil and water interface, and about 1% is dissolved in the groundwater.

Contaminants such as benzene, toluene, ethylbenzene, and xylene (BTEX) are of the greatest concern because they have a direct exposure link to development of cancer in humans (see Table 1.7).<sup>16</sup>

**Table 1.7** Principal groundwater contaminants found in petroleum.

Element	Avg. amount in petroleum % by weight	Range of concentrations in crude oil	Solubility in H <sub>2</sub> O @ 20–25 °C(mg l <sup>-1</sup> )	Henry's law constant
Benzene	0.16	0.04–0.41	1800	0.228
Toluene	0.67	0.08–2.5	530	0.272
Ethylbenzene	0.17	0.056–0.31	170	0.323
M-Xylene	0.66	0.08–2.0	407	160
O-Xylene	0.26	0.033–0.092	31	0.0198
p-Xylene	0.26	0.090–0.68	190	0.314
Naphthalene	0.069	0.033–0.092	31	0.0198
Acenaphthalene	0.057	0.057–0.057	4.2	0.00636

Source: Table 1, Fate and transport of petroleum hydrocarbons in soil and groundwater at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002–2003, available at <http://pubs.usgs.gov/sir/2005/5104> and <http://pubs.usgs.gov/sir/2005/5104/PDF/SIR20055104.pdf>.

### 1.5.4 Movement of Groundwater

The ground is a porous medium but the groundwater moves very slowly. The principal factor that causes groundwater movement is a hydraulic gradient. The velocity of groundwater movement is measured in feet or meters per day, or per year, or in centimeters per second. The rate of fluid movement through the ground varies with the reciprocal of the viscosity of the fluid. The rate of fluid movement ranges between  $10^{-3}$  cm s $^{-1}$  for gravels or very coarse gravels (86.4 ft/day), to  $10^{-12}$  cm s $^{-1}$  ( $8.64 \times 10^{-8}$  ft/day) for very tight clays. By comparison, new uncracked concrete has a permeability of  $10^{-11}$  to  $10^{-12}$  cm s $^{-1}$  (0.0000316 ft/year), and impermeable clay layers to be used in landfills must be compacted to  $10^{-9}$  cm s $^{-1}$ .

A later chapter in this book will discuss groundwater movement further.

## 1.6 Analytical Methods

In order to know what is in the water, we must also know something about how the medium is sampled and preserved, and how the contaminants are measured. This is not a text on analytical chemistry, but merely a brief mention of some of the methods of detecting the most common compounds dissolved in water. It is imperative that the sample for analysis be representative of the conditions or fluid being sampled, and often this is not as straightforward as it may at first appear. It is almost impossible to obtain representative samples of two-phase flows (consider water with an oil layer floating on it) or suspended solids in a channel or stream. Both are difficult to sample unless the samples are extremely well mixed in an area of very high turbulence.

Once the material is sampled, it must be preserved until it can be shipped to the laboratory and analyzed. Even after the sample is transmitted to the laboratory, the lab will have some holding times before the analyses can be scheduled. Some sampling protocols require preservatives to be added, and others prohibit the use of certain containers because of the chance of contamination or because the material in the liquid could adhere to the sides of the sampling container.

In the water industry there are two principal references on methods. The first and one of the oldest is *Standard Methods for the Examination of Water and Wastewater*, published by the American Water Works Association (AWWA.org), the Water Environment Federation (WEF.org), the American Public Health Association (APHA.org), the American Society of Civil Engineers, and others. The second principal reference has become important not only because of its publisher (USEPA), but also for many of the methods that are applicable to groundwater and wastewater: SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, Office of Solid Waste Research, principally for hazardous waste analyses. It has also become a de facto standard in the United States and elsewhere because of the many references in EPA-issued permits to the manual. The manual can be viewed and downloaded at <http://www.epa.gov/epaoswer/hazwaste/test/main.htm>. However, it often does not

include as thorough an explanation of the methods, and it often relies on methods that focus on the issue of the analysis of hazardous wastes, and occasionally relies on methods that use advanced and expensive analytical equipment not generally available in many laboratories. SW-846 often includes specialized analytical methods that are not covered by *Standard Methods*.

Table 1.8 briefly lists some of the more common analytical methods used in a modern laboratory.

Inorganic contaminants in water generally follow specific rules that are determined based upon the valence of the compounds and the reaction between the cations and anions, as cited above and in the following materials. The rules for predicting solubility of an inorganic compound are shown in Table 1.9.

A caveat is appropriate. Most chemistry texts, handbooks, and common definitions of solubility define insoluble compounds as those which are less than 1% soluble (solubility  $< 0.1 \text{ mol l}^{-1}$ ). However, for the environmental

**Table 1.8** Principal analytical methods for contaminants in water.

Element	Measurement method	Element n	Measurement method
Aluminum	Flame ionization	Carbonate ( $\text{CO}_3$ )	Calculation
Antimony	Flame ionization	Chloride (Cl)	Gravimetric
Arsenic	Flame ionization	Cyanide (CN)	Colorimetric
Calcium	Flame ionization	Fluoride (F)	Gravimetric
Chromium	Flame ionization	Hydronium ( $\text{OH}$ )	pH
Copper	Flame ionization	Hypochlorite ( $\text{HClO}_2$ )	pH
Hydrogen	pH	Hypochlorous ( $\text{ClO}_2$ )	pH
Iron	Flame ionization	Nitrate ( $\text{NO}_3$ )	Colorimetric
Lead	Flame ionization	Nitrite ( $\text{NO}_2$ )	Colorimetric
Magnesium	Flame ionization	Sulfate ( $\text{SO}_4$ )	Colorimetric
Manganese	Flame ionization	Sulfite (S)	Colorimetric
Mercury	Flame ionization	Other	
Potassium	Flame ionization	Alkalinity	Colorimetric
Silica	Flame ionization	Total org. carbon	Gravimetric
Silver	Flame ionization	Diss. $\text{O}_2$	Azide titr or probe
Sodium	Flame ionization	Org. nitrogen	Kjelldahl
Zinc	Flame ionization	Chem $\text{O}_2$ demand	Digestion/titration
Ammonia	Kjelldahl or Nesslerization	Biochemical. $\text{O}_2$ demand	Difference in oxygen uptake
Bicarbonate ( $\text{HCO}_3$ )	Calculation		

**Table 1.9** Solubility rules for simple inorganic compounds in water.

Rule number	Rule
1	Periodic Table Group 1 elements (Li, Na, K, Cs, Rb) are soluble.
2	Salts containing NH <sub>4</sub> ammonium ion and nitrate and nitrite ions (NO <sub>3</sub> and NO <sub>2</sub> ) are generally soluble
3	Most salts of Cl, Br, and I (halide salts) are soluble. Except for Ag, Pb <sup>+2</sup> and Hg <sub>2</sub>
4	Silver salts of AgNO <sub>3</sub> and Ag (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) are soluble. All other silver salts are insoluble
5	CaSO <sub>4</sub> , BaSO <sub>4</sub> , PbSO <sub>4</sub> , Ag <sub>2</sub> SO <sub>4</sub> , and SrSO <sub>4</sub> are insoluble, but most other Sulfate salts are soluble
6	Hydroxides: Group 1 metals are soluble; Group II metals are slightly soluble; Salts of transition metals and Al <sup>+3</sup> are insoluble. Reactions of Al(OH) <sub>3</sub> , Fe(OH) <sub>3</sub> , and Co(OH) <sub>2</sub> are also insoluble
7	Group II carbonate salts are insoluble, as are most other carbonates
8.	Sulfide salts are insoluble: CdS, FeS, Ag <sub>2</sub> S, As <sub>2</sub> S <sub>3</sub> , Bi <sub>2</sub> S <sub>3</sub> PbS are also insoluble
9	Reactions of chromates with cations often yield insoluble salts.
10	Fluoride reactions with Group II metals will often yield insoluble salts, except Calcium
11	Phosphates are also frequently insoluble.

Note: Insoluble is considered as less than 1% molar concentration of the salt.

Source: [http://chemwiki.ucdavis.edu/Physical\\_Chemistry/Equilibria/Solubility/Solubility\\_Rules](http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Solubility/Solubility_Rules) and <http://www2.ucdsb.on.ca/tiss/stretton/Database/solubility.htm>.

engineer and chemist, 1% solubility represents 1000 mmol l<sup>-1</sup>. The aquatic contaminants that turn water into sewage rarely exceed 400 mg l<sup>-1</sup> of solids, and waste with 1000 mg l<sup>-1</sup> of almost any contaminant would be considered extremely strong. Most of the waste treatment operations are required to meet a permit limit on oxygen-consuming substances (as measured by biochemical oxygen demand (BOD)) of less than 20 mg l<sup>-1</sup>, and in certain circumstances the limit is less than 5 mg l<sup>-1</sup>. Additional information on solubility for inorganic compounds can be found at the following website: [http://sites.chem.colostate.edu/diverdi/all\\_courses/CRC%20reference%20data/solubility%20of%20inorganic%20compounds.pdf](http://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/solubility%20of%20inorganic%20compounds.pdf).

When examining old data generated prior to the 1970s, some caution should be exercised with regard to the presence or absence of compounds. Until about 1970, it was uncommon to have environmental data reporting for metals under 5 mg l<sup>-1</sup>, and highly unusual to have organic compounds reported at levels less than 10 mg l<sup>-1</sup>. The development of new and better computer techniques and analytical instruments has improved accuracy ranges. For gas chromatographic analysis, a chemist can get concentrations to 1 mg l<sup>-1</sup> and sometimes lower.

For analysis by gas chromatograph/mass spectrography, the analytical limits are now down to the parts per billion ranges, micrograms per liter, and for many compounds, the analytical range is in nanograms per liter or ppt.

Inorganic analysis has also improved with new techniques. The modern laboratory uses inductively coupled plasma techniques for analysis, and the reporting limits are micrograms per liter.<sup>17</sup> The analytical techniques for metals often incorporate the need for a standards curve where known concentrations of substances are analyzed to develop a spectrum absorbance curve versus concentration for a particular set of samples to be analyzed.<sup>18</sup> There are often problems with interferences in the analysis from either competing elements with similar absorption spectra or similar emission spectra. Mercury and lead analyses use cold emission spectra, and the same general concerns about calibration apply.

If one is having samples analyzed for the purpose of submitting them to a regulatory agency, state, national, or regional certification of the laboratory is a must if the results are to be accepted. The same applies to samples analyzed in another country, and the quality control data should always accompany the results.

## 1.7 Laboratory Guidance

When you examine water analyses, quality control in the laboratory is as important as the detection limits of the analytical equipment. One has to be familiar with the measurement techniques and some of the quality control procedures in order to understand the analyses. The equipment, the detection limits, the analytical methods, and interferences for specific analytes are always important. In most cases, the result one gets from the laboratory is sufficient, but there are cases, especially when one looks at low detection limits, and especially with organic chemical analyses, when the detection equipment can become an important part of the answer. If the equipment cannot detect the compound, or if the wrong compound is analyzed, the analysis can be useless in solving a water quality puzzle or in understanding the analysis.

For all samples delivered to the laboratory, strict protocols for sampling, preservation and transportation must be followed. Chain of evidence/custody protocols must be observed for all samples collected and submitted to a regulatory agency.<sup>19</sup> Some of those protocols include:

1. Packing the samples in ice and making sure that they are delivered to the laboratory before the ice melts.
2. All samples must be collected in thoroughly cleaned glassware (most often specially cleaned glassware).
3. Samples must be delivered within a specific timeframe (generally 48 hours).
4. The samples must have a completed chain of custody form for each sample.

5. The sample container must be sealed and be tamper-proof, or have seals that indicate whether it has been opened and examined prior to receipt.<sup>20</sup>

An aside is necessary here to indicate the manner in which planning for all contingencies is necessary. In 2004 my team was collecting water and soil samples in Ecuador under the supervision of the Ecuadorian Court. Initially, a laboratory with the required equipment to analyze soil and water samples at very low detection limits required for the project was not available.<sup>21</sup> So, we chose a US-based laboratory which had the required equipment, and which had a US Department of Agriculture soils permit for our analyses. (The soils permit was required to allow the samples to enter the US, ensuring that they would be sent to a laboratory or other location which would prevent foreign disease and insect vectors from entering the US, and to prevent the USDA from destroying the samples.)

The samples were to be delivered by Federal Express, and we were assured that the samples should be in the laboratory within the allowable holding times.

We packed the samples in a lot of ice, sealed the sample containers (big blue coolers) and executed the chain of custody forms, and placed a note in the paperwork indicating that the samples were for analyses and included the Soil Permit Number of the designated laboratory, along with a copy of their permit.

The Department of Agriculture placed a three days hold on the samples, causing the cooling ice to melt, raising the temperature of the samples beyond the protocol temperature limits, and the delay also caused the samples to exceed the protocol's holding times. Because of the protocol violations, we could not use the analyses. The point is that we should have planned better and accompanied the samples.

It is also important to decide in advance, especially in a regulatory situation, how non-detects and below quantification limits are to be handled and reported.<sup>22</sup>

The laboratory must have a quality control/quality assurance manual that includes use of duplicate and matrix spike samples. This is especially important in the analyses of organic compounds.

For specific information on sample holding times and preservation techniques for US regulatory programs, and most other countries' analytical protocols,<sup>23</sup> see the US Code of Federal Regulations, Chapter 40, Part 136, ([http://www.epa.gov/region9/qa/pdfs/40cfr136\\_03.pdf](http://www.epa.gov/region9/qa/pdfs/40cfr136_03.pdf)), and analyses involving hazardous wastes are specified in SW-846, Chapter 2, starting at about page 60: (<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap2.pdf>). It is important to recognize that detection limits between various programs and analytical methods are substantially different, and what is invisible

(non-detectable) in one set of analyses may be measured to two or three significant places with other methods. In general, *Standard Methods* is most often used for water analyses, and the methods are direct and often require less expensive equipment.

The analytical procedures in the EU are sufficiently different from the procedures in the US that the EU procedures follow ISO-9000 series standards.<sup>24</sup>

## 1.8 Regulatory Framework of Water Regulations

### 1.8.1 What Is Quality Water?

Defining quality water is difficult because the perception of water quality depends upon who is asking, and the uses for the water. The simplest definition of quality water would be a lack of contaminants, often equated with pure water. However, pure water is difficult and expensive to obtain. The perceived quality of water depends upon the types of contaminants it contains. The removal of contaminants from water is an expensive process, and the cost of that removal is directly related to the requirements for purity or the perceived quality of the water. For practical purposes, we have to compromise about the contaminants that we can accept in the water, regulating or eliminating those that are harmful, and ignoring those that are too difficult, impractical or expensive to regulate or remove.

The function of water quality standards is to specify minima and maxima that can be used to protect the environment in accordance with overall objectives. Substances that are harmful are regulated, and specific water quality floors are set for those contaminants deemed to be beneficial. Note that this does not mean that criteria or regulations need to be meaningful, nor tied to controllable parameters – only that they can be measured and regulated.

Two good examples of this can be found in stream standards. First, in many areas, minimum dissolved oxygen (DO) concentrations are mandated for certain classes of aquatic life (trout streams) at  $6.0 \text{ mg l}^{-1}$  of DO, at all times. Given diurnal variations and seasonal variations in groundwater, runoff quality, and so on, it is functionally impossible to mandate that the DO concentration of  $6.0 \text{ mg l}^{-1}$  be achieved at all times because Mother Nature's activities upstream will govern the quality of the water and the oxygen content.

Secondly, turbidity standards (a measurement of the cloudiness of the water) have been imposed on many watercourses and streams. This is an attempt to control runoff from lands that are under development and which may have had their vegetative cover removed in preparation for earthwork. The regulation sets

limits on turbidity increases on runoff from a property with an active construction activity thereupon. Turbidity is measured in either Jackson Turbidity Units (JTUs, an older style measurement)<sup>25</sup> or nephelometric units (NTUs),<sup>26</sup> where both measure light scattered in water, or the relative cloudiness of the water. The amount of light scattered depends upon particle size, shape, albedo, and color. For example, suspensions containing mica would have a higher albedo and thus a higher NTU than soils with a darker color for the same level of suspended solids in the water.<sup>27</sup> For low values of NTU, there is no calibration, and for soils, both measurements have a minimal relationship to suspended solids and the test has low repeatability.

In the first case, development can be restricted if the water quality is not maintained. In the second case, the property owner can be fined and his activity halted based upon the results of the test, even though the owner has done everything requested by the governing legal authority.

We often judge the environmental quality of water by its suitability to support aquatic life, and its suitability for public recreational and drinking water purposes, and freedom from contaminants that would prevent a specific use. For example, distilled water has high quality, but it is unsuitable for many purposes because it cannot support aquatic life, nor is it safe to use as drinking water. Freshwater is unsuited for saltwater organisms, and vice versa.

By comparison, the quality requirement for cooling water is much lower. The water has a tolerance for impurities because it is non-potable, and it is recirculated through process piping where it can pick up contaminants. The principal requirement for cooling water is its temperature, and it should be relatively free of suspended solids. Cooling tower water is often treated chemically to reduce corrosion in the plant piping, so it is generally non-potable and will require treatment before it is discharged to the environment.

### 1.8.2 Water Quality Standards

The next couple of sections will cover the US water quality standards and the EU and UK Water Quality Standards and effluent setting processes. The US Standards will be discussed in greater detail because: (i) the author is US-based and more familiar with the US regulations; (ii) the UK Regulations are set by a slightly different procedural basis which will be discussed in overview; (iii) the EU Regulations are set by policy which is then enforced by individual EU member countries; and (iv) because the US represents the largest single market in the world, with the exception of China, which at the time of writing, does not have a well-defined market nor structure.

### 1.8.3 Water Quality Standards in the United States

US surface water quality standards are established by classification and proposed use. The legal authority for the establishment of surface water quality standards is the Clean Water Act 1972 (CWA), and accompanying US regulations found in Chapter 40 of the Code of Federal Regulations Part 131. The CWA provided the authority for the Federal Government to establish standards for the navigable waters of the US.<sup>28</sup> These standards establish minimum concentrations of specific water quality parameters that must be met at all times. Depending upon the declared use for the waters, the provisions include temperature, dissolved oxygen, and other limits that are generally protective of aquatic life and protective of the proposed use. It is the water quality standards which drive effluent standards.

Water quality criteria are slightly different from standards as they express the intent to create water free from certain contaminants, but they do not have the force of law.

Groundwater in the US is generally regulated by the Clean Drinking Water Act. Because it is regulated by a different law, it is treated differently here. Drinking Water Quality Standards, are based on a requirement to protect health and the Water Quality Standards are requirements designed to protect aquatic life and river quality (and drinking water sources).

### 1.8.4 Establishing Water Quality Standards

In the US, waters are classified on a watershed basis or geographical area, and within that area, the individual rivers, streams, and water bodies are classified with regard to specific use. The use sets the water quality standards. An example of the classification and standards setting is shown in Section 1.8.10, taken from Georgia Environmental Law.

### 1.8.5 Effluent Standards and Guidance

Starting in the 1970s, the Federal and State and international communities started to publish water quality criteria (WQC). In the US, the earliest WQC can be tracked back to the Rivers and Harbors Act of 1899, where it was determined that unauthorized dumping of garbage or refuse matter of any kind into navigable waters of the US was a misdemeanor. The provisions of the Act were later used to control certain types of water pollution discharges, principally prior to the development of the Clean Water Act, and it is still used today to govern the discharge of dredge and fill materials to the “navigable waterways”<sup>29</sup> of the US.

The existence of water quality standards in the US dates back to the Ohio River Valley Sanitary Commission, formed in 1948 in an attempt to regulate

the discharge of industrial waters into the tributaries of the Ohio River. The compact was historic because any one state could bring an action against individual companies in other states, based on water pollution.

Later, when the Clean Water Act first became law in the early 1970s, the responsibility for discharge to waters of the Ohio and its tributaries was transferred from the Corps of Engineers to the agency that later became the US Environmental Protection Agency. The purpose of this bit of history is to set the stage for the next material in this chapter: regulations and their effect on water discharges and treatment.

We now live in a regulated environment and must comply with good practice and the appropriate regulations for treatment of water prior to discharge, in order to protect the environment. Many states and the Federal Government, the EU government, and almost every country have their own water quality standards that govern the discharge to surface waters. There are different ways of protecting the surface waters, depending upon the country and the philosophy with regard to protection. Section 1.8.10 contains an excerpt from the State of Georgia Code which describes the water quality standards and how they are established.

### 1.8.6 Mixing Zones

Before we go into stream quality and surface water quality standards, it is important to consider the definition of a mixing zone because it is generally an exception to the water quality standards and criteria.

A mixing zone is a small area where water quality standards do not apply. It can be on a stream, a lake, or a river, but it is an area where the effluent from a process is allowed to mix with the receiving waters for the purpose of allowing the contaminants in the effluent to equalize into the water column.<sup>30</sup>

There are a number of qualifications to a mixing zone, and it can be a complex issue. The purpose of mixing zones is to allow the effluent to mix with the local water, and after a fashion, allow the effluent stream to mix fully with the receiving water body. The USEPA has developed a licensing and recommendation program with Mixzon, for their program called Cormix. The program constructs a detailed mathematical model of a mixing zone, and the diffusion and mixing that occurs when an effluent discharges into a body of water or stream. The Cormix program is available for a relatively expensive annual license fee.<sup>31</sup> Manually established mixing zones generally have a maximum width of a third to half of the stream width and a specified length where the effluent will be assumed to be fully diluted.<sup>32</sup>

If a wastewater discharge, legally permitted, is flowing into an intermittent stream, it can pose a significant industrial challenge. During dry weather, the only flow in the stream is the plant effluent. Since water quality standards are significantly lower than effluent standards, and are always applicable, the industry must achieve a higher level of treatment in order to comply with the water quality standards.

### 1.8.7 Discharge Permits

There are three prominent and distinct philosophies regarding effluent discharges and water quality protection. The US regulations characterize one type of approach, while the EU regulations characterize another approach, and the UK uses a third but similar approach. We will look at all three approaches, but will give the most attention to the US regulations. It should be noted that the EU regulations are set by a framework directive published by the EU governing body, but enforced individually and differently in each of the EU Member States.

The US approach is statistically based using a normal distribution (which will be covered in detail later), and sets limits on general pollutants, as well as individual chemical parameters. Most, if not all, US permits will have a daily maximum discharge quantity, and a monthly average discharge quantity, where the limits are derived from Stream Quality Standards, and Public Health Drinking Water Quality Criteria, with an adequate reserve or allowance for safety and expansion. In the vast majority of cases, the conventional and priority pollutants regulated will have mass-based quantity limits where the total daily average discharge mass limit is two times the monthly average figure. There is also a monthly average concentration where the daily maximum concentration cannot exceed the monthly average concentration by more than two times. Violation of either of these provisions can generate substantial fines. It is also not uncommon for the permits to have a biological monitoring component which requires aquatic testing of target organisms (usually *Daphnia magna*, or water fleas) for their survival rate in various concentrations of the facility effluent, as a check on the potential aquatic toxicity of the effluent stream.

### 1.8.8 US Penalty Policies – Enforcement of Permit Conditions

The US Water Pollution Control Penalty Policy starts at \$10 000 per day, per violation. If the discharge is wilful or negligent, the fines can be quickly increased to between \$37 500 and \$50 000 per day of violation, plus a year in jail for each day of violation if the violation is found to be wilful or negligent, or fraudulent. The fine for spilling hazardous materials into public waterways is now set at \$2100 per barrel or unit, plus administrative penalties starting at \$137 000.<sup>33</sup> This regulatory approach is a huge hammer poised to be painful when dropped upon a violator. This, plus severe penalties for falsification of data, and a requirement

for self-monitoring and self-mandated reporting of all pollution permit conditions, plus any special circumstances, create a sometimes hostile relationship between industry and the EPA.<sup>34</sup> It is also a truism that while the EPA has been quick to bring suit against industry, even to the point of giving responsible parties prison time, it has been less enthusiastic about applying the same standards to municipal and governmental offices and locations. (The mayor does not go to jail over EPA violations, but the CEO of a company might!)

### 1.8.9 Water Quality Discharge Basics in the US

The following is a summary of the framework and the legal basis for development of Water Quality Regulations in the US.<sup>35</sup>

In the US, it is the State that must designate its waters with respect to the following objectives:

1. It is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985;
2. It is the national goal that wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water be achieved by July 1, 1983;
3. It is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited;
4. It is the national policy that Federal financial assistance be provided to construct publicly owned waste treatment works;
5. It is the national policy that area-wide waste treatment management planning processes be developed and implemented to assure adequate control of sources of pollutants in each State;
6. It is the national policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans; and
7. It is the national policy that programs for the control of nonpoint sources of pollution be developed and implemented in an expeditious manner so as to enable the goals of this Act to be met through the control of both point and nonpoint sources of pollution.

Section 303 (c) (2) of the Clean Water Act further refines the requirements to require the States to issue and review triennially (once in every three years) water quality designations and standards which:

(s)hall consist of the designated uses of the navigable waters involved and the water quality criteria for such waters based upon such uses. Such standards shall be such as to protect the public health or welfare, enhance the quality of water and serve the purposes of this Act. Such standards

**Table 1.10** The 65 priority water pollutants according to the US code.

1. Acenaphthene	23. Cyanides	45. Mercury and compounds
2. Acrolein	24. DDT and metabolites	46. Naphthalene
3. Acrylonitrile	25. Dichlorobenzenes (1,2-, 1,3-, and 1,4-dichlorobenzenes)	47. Nickel and compounds
4. Aldrin/Dieldrin	26. Dichlorobenzidine	48. Nitrobenzene
5. Antimony and compounds	27. Dichloroethylenes (1,1-, and 1,2-dichloroethylene)	49. Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
6. Arsenic and compounds	28. 2,4-dichlorophenol	50. Nitrosamines
7. Asbestos	29. Dichloropropane and dichloropropene	51. Pentachlorophenol
8. Benzene	30. 2,4-dimethylphenol	52. Phenol
9. Benzidine	31. Dinitrotoluene	53. Phthalate esters
10. Beryllium and compounds	32. Diphenylhydrazine	54. Polychlorinated biphenyls (PCBs)
11. Cadmium and compounds	33. Endosulfan and metabolites	55. Polynuclear aromatic hydrocarbons (including benzoanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)
12. Carbon tetrachloride	34. Endrin and metabolites	56. Selenium and compounds
13. Chlordane (technical mixture and metabolites)	35. Ethylbenzene	57. Silver and compounds
14. Chlorinated benzenes (other than dichlorobenzenes)	36. Fluoranthene	58. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

15. Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)	37. Haloethers (other than those listed elsewhere; includes chlorophenylphenyl ethers, bromophenylphenyl ether, bis(dichloroisopropyl) ether, bis-(chloroethoxy) methane and polychlorinated diphenyl ethers)	59. Tetrachloroethylene
16. Chloroalkyl ethers (chloroethyl and mixed ethers)	38. Halomethanes (other than those listed elsewhere; includes methylene chloride, methylchloride, methylbromide, bromoform, dichlorobromomethane	60. Thallium and compounds
17. Chlorinated naphthalene	39. Heptachlor and metabolites	61. Toluene
18. Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	40. Hexachlorobutadiene	62. Toxaphene
19. Chloroform	41. Hexachlorocyclohexane	63. Trichloroethylene
20. 2-chlorophenol	42. Hexachlorocyclopentadiene	64. Vinyl chloride
21. Chromium and compounds	43. Isophorone	65. Zinc and compounds
22. Copper and compounds	44. Lead and compounds	

shall be established taking into consideration their use and value for public water supplies, propagation of fish and wildlife, recreational purposes, and also taking into consideration their use and value for navigation.

The State must, at a minimum, adopt the Federal Water Quality Regulations, and issue and adopt criteria for conventional and toxic pollutants which contain numerical standards, or which refer to biological monitoring or assessment methods. Table 1.10 contains the list of the 65 toxic pollutants that the EPA has identified.<sup>36</sup> The State must submit their Water Quality Standard to the Federal Government for approval, or certain portions of Federal revenues will be withheld from the non-compliant states. The Federal regulations represent a minimum floor for regulations and standards. The States are free to exceed the Federal requirements but must meet them as a minimum condition (44 FR 44502, July 30, 1979, as amended at 46 FR 2266, Jan. 8, 1981; 46 FR 10724, Feb. 4, 1981).

Other basic effluent standards are often specified by the type of industry and are regulated on a case-by-case basis. The CWA regulations at 40 CFR 401.16 identifies biochemical oxygen demand ( $BOD_5$ ), total suspended (non-filterable) solids (TSS), pH, fecal coliform, and oil and grease as conventional pollutants which need to be regulated in discharge permits. 40CFR 401.17 contains limits on pH of the liquid discharged.

### 1.8.10 How Water Quality Standards Are Established

Water quality standards are established by watershed or geographical location and then by proposed use. All water quality standards have to be maintained at all times, even at very low flows. The definition of low flow is consistent in the US, as the lowest flow that occurs in a stream for seven consecutive days on an average of once in every 10 years. This is known as the "7Q10 Flow."

A sample of the classification and water quality standards follows. The regulations are similar in all the states in the US, and the specific samples of regulations are taken from the Georgia Code for protection of the environment. Specific references to Georgia have been removed, and the regulations have been edited to follow generally the appropriate sections of US Code.

In the following, ellipses and brackets are used to indicate comments or deleted sections of material that are largely irrelevant to the subject of water quality or development and promulgation of the Standards.

### 391-3-6-.03 Water Use Classifications and Water Quality Standards

- (1) *Purpose.* The establishment of water quality standards.
- (2) *Water quality enhancement:*
  - (a) The purposes and intent of the State in establishing Water Quality Standards are to provide enhancement of water quality and prevention of pollution; to protect the public health or welfare in accordance with

- the public interest for drinking water supplies, conservation of fish, wildlife and other beneficial aquatic life, and agricultural, industrial, recreational, and other reasonable and necessary uses and to maintain
- (b) and improve the biological integrity of the waters of the State.
- (i) Existing instream water uses and the level of water quality necessary to protect the existing uses shall be maintained and protected.
- (ii) Where the quality of the waters exceed levels necessary to support propagation of fish, shellfish, and wildlife and recreation in and on the water, that quality shall be maintained and protected unless the division finds, ... that allowing lower water quality is necessary to accommodate important economic or social development in the area in which the waters are located.
- (3) [is Irrelevant]
- (4) *Water use classifications.* Water use classifications for which the criteria of this Paragraph are applicable are as follows:
- (a) Drinking Water Supplies
- (b) Recreation
- (c) Fishing, Propagation of Fish, Shellfish, Game and Other Aquatic Life
- (d) Wild River
- (e) Scenic River
- (f) Coastal Fishing
- (5) *General criteria for all waters.* The following criteria are deemed to be necessary and applicable to all waters of the State:
- (a) All waters shall be free from materials associated with municipal or domestic sewage, industrial waste or any other waste which will settle to form sludge deposits that become putrescent, unsightly, or otherwise objectionable.
- (b) All waters shall be free from oil, scum, and floating debris associated with municipal or domestic sewage, industrial waste or other discharges in amounts sufficient to be unsightly or to interfere with legitimate water uses.
- (c) All waters shall be free from material related to municipal, industrial, or other discharges which produce turbidity, color, odor, or other objectionable conditions which interfere with legitimate water uses.
- (d) *Turbidity.* The following standard is in addition to the narrative turbidity standard ... above: All waters shall be free from turbidity which results in a substantial visual contrast in a water body due to a man-made activity. [Note the vagueness of the standard.] The upstream appearance of a body of water shall be as observed at a point immediately upstream of a turbidity-causing man-made activity. That upstream appearance shall be compared to a point which is located sufficiently downstream from the activity so as to provide an appropriate mixing zone. For land disturbing activities, proper

- design, installation, and maintenance of best management practices and compliance with issued permits shall constitute compliance ....
- (e) All waters shall be free from toxic, corrosive, acidic, and caustic substances discharged from municipalities, industries, or other sources, such as nonpoint sources, in amounts, concentrations, or combinations which are harmful to humans, animals, or aquatic life.
- (i) Instream concentrations of the following chemical constituents which are considered to be other toxic pollutants of concern in the State of Georgia shall not exceed the criteria indicated below under 7-day, 10-year minimum flow (7Q10) or higher stream flow conditions except within established mixing zones:
- [List of specific chemicals with concentrations follows for both 1Q10 and 7Q10 flows but is omitted here.]
- (6) *Specific criteria for classified water usage.* In addition to the general criteria, the following criteria are deemed necessary and shall be required for the specific water usages shown:
- (a) *Drinking water supplies.* Those waters approved as a source for public drinking water systems permitted or to be permitted by the Environmental Protection Division. Waters classified for drinking water supplies will also support the fishing use and any other use requiring water of a lower quality.
- (i) *Bacteria.* [The standard for bacterial quality is based on a geometric mean for May through October and a different level of quality for the months of November through April.]
- (ii) *Dissolved oxygen.* A daily average of  $6.0 \text{ mg l}^{-1}$  and no less than  $5.0 \text{ mg l}^{-1}$  at all times for waters designated as trout streams by the Wildlife Resources Division. A daily average of  $5.0 \text{ mg l}^{-1}$  and no less than  $4.0 \text{ mg l}^{-1}$  at all times for water supporting warm water species of fish.
- (iii) *pH.* Within the range of 6.0–8.5.
- (iv) No material or substance in such concentration that, after treatment by the public water treatment system, exceeds the maximum contaminant level established for that substance by the Environmental Protection Division pursuant to the [Name of the State] Rules for Safe Drinking Water.
- (v) *Temperature.* Not to exceed 90 °F. At no time is the temperature of the receiving waters to be increased more than 5 °F above intake temperature except that in estuarine waters the increase will not be more than 1.5 °F. In streams designated as primary trout or smallmouth bass waters by the Wildlife Resources Division, there shall be no elevation of natural stream temperatures. In streams designated as secondary trout waters, there shall be no elevation exceeding 2 °F of natural stream temperatures.

- (b) *Recreation.* General recreational activities such as water skiing, boating, and swimming, or for any other use requiring water of a lower quality, such as recreational fishing. These criteria are not to be interpreted as encouraging water contact sports in proximity to sewage or industrial waste discharges regardless of treatment requirements:
- (i) *Bacteria.* [Fecal coliform standards for coastal and other recreational waters – omitted.]
  - (ii) *Dissolved oxygen.* A daily average of  $6.0 \text{ mg l}^{-1}$  and no less than  $5.0 \text{ mg l}^{-1}$  at all times for waters designated as trout streams by the Wildlife Resources Division. A daily average of  $5.0 \text{ mg l}^{-1}$  and no less than  $4.0 \text{ mg l}^{-1}$  at all times for waters supporting warm water species of fish.
  - (iii) *pH.* Within the range of 6.0–8.5.
  - (iv) *Temperature.* Not to exceed  $90^{\circ}\text{F}$ . At no time is the temperature of the receiving waters to be increased more than  $5^{\circ}\text{F}$  above intake temperature except that in estuarine waters the increase will not be more than  $1.5^{\circ}\text{F}$ . In streams designated as primary trout or smallmouth bass waters by the Wildlife Resources Division, there shall be no elevation of natural stream temperatures. In streams designated as secondary trout waters, there shall be no elevation exceeding  $2^{\circ}\text{F}$  natural stream temperatures.
- (c) *Fishing.* Propagation of Fish, Shellfish, Game and Other Aquatic Life; secondary contact recreation in and on the water; or for any other use requiring water of a lower quality:
- (i) *Dissolved oxygen.* A daily average of  $6.0 \text{ mg l}^{-1}$  and no less than  $5.0 \text{ mg l}^{-1}$  at all times for water designated as trout streams by the Wildlife Resources Division. A daily average of  $5.0 \text{ mg l}^{-1}$  and no less than  $4.0 \text{ mg l}^{-1}$  at all times for waters supporting warm water species of fish.
  - (ii) *pH.* Within the range of 6.0–8.5.
  - (iii) *Bacteria.* [Bacterial standards repeated and omitted.]
  - (iv) *Temperature.* [Temperature standard repeated and omitted.]
- (d) *Wild river.* For all waters designated in 391-3-6-.03(13) as “Wild River,” there shall be no alteration of natural water quality from any source.
- (e) *Scenic river.* For all waters designated as “Scenic River,” there shall be no alteration of natural water quality from any source.
- (f) *Coastal fishing.* This classification will be applicable to specific sites when so designated by the Environmental Protection Division. For waters designated as “Coastal Fishing,” site specific criteria for dissolved oxygen will be assigned. All other criteria and uses for the fishing use classification will apply for coastal fishing.

- (i) *Dissolved oxygen (D.O.).* A daily average of  $5.0 \text{ mg l}^{-1}$  and no less than  $4.0 \text{ mg l}^{-1}$  at all times. [Qualifying statements omitted.]
- (7) *Natural water quality.* It is recognized that certain natural waters of the State may have a quality that will not be within the general or specific requirements contained herein. These circumstances do not constitute violations of water quality standards. This is especially the case for the criteria for dissolved oxygen, temperature, pH and fecal coliform. NPDES permits and best management practices will be the primary mechanisms for ensuring that discharges will not create a harmful situation.
- (8) *Treatment requirements.* Notwithstanding the above criteria, the requirements of the State relating to secondary or equivalent treatment of all waste shall prevail. The adoption of these criteria shall in no way preempt the treatment requirements.  
[Definition of low flow conditions follows.]
- (9) *Streamflows.* Specific criteria or standards set for the various parameters apply to all flows on regulated streams. On unregulated streams, they shall apply to all streamflows equal to or exceeding the 7-day, 10-year minimum flow (7Q10) and/or the 1-day, 10-year minimum flow (1Q10). All references to 7-day, 10-year minimum flow (7Q10) and 1-day, 10-year minimum flow (1Q10) also apply to all flows on regulated streams. All references to annual average stream flow also apply to long-term average stream flow conditions. Numeric criteria exceedences that occur under streamflows lower than 7Q10 or 1Q10, whichever applies, do not constitute violations of water quality standards as long as all current permit conditions are met.
- (10) *Mixing zone.* Effluents released to streams or impounded waters shall be fully and homogeneously dispersed and mixed insofar as practical with the main flow or water body by appropriate methods at the discharge point. Use of a reasonable and limited mixing zone may be permitted on receipt of satisfactory evidence that such a zone is necessary and that it will not create an objectionable or damaging pollution condition. Protection from acute toxicity shall be provided within any designated mixing zone to ensure a zone of safe passage for aquatic organisms.
- (11) *Toxic pollutant monitoring.* The Division will monitor waters of the State for the presence or impact of Section 307 (a)(l) Federal Clean Water Act toxic pollutants, and other priority pollutants. The monitoring shall consist of the collection and assessment of chemical and/or biological data as appropriate from the water column, from stream bed sediments, and/or from fish tissue. Specific stream segments and chemical constituents for monitoring shall be determined by the Director on the basis of the potential for water quality impacts from toxic pollutants from point or nonpoint waste sources. Singulaly or in combination, these constituents may cause an adverse effect on fish propagation at levels lower than the criteria.

Additional toxic substances and priority pollutants will be monitored on a case specific basis using Section 304(a) Federal Clean Water Act guidelines or other scientifically appropriate documents.

- (12) *Fecal coliform criteria.* The criteria for fecal coliform bacteria provide the regulatory framework to support the USEPA requirement that States protect all waters for the use of primary contact recreation or swimming.... The assessment of streams, rivers, lakes, and estuaries in Georgia and other States is based on fecal coliform organisms....
- (13) *Acceptance of data.* [The State will accept data for listing if it is sampled in accordance with the State's water quality assurance manual and analyzed by a Federal or State certified laboratory.]
- (14) *Specific water use classifications.* Beneficial water uses assigned by the State to all surface waters ... stream reaches not specifically listed are classified as Fishing. The specific classifications are as follows:  
[What follows is a very abbreviated listing of some watersheds with their classifications excerpted directly from the Code and provided as an example of the type of classification system used and the classes of waters considered]:

<i>Altamaha River Basin</i>	<i>Classification</i>
All littoral waters on the ocean side of St. Simons, Sea, and Sapelo Islands	Recreation
<i>Chattahoochee River Basin</i>	<i>Classification</i>
Alexander Creek	Headwaters to confluence with Cedar Creek
Bear Creek	Headwaters to confluence with Chattahoochee River
Chattahoochee River	Soque River to White Creek
Jacks Creek	Waters within the Cohutta wilderness area
	Drinking water
	Drinking water
	Recreation and drinking water
	Wild and scenic

- (15) *Specific criteria for lakes and major lake tributaries.* In addition to the general criteria, the following lake specific criteria are deemed necessary and shall be required for the specific water usage as shown. [Specific water quality criteria are not shown.]

### 1.8.11 UK Water Effluent Quality Standard<sup>37</sup>

The UK has a regulatory regime that is different from much of the rest of the EU. The water standards are set by the UKTAG group, and they have established a number of control parameters that are very similar to the priority pollutants in

**Table 1.11** UK list of priority pollutants.*See the UK Water Quality Directive*

ammonia, arsenic, chlorine, chromium(III), chromium(VI), copper, cyanide, cypermethrin, diazinon, 2,4-dichlorophenol, 2,4-dichlorophenoxyacetic acid (2,4-D), dimethoate, iron, linuron, mecoprop, permethrin, phenol, toluene, zinc, and the following recently added pollutants: benzyl butyl phthalate, carbendazim, chlorothalonil, 3,4-dichloroaniline, glyphosate, manganese, methiocarb, pendimethalin, tetrachloroethane and triclosan.

Source: <http://www.wfd.uk.org/sites/default/files/Media/Environmental%20standards/UKTAG%20Environmental%20Standards%20Phase%203%20Final%20Report%2004112013.pdf>.

the US. Briefly, the Water Quality Directive has identified the following pollutants shown in Table 1.11.

The UK government has determined that sampling and analyzing water quality 12–20 times per year will establish that river water quality standards have been met approximately 90–95% of the time. Table 4 of the UK standards establishes the number of permissible failures in a dataset that will lead to indicating that water quality standards have not been met, as shown in Table 1.12.

Most of the UK effluent standards have an “upper tier” (do not exceed limit) and an effluent value which must be achieved 95% of the time. The 95% effluent standard is established using river water quality modeling, where the  $BOD_5$  and other minimum river water quality parameters should be achieved approximately 90% of the time. The 95% effluent limit is also based upon a log-normal statistical distribution, which will be discussed later. The exceedances to the permit limits are determined by a look-up table (presented above) which considers the accuracy of the test, and the likelihood that the reported values may actually be within permit parameters because of the test’s accuracy.

**Table 1.12** UK water quality sampling table for determining compliance with standards UK directive Table 4.

Look-up table for 95% confidence of failing a 95 percentile standard	
Number of samples	Required number of samples exceeding standard
4–7	>1
8–16	>2
17–28	>3
29–40	>4
41–53	>5
54–67	>6

The UK water quality standard is found here: <http://www.wfd.uk.org/sites/default/files/Media/Environmental%20standards/UKTAG%20Environmental%20Standards%20Phase%203%20Final%20Report%2004112013.pdf>.

There is a further complication, which seems to be used more in Scotland than England, Wales, or Northern Ireland. If one fails the 95-percentile requirement but meets a percentage removal of the influent load, the plant is determined to have been in compliance.<sup>38</sup>

Prosecution of the violator is also not automatic. The EA (England/Wales) or SEPA (Scotland) may decide that there were exceptional circumstances, or they were warned in advance of the cause and what was being done to prevent it, or that they accept that measures are in place to prevent it from happening again. Should they decide to prosecute, the fine is still not fixed; it goes to court. There is an upper limit to the fine, but what is paid may be less – (if) the court decides.

The maximum fine appears to be £20 000.<sup>39</sup>

The water quality standards are established on a watershed-by-watershed basis, by assessing what is ecologically acceptable to the river, and are enforced and compared with a set of standards designed to ensure that benefit of the doubt goes to the polluter.<sup>40</sup> The preference is to avoid prosecution, and the authorities will work with companies to ensure that steps are taken to avoid the problem in the future. If the case goes to court there is no control by the EA on the level of fine, but it will not exceed £20 000.

### 1.8.12 EU Water Quality Standards and Effluent Limits

The European Union approach to water pollution discharges is very different. There are a number of details involved in obtaining a permit, but the basic philosophy is very similar to an odometer. The permittee pays a fee for the right to discharge pollutants to the environment, based upon negotiated values and water quality criteria, and the permittee pays per kilogram of materials discharged.<sup>41</sup> It is analogous to an odometer because the meter is running and the higher the discharge amount, the faster the meter runs and the higher the fees.

When it comes to determination of individual water quality parameters and effluent standards, the EU is a bit of a mixed bag. Germany has national mass limits, a national consent value, with a multiplier of the mass discharged above the consent value. But, like the UK, “exceptional circumstances” is a defense, and, unlike the UK system, severe winter or heavy rainfall is accepted as an exceptional circumstance.<sup>42</sup> The discharge limits are based on the Water Framework Directive (WFD) ([http://ec.europa.eu/environment/water/water-framework/index\\_en.html](http://ec.europa.eu/environment/water/water-framework/index_en.html)). This states that all water bodies are required to have a good ecological water quality by 2015.

If technical or financial circumstances make timely compliance prohibitive, an extension can be granted if there is sufficient excuse. The EU also has an Urban Wastewater Directive whose objective is to protect the environment from the adverse effects of urban wastewater discharges and discharges from certain industrial sectors.<sup>43</sup>

Every member state can then apply this directive as they wish, as long as they meet the standards set forth. In most countries, although the WFD allows for variable discharge limits, many still use fixed discharge limits. There are some exemptions, usually for industry where it does not make technical or financial sense.<sup>44</sup>

The EU also has a list of its own priority pollutants that member states must regulate (Table 1.13). That list of priority pollutants is very similar to the USEPA's priority pollutants, except that the enforcement is left to the member states.

### 1.8.13 Other Water Quality Requirements

We have seen how the stream and river water quality requirements for fish and for recreational activities are established. There are many other types of requirements for water: drinking water, agricultural water, industrial water (boiler and cooling water), to name but a few. In all of these categories, the water quality requirements are tailored to the use, and if the available water is not of sufficient quality for the intended use or purpose, it must be treated to conform to the requirements.

#### 1.8.13.1 US Primary and Secondary Drinking Water Standards

One of the most important uses and highest classifications of use is for drinking water. The water must be free of any harmful substances or organisms.<sup>45</sup> Drinking water has some of the greatest restrictions on water contaminant levels (from USEPA)<sup>46</sup>: nitrate,  $\text{NO}_3\text{-N}$   $10 \text{ mg l}^{-1}$ ; benzene,  $0.005 \text{ mg l}^{-1}$ ; bacterial contamination such as Cryptosporidium and *Giardia lamblia*, zero; uranium,  $0.03 \text{ mg l}^{-1}$ ; pesticides such as Lindane,  $0.0002 \text{ mg l}^{-1}$ ; chromium (total)  $0.1 \text{ mg l}^{-1}$ ; cadmium  $0.005 \text{ mg l}^{-1}$ .

The USEPA uses a two-tier list of Primary and Secondary Drinking Water Standards, and Maximum Contaminant Levels and Treatment Technology Standards to establish the requirements for limitations on drinking water. The Treatment Technology Goals have been established for those contaminants that cannot be effectively removed. The EPA also has a more extensive list of microbiological contaminants than the EU, UK, or WHO.

**Table 1.13** EU list of priority water pollutants.

	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	X
(3)	1912-24-9	217-617-8	Atrazine	
(4)	71-43-2	200-753-7	Benzene	
(5)	Not applicable	Not applicable	Brominated diphenyletheriv	X
	32534-81-9	Not applicable	Pentabromodiphenylether (congener numbers 28, 47, 99, 100, 153, and 154)	
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	Chloroalkanes, C10-13 iv	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos (chlorpyrifos-ethyl)	
(10)	107-06-2	203-458-1	1,2-dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	
(13)	330-54-1	206-354-4	Diuron	
(14)	115-29-7	204-079-4	Endosulfan	X
(15)	206-44-0	205-912-4	Fluoranthenevi	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-158-9	Hexachlorocyclohexane	X
(19)	34123-59-6	251-835-4	Isoproturon	
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-nonylphenol)	X
(25)	1806-26-4	217-302-5	Octylphenols	
	140-66-9	Not applicable	(4-(1,1',3,3'-tetramethylbutyl)-phenol)	
(26)	608-93-5	210-172-5	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	

(continued)

**Table 1.13 (Continued)**

	<b>CAS number</b>	<b>EU number</b>	<b>Name of priority substance</b>	<b>Identified as priority hazardous substance</b>
(28)	Not applicable 50-32-8 205-99-2 191-24-2 207-08-9 193-39-5	Not applicable 200-028-5 205-911-9 205-883-8 205-916-6 205-893-2	Polyaromatic hydrocarbons (Benzo(a)pyrene) (Benzo(b)fluoranthene) (Benzo(g,h,i)perylene) (Benzo(k)fluoranthene) (Indeno(1,2,3-cd)pyrene)	X X X X X
(29)	122-34-9	204-535-2	Simazine	
(30)	Not applicable 36643-28-4	Not applicable	Tributyltin compounds (Tributyltin-cation)	X X
(31)	12002-48-1	234-413-4	Trichlorobenzenes	
(32)	67-66-3	200-663-8	Trichloromethane (chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	

**Additional pollutants added by amending directive 88/347/EEC and 90/415/EEC**

	<b>CAS number</b>	<b>Name of other pollutant</b>
(6a)	56-23-5	Carbon-tetrachloride <sup>a)</sup>
(9b)	Not applicable 50-29-3	DDT total <sup>a)</sup> b) Para-para-DDT <sup>a)</sup>
(9a)	309-00-2 60-57-1 72-20-8 465-73-6	Cyclodiene pesticides Aldrin <sup>a)</sup> Dieldrin <sup>a)</sup> Endrin <sup>a)</sup> Isodrin <sup>a)</sup>
(29a)	127-18-4	Tetrachloro-ethylene <sup>a)</sup>
(29b)	79-01-6	Trichloro-ethylene <sup>a)</sup>

- a) This is not a priority substance but one of the other pollutants for which the environmental quality standards (EQS) are identical to those laid down in the legislation that applied prior to 13 January 2009.
- b) DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU number 200-783-0).

Source: [http://ec.europa.eu/environment/water/water-framework/priority\\_substances.htm](http://ec.europa.eu/environment/water/water-framework/priority_substances.htm).

#### 1.8.13.2 WHO Drinking Water Quality Guidelines

By comparison, the World Health Organization (WHO) has a slightly different list of recommended water quality guidelines. The guidelines are explained in a 564-page document available from the WHO website.<sup>47</sup> The WHO publishes guidelines rather than standards because they generally lack the power to enforce the guidelines in the various countries around the world. Of significance is the fact that the WHO guideline on nitrate is five times the maximum permitted value in the US. Higher nitrate levels may have an association with methemoglobinemia, or the “blue baby syndrome,”<sup>48</sup> and several other diseases.

#### 1.8.13.3 EU Drinking Water Directives

The EU publishes directives that serve as guidelines for the member states. The language is “should comply” rather than “must comply” when compared with the US. One of the principal differences in the EU directives is in the area of nitrate. The *EU Directive on Water Quality* limits the concentration of nitrate to no more than  $50 \text{ mg l}^{-1}$   $\text{NO}_3\text{-N}$ .<sup>49</sup> The US requires an upper limit of  $10 \text{ mg l}^{-1}$  of nitrate, and a different set of bacteriological parameters, and generally comparable but generally slightly higher levels of individual contaminants, such as lead and pesticides.

#### 1.8.13.4 UK Drinking Water Standards

The UK Drinking Water Standards are also generally comparable with the US standards, with some numerical limits higher and some lower than US standards.<sup>50</sup> The UK standards are also comparable with the EU standards, but are a bit more restrictive overall.

### 1.9 Water Use Data and Some Discharge Characteristics

Industrial water use varies widely with the industry and the technology used. Most if not all industries can be categorized on the basis of water use and product involved. The industrial effluents consist of a base flow (including sanitary flows and some consistent operations) and process-related flows that are often in proportion to the process production. This is true for both quantity of water use and the amount of pollutants produced by a plant or a process. Sometimes, in larger plants, things like boiler blowdown and cooling flows are more constant than the flows and pollutant loadings from individual processes. About the only way to make an accurate determination is to attempt to perform a water balance for the entire plant and account for the flows and water use. (The word “attempt” is used with “water balance” because, more often than not, water use balances do not balance despite one’s best efforts!)

One of the best sources for information on industrial water use is somewhat outdated, but only because some of the technologies described have changed. In the 1970s through to the early 1980s, the USEPA published Effluent Guidelines for discharges to surface waters. The summary of the documents are reflected in the water pollution control regulations published in the Federal Register 40 CFR Chapter I, Subchapter N – Effluent Guidelines and Standards Parts 400 through 471.<sup>51</sup> The regulations are both broad and deep. The headings of each of the Subparts contain a number of subcategories which deal with individual manufacturing products within a broader industrial category. An example of the organization and breakdown of a typical category can be found in Table 1.14.

**Table 1.14** Typical breakout of Federal Register effluent guidelines and standards for the pesticide chemicals subpart.

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PART 455 – PESTICIDE CHEMICALS (§§ 455.10–455.67)
§ 455.10 – General definitions.
SUBPART A – Organic Pesticide Chemicals Manufacturing Subcategory (§§ 455.11–455.27)
SUBPART B – Metallo-Organic Pesticide Chemicals Manufacturing Subcategory (§§ 455.30–455.37)
SUBPART C – Pesticide Chemicals Formulating and Packaging Subcategory (§§ 455.40–455.47)
SUBPART D – Test Methods for Pesticide Pollutants (§§ 455.50–455.50)
SUBPART E – Repackaging of Agricultural Pesticides Performed at Refilling Establishments (§§ 455.60–455.67)
Table 1 to Part 455 – List of Organic Pesticide Active Ingredients
Table 2 to Part 455 – Organic Pesticide Active Ingredient Effluent Limitations Best Available Technology Economically Achievable (BAT) and Pretreatment Standards for Existing Sources (PSES)
Table 3 to Part 455 – Organic Pesticide Active Ingredient New Source Performance Standards (NSPS) and Pretreatment Standards for New Sources (PSNS)
Table 4 to Part 455 – BAT and NSPS Effluent Limitations for Priority Pollutants for Direct Discharge Point Sources that use End-of-Pipe Biological Treatment
Table 5 to Part 455 – BAT and NSPS Effluent Limitations for Priority Pollutants for Direct Discharge Point Sources that do not use End-of-Pipe Biological Treatment
Table 6 to Part 455 – PSES and PSNS for Priority Pollutants
Table 7 to Part 455 [Reserved]
Table 8 to Part 455 – List of Pollution Prevention Alternative Practices
Table 9 to Part 455 – Group 2 Mixtures
Table 10 to Part 455 – List of Appropriate Pollution Control Technologies

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*Note:* There are 10 Appendices (Tables 1–10) that address active ingredients, mixtures, priority pollutants, alternative practices, and other similar subjects.

*Authority:* Secs. 301, 304, 306, 307, and 501, Pub. L. 92-500, 86 Stat. 816, Pub. L. 95-217, 91 Stat. 156, and Pub. L. 100-4 (33 U.S.C. 1311, 1314, 1316, 1317, and 1361).

*Source:* 43 FR 17776, Apr. 25, 1978, unless otherwise noted.

The regulations were developed by the USEPA through studying the associated industries in detail, and selecting the best technologies available and setting effluent guidelines on those industries. The source documents have useful information, and most if not all can be found with a search for the Effluent Guidelines Development Documents on the USEPA's website. Many of the development documents are available in portable document format (PDF) and are free to download, while others must be ordered from the National Technical Information at a reasonable price. The Development Documents contain recommendations for best available technology, which, in some cases, is still in use, and new source performance standards for any facilities built or rebuilt after the date of issue of the individual regulations. The new source performance standards (NSPS) Regulations are applicable to new industries and processes.

The Development Documents also contain process descriptions and block flow diagrams for many of the regulated processes, but do not contain equipment sizes, flow rates, or technical details, as many of the details are considered proprietary to the companies. The Development Documents also estimate the water usage per unit of production for the various processes. As such, they are extremely helpful for initial investigations and process evaluations.<sup>52</sup>

### 1.9.1 Water Use by Municipalities

Water use by municipalities is often regulated by both design codes and fire codes. The fire codes specify the amount of water that must be supplied in an emergency, and the minimum pressure in the distribution system. The actual water use depends upon the economic activity and development base of the country. UNESCO cites that municipal water use is expected to grow to between 500 and 1000 liters per person per day (l/d) by the year 2100. In many places in the US, the water consumption rates are already at that figure. In less developed countries, water use is often less than 100–150 l/d.

Figures on how water is used in US households vary widely. A typical family of four living in an older house with 8 l flush toilets, and larger shower heads will use between 480 and 525 liters per capita per day (l/c/d) for interior use, and 280–446 l/c/d for exterior use (lawn watering, etc.).<sup>53</sup> Add to that figure commercial and industrial water use in cities and towns, and system water losses. On average, the domestic water use in the US accounts for 57% of the total water use; commercial water use 15%; industrial water use 13%; thermoelectric power use <1%; and public use losses 14%.<sup>54</sup>

Note that approximately 14% of the treated water used in the United States is lost through leaks, broken piping, cracks, and other sources. The wastewater collection system figures tell quite another story. The wastewater figures in terms of household uses range from 290 l to over 775 l per day, and the projections used for sewer and sewage treatment plant design are generally by code rather than by measurement.<sup>55</sup> Other studies indicate that the wastewater return rate is between 56% and 79% of the water supplied, based on a study of the cities of Lockhart and Luling, Texas, in 2011.<sup>56</sup> The point is that the

wastewater flows coming from residential areas are less than the water supplied to those areas, in dry weather, and may be substantially greater in wet weather. The water use and the wastewater flows have two diurnal peak flows. The first is between 6 and 9 a.m. (weekdays) and the second is between 6 and 8 p.m. weekdays. The peak flow rates are between three and four times the average daily consumption. The night-time low flows are between 20% and 40% of the daily average flow, and during the middle of the day, the residential generation of wastewater generally drops to about 70% of the daily average flow. However, the flow patterns for an individual household vary significantly, and only when one gets above about 20–30 dwelling units does a more uniform pattern exist.

Sewers leak into the groundwater, and they can serve as a good collection source for groundwater. When the local water table is above the sewer line, one can count on infiltration. In fact, there are American Society for Testing Materials (ASTM) standards and American Society of Civil Engineers (ASCE) standards for acceptance of new sewers based upon infiltration. The infiltration allowance is quite wide and varies from 100 to 100 000 gal/d-inch of diameter-mile ( $90\text{--}95\text{ l cm}^{-1}$  diameter/km of pipe to  $90\,000\text{--}95\,000\text{ l cm}^{-1}/\text{km}$ ) or 30–3000 gal/in. of circumference-mile ( $27\text{--}30\text{ l cm}^{-1}$  circumference/km to  $2700\text{--}3000\text{ l cm}^{-1}/\text{km}$ ).

Another way of checking the water infiltration rates is by comparison of the  $\text{BOD}_5$  loading and the strength of the wastewater. The standard figure for generation of  $\text{BOD}_5$  per person per day for the US is 0.17 lb or 77 g. At a flow rate of 100 gal per person/per day, the wastewater would have a strength of around  $203\text{ mg l}^{-1}$ . Industrial and commercial wastes have a much greater strength and can influence the estimate of the waste strength. In other countries, the figures do not necessarily apply: in Zambia and Kenya, the per capita waste loadings contributed by each individual are 36 and 23 g respectively, according to a Water Research Commission report dated 1993.<sup>57</sup>

In times of wet weather, such as snow-melt or rainfall, the quantity of storm-water can increase by three to five times because of increased infiltration, and connections of household downspouts and surface drains to the sanitary sewer. In older parts of the world, combined sewers are used. The dry weather flow may represent between 1% and 10% of the capacity of the sewer system. Surface drainage during wet weather can cause immense increases in flows, and the sewer systems have been connected to bypasses, so that they can discharge directly to a river. In recent times, there has been a movement to capture and contain the “first flush,” that portion of the storm flow that contains the majority of the surface dust and contamination from surface drainage that occurs with the onset of precipitation. A number of US cities have large underground structures designed to capture the first flush, and then, after the storm subsides, pump it to the treatment works.

### 1.9.2 Agricultural Water<sup>58</sup>

Water used for agricultural purposes must be relatively free from salts, especially boron, sediments, and herbicides. Water used for certain vegetable and fruit crops where the product is generally eaten raw, should also be free from pathogens and parasites. All water used in canning or cooking operations should be drinking water quality, and free from metals, various carbonate salts, and especially free from bacterial contamination. In certain areas of southeast Asia, where crops are fertilized and irrigated with human wastes, the cultural practice is only to eat cooked vegetables. The WHO limits on bacterial quality for irrigation water are more related to clogging of drip systems.<sup>59</sup>

Irrigation water uses a combination of measures, including some restrictions on contents such as boron  $0.75 \text{ mg l}^{-1}$ ; iron  $5 \text{ mg l}^{-1}$ ; selenium  $0.02 \text{ mg l}^{-1}$ ; and a balance of different types of salts such as the sodium absorption ratio, which is a proportioning of the sodium, calcium, and magnesium salts dissolved in the water. Calcium and magnesium tend to counter the adverse effects of sodium on the structure of the soil, to maintain its porosity and other characteristics. For many agricultural uses, the users plot the sodium absorption ratio (SAR) against the conductivity to determine the potential for salt damage to the crops. The classical reference on the subject of SAR is listed Handbook 60 from the US Agricultural Research Service.<sup>60</sup>

The principal concern for agricultural crops is the *adjusted* sodium absorption ratio or SAR. The SAR is given by the formula:

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca} + \text{Mg})/2}}$$

where Na, Ca, and Mg are the concentrations of sodium, calcium, and magnesium ions expressed in milliequivalents per liter. Various authors have suggested modifications to the equation to help account for carbonate and bicarbonate alkalinity.<sup>61</sup> Among the principal concerns are the buildup of sodium and potassium in the soils, and the reduction of soil permeability and reduction in crop yields up to about 50% for high SAR values of around 30.

### 1.9.3 Cooling Water

Cooling water is a heat receiver from hot process equipment. As such it needs to be relatively clean (low in suspended solids), a near-neutral pH, and relatively free of chemicals that will cause deposition on hot and warm surfaces, such as silicates and calcium bicarbonate, and free of chemicals that will corrode the equipment it is cooling. The cooling water is used and re-used between an average of three times and a maximum of eight times before it is too concentrated to

use and must be removed from the system to reduce the corrosion and fouling potentials of the water. The principal factors that cause the tower to lose water include evaporation, drift, and splashing. Tower losses from drift and splashing represent about 0.01% of the tower throughput. The principal loss is from evaporation, where 1000 BTU (British Thermal Units) of heat loss represents the evaporation of 1 pt of water, or 2260 kJ per kg of liquid evaporated.

The tower water is chemically treated to reduce the tendency of the dissolved materials to deposit on the inside of pipes and heat exchangers, and it also has to be passivated so that it does not attack metal used in the tower internals, or form “white rust” (zinc oxides) on galvanized metals. Control of algae and bacteria in the tower is also necessary, as algal buildup can also lead to corrosion. Depending upon the location of the facility and the water quality, silicate buildup often tends to be a limiting factor which controls the amount of blowdown to maintain the tower water quality. At one time in the US, hexavalent chromium ( $\text{Cr}^{6+}$ ) was used to prevent corrosion and bacterial fouling. This practice was banned in 1994 under the provisions of the Toxic Substances Control Act for all systems used in “comfort cooling” (air conditioning), but is still permitted in certain other industrial applications.<sup>62</sup> Other chemical treatment systems use a variety of organic compounds to prevent bacterial growth, and zinc, antimony, molybdenum, and phosphorus compounds, to prevent corrosion and passivate the metals in the cooling water system.<sup>63</sup>

Baltimore Air Coil<sup>64</sup> provides the following guidance: pH 6.5–9; hardness as  $\text{CaCO}_3$  30–750 mg l<sup>-1</sup>; silica (maximum) 150 mg l<sup>-1</sup>. The numbers are higher because the cooling tower loses up to 3% due to drift (droplets of water being blown out of the tower by wind), and much greater quantities due to evaporation. Another handy reference is the San Diego, CA, County Water Authority,<sup>65</sup> and more detailed guides are available from EPRI, the Electric Power Research Institute,<sup>66</sup> the Water District for San Jose, California,<sup>67</sup> and a Best Management Practices Guide prepared by Jacksonville Environmental Authority.<sup>68</sup> The water in the towers is always balanced with makeup and blowdown waters to maintain the water chemistry at certain ranges. In areas where water is in short supply, it is not uncommon for power and other companies to use treated municipal effluent and other wastewater sources for tower makeup water.<sup>69</sup>

#### 1.9.4 Boiler Water

The two types of boilers in use are fire tube and water tube. The fire tube boilers are also called Scotch Marine Boilers. For safety and heat transfer reasons, the fire tube boilers do not usually operate at pressures in excess of 16 bar.<sup>70</sup> Some specially designed water tube boilers operate at pressures well above 100 bar.

The two types have slightly different water quality requirements. A boiler has been described as a firebox with a metal oxide housing, and it is important to provide and condition the water so that it does not cause unwanted deposits

**Table 1.15** ASME boiler water quality guidelines.

Pressure (PSI)/bar	Hardness (mg l <sup>-1</sup> as CaCO <sub>3</sub> )	Iron (mg l <sup>-1</sup> )	Copper (mg l <sup>-1</sup> )	Silica (SiO <sub>2</sub> ) (mg l <sup>-1</sup> )	Total alkalinity (mg l <sup>-1</sup> CaCO <sub>3</sub> )	Specific conductance – un-neutralized ( $\mu\Omega\text{ cm}^{-1}$ )
(0–300) 0–20.5	0.3	0.1	0.05	150	700	7000
(301–450) 20.5–30.6	0.3	0.05	0.025	90	600	6000
(451–600) 30.6–41	0.2	0.03	0.02	40	500	5000
(601–750) 41–51	0.2	0.025	0.02	30	400	4000
(751–900) 51–61	0.1	0.20	0.015	20	300	3000
(901–1000) 61–67	0.05	0.02	0.015	8	200	2000
(1001–1500) 67–102	0.0	0.10	0.01	2	0	150
(1501–2000) 102–136	0.0	0.10	0.01	1	0	150

in turbines or pipes, and it is not corrosive to the iron oxide coating. Solids in the water will accumulate in the boiler water, and there is the added requirement that the water has little or no measurable dissolved oxygen and carbon dioxide because the presence of either will attack the boiler and the steam distribution system. Boilers also use oxygen scavengers to control corrosion. An excellent guide to boiler water treatment is available as a free download from EPRI Publication NP-6377-SLV2.<sup>71</sup>

A high-pressure boiler will have much more restrictive water quality requirements than low-pressure systems. The recommendations from the American Society of Mechanical Engineers (ASME) give water quality limits for the different types of boilers, based on their operating pressures (Table 1.15). The dissolved oxygen water quality requirement for the feed water is shown before the oxygen scavenger chemicals are added to reduce the oxygen concentrations in the boiler system to zero.

Cooling tower water quality and heat exchanger water quality are often linked or interchangeable. In one unusual instance, a combination of phosphate, ammonia, and calcium in groundwater which was used for cooling heat exchangers was found to cause hard scale-forming deposits in a refinery in southern Ohio. The source of the scale was attributed to struvite, a phosphorus-magnesium-ammonia compound which has the general formula of  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ , which can form when the principal components are present in approximately 1 : 1 : 1 M ratios. It can be removed by acid dissolution.

### 1.9.5 Other Industrial Water Quality Requirements

We covered the water requirements for boilers, agriculture, drinking, and cooling towers above. There are a few more we need to examine: the petrochemical, petroleum, and steel and paper industries, and fracking.

### 1.9.5.1 Steel Industry

Water quality is generally for cooling and quenching. The water should have low bacterial content, and generally be free from excessive carbonate hardness or other chemicals that could cause deposits in the piping or on steel slabs during quenching. Similarly, the water should not have a pH less than 5, and should be free from suspended solids. Steel production in North America and Europe has declined about 20% between 1980 and 2013, but still represents two of the largest two components of manufacturing, producing a total of almost 374 000 000 tons, with the Asian subcontinent excluding China producing 827 313 000 tons annually. Integrated steel plants consume about 93 000–109 500 l of water per MT of steel produced. Cooling water use is between 1000 and 2200 l per ton of steel produced, depending upon the process.<sup>72</sup>

### 1.9.5.2 Paper Industry

According to a study by the University of Minnesota, the “US Benchmark for water use within pulp and paper mills is approximately 17 000 gal/ton of paper (58 336 l/MT) with one of the most efficient Kraft pulp and paper mills using 4500 gal/ton (15 441 l/MT).”<sup>73</sup> The entire paper industry has been attempting to reduce water use since the 1970s, and their efforts to recover black liquor, implement new changes in non-chlorine bleaching, using counter-current washing techniques, water recycling in the press section, and generally implementing water conservation and recycling practices has reduced the water use in some plants by up to 40%, at an annual saving of over \$700 000.

### 1.9.5.3 Petrochemical Industry

The petrochemical industry is a major user of water. The world-wide production of oil is estimated at 90.5 million barrels per day. The US is a major producer of oil, estimated at 12.4 million barrels per day.<sup>74</sup> Of that, approximately 17.7 million barrels per day are refined. (The difference between refinery capacity and production is the approximate quantity of oil imports).

The World Bank, in a 1999 study, estimated the water use for production at 0.7–0.83 m<sup>3</sup> of water per barrel of oil produced on an industry average. The estimated total water use figure for the US is then in the range of 12.4–14.7 million m<sup>3</sup>/day (3.275–3880 Mgal/day).

Most of the wastewater generated is from cooling, but some of the water is also from desalting operations and includes moderate chlorides in the effluent (see Table 1.16).

Other waste streams may have greater quantities of oil, but most have some levels of heavy metals including lead, chromium, cadmium, nickel, and vanadium.

**Table 1.16** Wastewater characteristics from petroleum refining.

Pollutant	Strength ( $\text{mg l}^{-1}$ )
BOD <sub>5</sub>	150–250
COD	300–600
Phenol	20–200
Oil in the desalter	100–300
Benzene	1–100

#### 1.9.5.4 Petroleum Exploration and Production Operations

The petroleum industry uses a lot of water for production operations. The Texas Railroad Commission (who regulates the production of oil in Texas) has indicated that the act of fracking in Texas uses significant quantities of water. There is a difference between fracking of vertical and horizontal wells, principally due to the difference between the length of the horizontal well in the formation versus the vertical thickness of the formation. Vertical well fracking uses about 1.2 million gallons of water ( $4540 \text{ m}^3$ ) per well, while horizontal well fracking uses about three times as much water.<sup>75</sup> The effluent characteristics for fracking water are difficult to determine because of what is added by the geologists drilling the wells. Table 1.17 from the Penn State University study of fracking in the Marcellus Shale (principally in Pennsylvania and West Virginia) indicates some of the chemicals added to the water by the geologists who drill the wells.

There are well over 150 different additives used in fracking. The principal compounds include propants (sand and other compounds to hold the frack

**Table 1.17** Principal chemicals added to enhance one fracked well in Pennsylvania.

3.81 million gallons of water
4.57 million pounds of sand
1333 gal of hydrochloric acid
1695 gal of a friction reducer
2211 gal of an antimicrobial agent
386 gal of a scale inhibitor (which includes ethylene glycol, a component of antifreeze).

Source: <http://extension.psu.edu/natural-resources/water/marcellus-shale/waste-water/current-and-emerging-treatment-and-disposal-technologies>.

open), antimicrobial compounds, hydrochloric (muriatic) acid, gel compounds such as guar gum, friction-reducing compounds, petroleum derivatives, and just about anything else the geologist in charge of the well drilling believes will increase the production. All of these compounds will come out of the well in varying concentrations as the well is producing. The acids added to the well will tend to dissolve the fracked rock and open the cracks, but will dissolve the metals and other compounds in the rock, so heavy metals are also expected in the effluent. The quantity of formation water produced will initially be high, depending upon the tightness of the formation and other factors. The quantity of the formation water will drop off over time, on a power curve until it stabilizes between 90 and 120 days.

If left untreated, the fracking water will comprise hazardous waste and must be treated or sent to a chemical disposal facility. Disposal of the water into a publicly owned treatment works (POTW) is possible, but some pretreatment may be required, and the sludges from the treatment will also be hazardous wastes in need of proper labeling, packaging, transportation, and disposal at an approved disposal facility. In some instances, fracking wastewaters can be disposed of in underground wells specially designed for the purpose, but these wells are in different formations and deep underground so as to contain the pumped wastes.

## Notes

- 1 Distilled water has no dissolved solids. The human intestines are membranes. Low dissolved solids in the intestine can cause the membrane to pass dissolved solids, extracting them from the blood in an attempt to equalize the concentrations and reduce trans-membrane pressures.
- 2 Some typical ranges for various types of water are: deionized water  $\sim 0.1 \mu\text{S cm}^{-1}$ ; distilled water  $\sim 0.5 \mu\text{S cm}^{-1}$ ; tap water  $\sim 500\text{--}800 \mu\text{S cm}^{-1}$ ; seawater  $\sim 56\,000 \mu\text{S cm}^{-1}$ , and brackish water  $\sim 100\,000 \mu\text{S cm}^{-1}$ . (*Source:* MBH Engineering Systems: [http://www.mbhес.com/conductivity\\_measurement.htm](http://www.mbhес.com/conductivity_measurement.htm)).
- 3 See <http://www.analyticexpert.com/2012/08/measuring-total-dissolved-solids-tds-with-a-tds-meter> for more information.
- 4 For example, G.W.C. Kaye and T.H. Laby (1986) *Tables of Physical and Chemical Constants*, 15, New York, Longman; *The Handbook of Physics and Chemistry*, CRC Press.
- 5 *Solubility of Selected Gases in Water*, by L.E. Geventman. Found in [http://sites.chem.colostate.edu/diverdi/all\\_courses/CRC%20reference%20data/solubility%20of%20gases%20in%20water.pdf](http://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/solubility%20of%20gases%20in%20water.pdf).
- 6 American Public Health Association, American Water Works Association, and the Water Environment Federation (2017). Oxygen Dissolved Method

- 4500/Azide Modification. In: *Standard Methods for the Examination of Water and Wastewater*, 23e. Or see [www.standardmethods.org](http://www.standardmethods.org).
- 7 A table of aqueous solubility and Henry's law constants for almost 600 organic compounds can be found at: [http://chemistry.mdma.ch/hiveboard/rhodium/pdf/chemical-data/solubility\\_organic.pdf](http://chemistry.mdma.ch/hiveboard/rhodium/pdf/chemical-data/solubility_organic.pdf).
  - 8 The solubility of nitrogen in water at ambient temperature is approximately  $20 \text{ mg l}^{-1}$ , which we have ignored in the calculations. Similarly the solubility of oxygen in water is about  $16 \text{ mg l}^{-1}$  at the same temperature.
  - 9 [http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part\\_5.pdf](http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf).
  - 10 <http://cece.ucf.edu/people/taylor/teaching/pdf/Coagulation-Softening.pdf>.
  - 11 pH will vary somewhat with temperature. The value of pH = 7.0 is only valid for  $25^\circ\text{C}$ . At  $100^\circ\text{C}$  the value of pH for pure water is approximately pH  $\approx 6.75$ , and at  $10^\circ\text{C}$ , pH  $\approx 7.24$ . See the following articles: [http://reagecon.com/pdf/technicalpapers/Effects\\_of\\_Temperature\\_on\\_pH\\_v4-\\_TSP-01-2.pdf](http://reagecon.com/pdf/technicalpapers/Effects_of_Temperature_on_pH_v4-_TSP-01-2.pdf), and: [http://chemwiki.ucdavis.edu/Physical\\_Chemistry/Acids\\_and\\_Bases/Aqueous\\_Solutions/The\\_pH\\_Scale/Temperature\\_Dependent\\_of\\_the\\_pH\\_of\\_pure\\_Water](http://chemwiki.ucdavis.edu/Physical_Chemistry/Acids_and_Bases/Aqueous_Solutions/The_pH_Scale/Temperature_Dependent_of_the_pH_of_pure_Water).
  - 12 See <http://www.atsdr.cdc.gov/csem/csem.asp?csem=10&po=10> for human toxicity, and according to the USGS, trivalent chromium is between one third and one tenth as toxic as the hexavalent form of chromium. See [https://www.pwrc.usgs.gov/eisler/CHR\\_6\\_Chromium.pdf](https://www.pwrc.usgs.gov/eisler/CHR_6_Chromium.pdf).
  - 13 Sources for these figures are personal laboratory experience in treating chromium wastewaters from a cooling tower, and <http://www.hofflandenv.com/hydroxide-precipitation>.
  - 14 The US Geological Survey and the USEPA monitor the concentrations of certain contaminants in US waters. Their website <http://water.usgs.gov/nawqa/trace/arsenic> lists areas where arsenic is a potential contaminant. Radium contamination is tracked at <http://water.usgs.gov/nawqa/trace/radium>. It should also be noted that radium and radon are potential exposure problems in areas where the geology contains granite. Uranium is a natural contaminant of granite rock, and the daughter product is radium. In other parts of the world, arsenic is a natural contaminant found in waters from coal mining, and commonly in India. The issue was first identified in 1983, and since that time, West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, and Manipur in the flood plain of the Brahmaputra and Imphal rivers have had groundwater concentrations of arsenic in excess of  $50 \mu\text{g l}^{-1}$ . These concentrations are well above the recommended drinking water concentrations. See [www.cgwb.gov.in/documents/papers/incidpapers/Paper%208%20-%20Ghosh.pdf](http://www.cgwb.gov.in/documents/papers/incidpapers/Paper%208%20-%20Ghosh.pdf) for additional information.
  - 15 <http://www.epa.gov/region02/ust>.
  - 16 The Atlanta Toxic Substances and Disease Registry (ATSDR) has a paper on the health effects of BTEX. See: <http://www.atsdr.cdc.gov/interactionprofiles/IP-btex/ip05.pdf>. The individual constituents each have a TOX profile:

- <http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=468&tid=83>, as do many of the other individual components in petroleum.
- 17 See the following for more information: [https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&cad=rja&uact=8&ved=0CDUQFjAB&url=http%3A%2F%2Fwater.epa.gov%2Fscitech%2Fmethods%2Fcwa%2Fbioindicators%2Fupload%2F2007\\_07\\_10\\_methods\\_method\\_200\\_7.pdf&ei=5BfVICnL4m4ggTei4SQDA&usg=AFQjCNHGXd8BmBbcQ93nFICfVbw0W oDjw&sig2=9YRKvuVxdYpy2qkcMvETO&bvm=bv.84349003,d.eXY](https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&cad=rja&uact=8&ved=0CDUQFjAB&url=http%3A%2F%2Fwater.epa.gov%2Fscitech%2Fmethods%2Fcwa%2Fbioindicators%2Fupload%2F2007_07_10_methods_method_200_7.pdf&ei=5BfVICnL4m4ggTei4SQDA&usg=AFQjCNHGXd8BmBbcQ93nFICfVbw0W oDjw&sig2=9YRKvuVxdYpy2qkcMvETO&bvm=bv.84349003,d.eXY)
- 18 <http://eclabs.seas.wustl.edu/files/Flame%20AA%20Operating%20Manual.pdf>.
- 19 For example: See [http://www.epa.gov/watersecurity/pubs/guide\\_watersecurity\\_samplingforunknown.pdf](http://www.epa.gov/watersecurity/pubs/guide_watersecurity_samplingforunknown.pdf).
- 20 For example, see <http://chemistry.about.com/od/chemistrylabexperiments/a/cleanglassware.htm> and the fact that there are several companies that supply specially cleaned glassware and plastic for collecting environmental samples including [www.uline.com](http://www.uline.com), [www.coleparmer.com](http://www.coleparmer.com), [www.fishersci.com](http://www.fishersci.com), etc. Another reference for sampling water, and other media can be found at the following site: [www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh9404.pdf](http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh9404.pdf).
- 21 Not all countries have the same detection capabilities; in the example, we had to settle for one with a higher detection limit than that available in the US.
- 22 Non-detects (ND) and values below the practical quantification limits (PQL) often occur, indicating the machine detection limits. There is a debate in the regulatory community about how to handle the reporting and interpretation of something that the laboratory either did not find, or had an indication that the compound was present even if was below the quantification limits. One school of thought requires reporting a PQL or ND at half of the detection limit for the compound. (There is some logic in the reporting of the former, but not the latter.) Another school of thought requires that a ND or PQL value be reported at the detection limit. Still a third school of thought reports a non-detect or a PQL value as a zero. This is often important when the regulatory agency wants to sum up the total for all the detects and non-detects, and have them considered as part of a permit scheme.
- 23 The references are specific to the US only, but many other countries use the USEPA definitions and analytical provisions for their regulatory work. If in doubt, check with the country environmental agency laboratory.
- 24 There is a good guide to EU analytical protocols and procedures, with an excellent guide to the analytical protocols in the Appendices to the documents. See: <http://www.european-accreditation.org/publication/citac-eurachem-ta>. The standards biogroup also has a guide to statistical protocols in the EU: <http://www.standardsproposals.bsigroup.com/Home/getPDF/830>.
- 25 [http://www.who.int/water\\_sanitation\\_health/hygiene/emergencies/fs2\\_33.pdf](http://www.who.int/water_sanitation_health/hygiene/emergencies/fs2_33.pdf).
- 26 See: <http://or.water.usgs.gov/grapher/fnu.html> and [http://www.optek.com/Turbidity\\_Measurement\\_Units.asp](http://www.optek.com/Turbidity_Measurement_Units.asp).

- 27 A suspension of 100 ppm of silica (principally as diatomaceous earth) had a JTU of 21.5 units, and it is considered the “standard” for that measurement. Also see: [http://www.optek.com/Real\\_World\\_Turbidity.asp](http://www.optek.com/Real_World_Turbidity.asp).
- 28 The definition of the navigable waters of the United States is actually quite complex. The definition used to be “any body of water in which one could float a log.” Since the passage of the CWA in 1972, and subsequent to legal challenges the new definition of “navigable waters” has been modified. The clearest summary of the extent of these waters can be found in the Federal Register, Vol. 79, No.76, Monday April 21, 2014, Proposed Rules, pp. 22192–22194. The currently proposed changes will be found in the 40 CFR 203.3 when fully adopted. In general “navigable waters” includes the following:
- All waters that are currently used, were used in the past, or may be susceptible to use in interstate or foreign commerce, including all waters that are subject to the ebb and flow of the tide;
  - All interstate waters, including interstate wetlands;
  - The territorial seas;
  - All impoundments of a traditional navigable water, interstate water, the territorial seas or a tributary;
  - All tributaries of a traditional navigable water, interstate water, the territorial seas or impoundment;
  - All waters, including wetlands, adjacent to a traditional navigable water, interstate water, the territorial seas, impoundment or tributary; and
  - On a case-specific basis, other waters, including wetlands, provided that those waters alone, or in combination with other similarly situated waters, including wetlands, located in the same region, have a significant nexus to a traditional navigable water, interstate water or the territorial seas.
- Note that in certain specific cases defined in the regulations, some ditches, culverts, and other activities may be exempt from regulation.
- 29 Here the definition of a navigable waterway can be critical. Generally, it is taken to mean anything that has links to interstate commerce and in which one can float a log. That definition has been expanded slightly to include an area of drainage basin, but as a practical matter there are several industrial sites in the State of Florida which discharge to sink holes in a Floridian aquifer that were exempt from Federal but not State regulation, principally because the discharge could not be tracked in the aquifer because it was greatly diluted to the point that it could not be identified in the aquifer, without a very intensive and expensive groundwater investigation.
- 30 [http://water.epa.gov/learn/training/standardsacademy/upload/module\\_mixingzone.pdf](http://water.epa.gov/learn/training/standardsacademy/upload/module_mixingzone.pdf).
- 31 <http://www.mixzon.com/sales/uspricing.php>.
- 32 For example, see the EPA’s guidance on mixing zones: [http://water.epa.gov/scitech/swguidance/standards/upload/2007\\_01\\_31\\_standards\\_mixingzone\\_compendium.pdf](http://water.epa.gov/scitech/swguidance/standards/upload/2007_01_31_standards_mixingzone_compendium.pdf).

- 33 See the following: <http://www.law360.com/articles/486315/epa-raises-fines-for-air-water-pollution-violations>, and [http://www.epa.gov/region7/public\\_notices/CWA/309.htm](http://www.epa.gov/region7/public_notices/CWA/309.htm), and starting on page (349) 13 of 36, look at the penalty provisions [http://www.emlf.org/clientuploads/directory/whitepaper/McLusky\\_Vining\\_07.pdf](http://www.emlf.org/clientuploads/directory/whitepaper/McLusky_Vining_07.pdf).
- 34 American humor sometimes is used to highlight the adversarial relations between government and industry, as in this joke. *There are 3 great lies told in the US. The first is, "The check is in the mail." The second occurs when the boyfriend says to his girlfriend, "If you let me make love to you tonight, I promise that we will get married in the morning." The third great lie is when the local regulatory person shows up at the industry gate and says to the plant manager, "Hi, I'm from the EPA and I'm here to help you!"*
- 35 From Section 101(a)(2) and Section 303(c)(2) of the Clean Water Act.
- 36 <http://www.gpo.gov/fdsys/pkg/CFR-2011-title40-vol29/pdf/CFR-2011-title40-vol29-sec401-15.pdf>.
- 37 Personal communications from Jeremy Dudley (WRc.Plc), and Youri Amerlinck (University of Ghent).
- 38 In some cases, the removal standard based upon influent values is approximately 50% for TSS but only 20% for BOD (see [https://www.google.com/url?q=www.sepa.org.uk/about\\_us/idoc.ashx%3Fdocid%3Dcf86e6d5-6e0f-4f7e-8c5a-f1aac520b5df%26version%3D-1&sa=U&ei=fFXRVIfmHMmBywPV2YLgCw&ved=0CAUQFjAA&client=internal-uds-cse&usg=AFQjCNFUzabYAwS0UATD\\_quHxHqnRuqcqA](https://www.google.com/url?q=www.sepa.org.uk/about_us/idoc.ashx%3Fdocid%3Dcf86e6d5-6e0f-4f7e-8c5a-f1aac520b5df%26version%3D-1&sa=U&ei=fFXRVIfmHMmBywPV2YLgCw&ved=0CAUQFjAA&client=internal-uds-cse&usg=AFQjCNFUzabYAwS0UATD_quHxHqnRuqcqA). The foregoing was supplied by personal communication with Dr Jeremy Dudley of WRc Plc.
- 39 <http://archive.defra.gov.uk/environment/policy/enforcement/pdf/envleg-enforce-wrcreport.pdf>
- 40 <http://www.fwr.org/WQreg/Appendices/uwwtreport2.pdf>. These maps may be slightly out of date but illustrate the manner in which the standards are established.
- 41 [www.legislation.gov.uk/uksi/2010/675/pdfs/uksi\\_20100675\\_en.pdf](http://www.legislation.gov.uk/uksi/2010/675/pdfs/uksi_20100675_en.pdf).
- 42 By comparison, the US does not have exceptional circumstances, partially because its infrastructure is younger and has a design philosophy that requires separation of sanitary and storm sewers, treatment of stormwater first flush, and regulation of groundwater infiltration and inflows into the stormwater sewer system to keep the sanitary flows as small as practicable, even in wet weather. It is not uncommon for wet weather flows in municipal sewer systems to increase by a factor of between 3x and 6x the dry weather flows.
- 43 [http://ec.europa.eu/environment/water/water-urbanwaste/index\\_en.html](http://ec.europa.eu/environment/water/water-urbanwaste/index_en.html).
- 44 Personal communication: Dr. Youri Amerlinck.
- 45 There are a host of waterborne diseases which can be transmitted by contaminated water. A good list of those diseases can be found on the Arizona Public Health site: <http://www.azdhs.gov/phs/oids/epi/waterborne/list.htm>. Of most recent concern has been the issue of *Giardia lamblia*, and certain types of spore-forming bacteria that tend to be more resistant to certain types of disinfection.

- 46 Source for Drinking Water Standards: <http://water.epa.gov/drink/contaminants/#List>. Note that these standards are considered to be health protective over many years, and the levels of toxicity or acute hazard or damage to an individual would be many times higher. For many contaminants, the active levels of those materials are found on the CDC website: <http://www.astdr.cdc.gov/toxfaqs/Index.asp>.
- 47 [http://www.who.int/water\\_sanitation\\_health/publications/2011/dwq\\_guidelines/en/](http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/).
- 48 <http://www.newscientist.com/article/mg18925380.200-blue-baby-links.html>.
- 49 <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0676:EN:HTML>. See Annex 1 (several pages into the text), and see page 2 of <http://ec.europa.eu/environment/pubs/pdf/factsheets/nitrates.pdf>. The majority of cases have occurred in the UK when nitrate levels have been over  $100 \text{ mg l}^{-1}$ . However, in many cases bacterial contamination of the water causing gut infections was present or suspected. There have been no cases in the UK since 1972.
- 50 <http://dwi.defra.gov.uk/consumers/advice-leaflets/standards.pdf>.
- 51 See <http://water.epa.gov/scitech/wastetech/guide/industry.cfm>, and look at industry studies for the regulations: <http://water.epa.gov/scitech/wastetech/guide/industry.cfm#studies>.
- 52 One important caution is to be noted when using the Development Documents: there is no substitute for recent analyses of the wastestream to be investigated. Some of the documents are over 40 years old, and describe technologies that are no longer in use, and the regulations regarding what can be discharged have changed dramatically. For example, some of the documents relating to discharge from cooling towers contain information that one could expect up to  $250 \text{ mg l}^{-1}$  of hexavalent chromium in the blowdown from a tower. The use of hexavalent chromium was banned in 1994 under the provisions of the Clean Air Act, as  $\text{Cr}^{6+}$  is a human carcinogen and can cause lung cancers. See <http://www.epa.gov/ttnatw01/cool/fscoolt.pdf> for the citation.
- 53 Source: Desert Water Agency public data and <http://www.csgnetwork.com/waterusagecalc.html> calculator.
- 54 Source: "How we use water in the United States," USEPA: <http://esa21.kennesaw.edu/activities/water-use/water-use-overview-epa.pdf>.
- 55 See Appendix A: <http://www.doh.wa.gov/Portals/1/Documents/Pubs/337-103.pdf>.
- 56 See Table 9.3: <http://www.gbra.org/documents/studies/caldwell/09-WastewaterFlows.pdf>.
- 57 <http://www.unep.or.jp/Ietc/Publications/TechPublications/TechPub-15/3-1Africa/1-1.asp>.
- 58 Source for Irrigation Water Quality Standards: Texas A&M Agrilife Extension Service. Values listed are for long-term use – see page 6 for a comparison: <http://soiltesting.tamu.edu/publications/B-1667.pdf>.

- 59 <http://www.fao.org/docrep/t0551e/t0551e07.htm>. See comments at Table 27.
- 60 See the following articles: <http://www.iaeess.org/publications/journals/piaees/articles/2011-1%283-4%29/assessment-of-groundwater-quality-for-drinking-and-irrigation.pdf>, and a second article that instructs the method of creating a salinity diagram: [http://aces.nmsu.edu/pubs/\\_a/A116/welcome.html](http://aces.nmsu.edu/pubs/_a/A116/welcome.html). A third article from the US Agricultural Research Service, Handbook 60, discusses the repair of alkaline and salty soils: [http://www.ars.usda.gov/SP2UserFiles/Place/20360500/hb60\\_pdf/hb60complete.pdf](http://www.ars.usda.gov/SP2UserFiles/Place/20360500/hb60_pdf/hb60complete.pdf).
- 61 Two different formulations for the modified SAR are found in the following publications: Water Quality for Agriculture, a 1977 publication by the Food and Agriculture Division of the UN, found at [www.calwater.ca.gov/Admin\\_Record/C-110101.pdf](http://www.calwater.ca.gov/Admin_Record/C-110101.pdf), and Sodium Adsorption Ratio-Exchangeable Sodium Percentage Relationships in a High Potassium Saline-Sodic Soil by Charles published in 1983 by Springer-Verlag, in *Irrig Sci* (1984) 5: 173–179 found at <http://eprints.nwslr.ars.usda.gov/422/1/532.pdf>.
- 62 See the US Code of Federal Regulations: 40 CFR 749.68 – Hexavalent chromium-based water treatment chemicals in cooling systems.
- 63 For greater detail see: [www.emsd.gov.hk/emsd/e\\_download/pee/wcacsCoP\\_Part\\_3.pdf](http://www.emsd.gov.hk/emsd/e_download/pee/wcacsCoP_Part_3.pdf).
- 64 Source: Baltimore Air Coil <http://www.baltimoreaircoil.com/english/resource-library/file/579>.
- 65 <http://www.sdcwa.org/sites/default/files/files/water-management/recycled/techinfo-cooling-towers.pdf>.
- 66 [http://mydocs.epri.com/docs/PublicMeetingMaterials/0712/watertreatment\\_RFI\\_Final.pdf](http://mydocs.epri.com/docs/PublicMeetingMaterials/0712/watertreatment_RFI_Final.pdf).
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- 70 In a water tube boiler the pressure is in the individual tubes inside the boiler. In a Scotch Marine or fire tube boiler, the boiler shell is under pressure. Failures of the shell, with its larger volume of pressurized water, could be much more catastrophic than failures of an individual pressurized water tube in a boiler.
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## 2

# What is Water Pollution?

In Chapter 1, we discussed some typical contaminants found in water, and the various major users of water and their water quality requirements. In this section we will look at some of the typical contaminants and wastewater quantities generated by typical industries, and examine a couple of the problems associated with pollution. The characterization of many of these wastewaters is general in nature, and it is definitely process-specific. This is a general guide of the types of things to look for in industrial discharges.

## 2.1 Pollution Defined

Before we begin, it is wise to consider a working definition of pollution. Pollution is any substance which, when contained in a larger substance or material, at or above prescribed levels, degrades the intended use of the larger substance. Pollution is partially defined by the purpose to which the larger material is to be used.

In cooling water, certain chemicals are deliberately added to the circulating cooling flows in order to prevent corrosion. Many of these additives are toxic, and would never be added to drinking water, but because they are used and enhance certain specific characteristics of the cooling water, they are additives, rather than pollution.

By comparison, ethylene glycol compounds are added to water in order to keep cold weather from freezing the cooling water in the engine, and cracking the engine block when it does. When the used cooling water is drained and sent off for disposal, the glycol and everything else in the cooling water become pollutants because the purpose of the water's use has changed, and the standards for wastewater treatment now apply.

Chlorine is a compound that is used for disinfection, and almost all drinking water supplies in the US contain small quantities of chlorine, generally between 0.05 and 3.0 mg l<sup>-1</sup>. Some people find that chlorine is a pollutant and take steps (carbon filtration and/or aeration) to remove the objectionable taste. At levels

above  $3 \text{ mg l}^{-1}$ , chlorine is an objectionable pollutant, but may be necessary for disinfection of swimming pools, tanks, etc. Chlorine is used to disinfect swimming pools at concentrations above  $0.3 \text{ mg l}^{-1}$  because it is long-lasting, and because it forms chloramines with ammonia compounds, and the chloramines also have some slight disinfecting power.

Oil in the environment can cause damage to plants and animals. Oil in a closed cooling water system is a contaminant, which may not interfere with the cooling function of the water. Oil, especially water-soluble oils, are necessary for machine shop operations where they lubricate the metal being cut, and cool the cutting bits as well.

## 2.2 Chemical Industry

Waste discharges from chemical plants are complex and varied. A number of years ago, the US Environmental Protection Agency (USEPA) attempted to use a “building block” approach in an attempt to characterize chemical industry wastes. The idea was to look at the building blocks or fundamental chemicals produced and develop a waste characterization scheme in order to estimate the kind and quantity of pollutants produced, so that they could be regulated. The attempt was ill-conceived and soon abandoned because it was unworkable due to the varied production routes and chemistry of even some of the most common chemicals in production.

In order to understand chemical industry wastes, one has to delve into the chemical processes and look at specifics of the manufacture. The chemical industry does have some generic information that can assist anyone seeking to characterize some of its parts. The USEPA has developed Effluent Guidelines and Development Documents for many parts of the chemical industry, including some plastics and synthetic fibers.

When faced with an unknown process, the Development Documents are a good place to begin one’s research in order to understand the product and processes employed, and to begin to characterize the process. In most cases, however, one will be working with an already established chemical plant, and will be asked to improve or enhance the treatment of a specific waste stream.

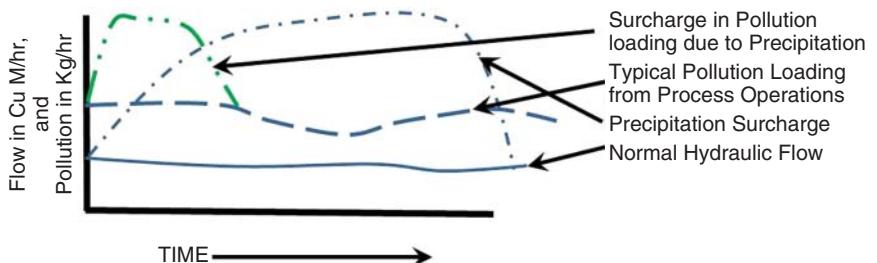
Chemical industry waste streams are most often derived from several sources: (i) process discharge; (ii) cooling water (recirculated or non-recirculated); and (iii) boiler water blowdown or boiler water conditioning treatments. For most if not all facilities, a plan of the plant sewer system may be available, showing the various process units that discharge to the sewer system. The plant map may or may not have waste flows indicated on it, but it is a start to understanding the process and the plant. At a minimum, you will need a process flow diagram that shows the various inputs and outputs to the

process. Typical Process flow diagrams are found on the Internet, but the best information is obtained from the chemical plant itself.

Process streams generally consist of water and the chemicals that come into contact with it. The wastewater streams from the process units depend upon the units' housekeeping (how clean are the floors, and are there product spills?), product wasted from transfer operations (tank car overfills, drum overfills, etc.), wastewater from equipment cleanup and wash-down (end of shift wastes), leaks from pumps, seals, and piping, spills, and, minor leaks from process equipment. The liquid discharged to the process sewer will have a high strength, may contain products of incomplete reactions, improperly formulated chemical batches and mixtures, and other concentrated materials. In some instances, the plant sewer may contain exceedingly strong materials from spills and wash-down.

Many chemical plant reactors are built in the open, on a drained concrete pad. The process portion of the plant, both for fire prevention and construction cost reasons, does not have a roof over the process, so rainwater regularly contributes to the wastewaters from the process pad. Precipitation can enter the process sewers, greatly increasing their flows during wet weather. A variation in plant sewer flows upwards of 1000% is not uncommon when the plant experiences intense rainfall, and the precipitation also washes accumulated dust and product from pipes and floors, increasing the organic loading from the plant by up to 200% or more; the peak hydraulic load is usually independent of the increased pollutant load. When the precipitation is light to moderate, there is a stronger correlation between increased hydraulic loading and increased pollutant loading, a phenomenon similar to a "first flush" condition experienced by municipalities when the runoff carries street washings and accumulated dirt into the storm sewers at the start of a rainfall. This is illustrated in Figure 2.1.

It is often important to be able to identify and characterize the source of various chemicals entering the plant sewer system. It is critically important to identify and attempt to separate the unavoidable plant discharges (process wastes) from the wash-down (usually third shift), and the plant volunteered



**Figure 2.1** Typical profiles for chemical plant wastewater discharges, showing the effect of rainfall.

discharges and spills.<sup>1</sup> The highest waste discharges often occur in the second and third shifts and are associated with the fact that the managers who work during the first shift have gone home, and with cleanup of the process and the floors, and the sewerage of off-specification batches of product.

One other major source of chemical plant discharges is from the loading and unloading operations, and an occasional draining of a process tank. Spills can often be prevented by careful operation and good facility design, including covered loading areas, dikes or spill catchment areas, and an intelligent, well-written and frequently rehearsed spill control plan including positive control measures for spill prevention. These measures represent good practice, and may include the use of spill kits, drain plugs, absorbent pads and booms, and other recovery devices, including, but not limited to, oil–water separators and skimmers.

The lesson here is to keep the process material out of the sewer by whatever means necessary. In one extreme case, where the operators in a particular area were non-cooperative, my colleagues and I had to (i) rename the environmental department from Environmental Control to Environmental Monitoring, and (ii) enforce our internal controls via use of curbing and quick-set cement.<sup>2</sup>

Chemical plants also have other significant sources of water discharge – cooling water. Cooling water may or may not be recirculated through a cooling tower. Depending upon the plant and the cooling water treatment system, the towers have to be blown down to control the silicate level in the tower water, and to prevent the cooling water from forming deposits in the heat exchangers within the plant.

Cooling tower flows are often very large, several hundred gallons or several cubic meters per minute. Depending upon the plant water chemistry and cooling water requirements, the plant will blow down between a third and a sixth of the total quantity of the cooling water used on a daily basis. The flows are consistent in quantity, but will contain small quantities of whatever is on the other side of the heat exchangers (the fluids being cooled), and tower water passivation and treatment chemicals. Cooling towers will be discussed below.

Most chemical plants have a significant loading and unloading area, and a rail car area for the movement of chemicals in and out of the plant – both finished chemicals and raw materials. These areas are often unpaved and poorly monitored, but they do have yard drains which can be a source of process waste contamination both through current and past spills, tank car leaks, and accidents which can cause leaks. Depending upon the age of the plant, its history, and dedication to environmental control, the groundwater and surface soils may also be contaminated with process chemicals and/or hazardous wastes which are, in wet weather, a part of the plant stormwater discharge, and which may not be routed to the wastewater treatment system, but will be conveyed directly to the storm sewer, river, or other water body.

If the plant has processes that generate particulate emissions or dust, and even sometimes gases, the runoff from the process areas and building roofs

can sometimes be a source of contamination during precipitation, but the only way to check for that condition is to perform a wipe test on the surfaces during dry weather, and estimate the pollution being discharged to the storm sewer system.

## 2.3 Cooling Towers

Almost every industrial building and all process plants, all manufacturing plants, power plants, every industry, and even warehouses, will have cooling towers in one form or another. In chemical plants and other industries where energy is used in quantities, cooling towers are a required part of the operations. In most humid and warm climates, air conditioning systems are the norm. Comfort cooling has led to dramatic increases in productivity of the workplace in warm climates. In computer systems, climate control is vital to prevent the computers from overheating, and in process control and operating centers, air conditioning is viewed as a necessity.

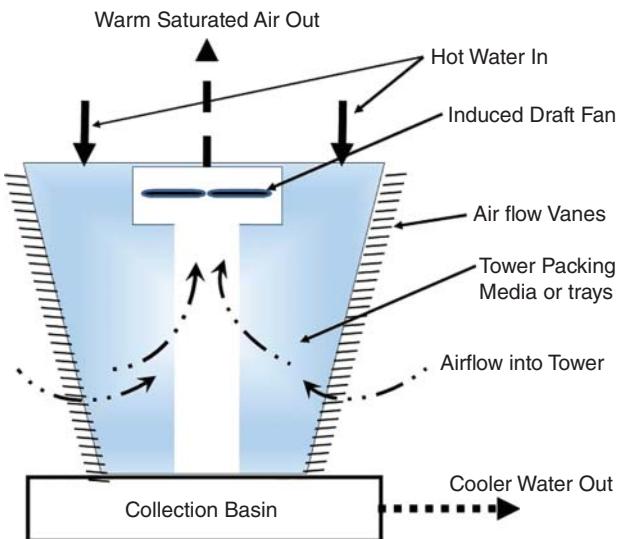
Larger systems often use water as a working fluid to keep the process equipment within required operating temperature ranges, and the heat absorbed from the process is transferred through heat exchangers, cooling the process fluids, and heating the cooling water. The now-hot cooling water is passed through a cooling tower where it is cooled by evaporation.<sup>3</sup>

A cooling tower functions by evaporating water and rejecting heat. Most are built along the lines of a set of sprays over a series of drip trays or chevron-like packing, and air is induced through the tower cooling the water by evaporation. A schematic of a cooling tower is shown in Figure 2.2.

Many of the older cooling towers were built with wooden slats, and some still are, but more modern towers are built with zinc-coated steel slats. When the passivation chemicals are out of balance, or insufficient, the zinc coating will oxidize and form “white rust,” as an indication of potential tower corrosion. It is important to maintain the corrosion inhibition because if the tower chemical system fails, the steel in the tower will be attacked, and that could lead to tower failure.

It is also important to note that the tower is a biological treatment facility of sorts. There are always bacteria in the air that are transferred to the tower water, along with dust. The dust and bacteria will often react with the leaked process chemicals in the tower water to form a bacterial slime similar to that found in a wastewater trickling filter. The tower water and blowdown will contain suspended solids, dusts, chemical precipitants, and biological solids from sloughing of the slime growths.

Most recently, there has been an uptick in *Legionella pneumonia* and Pontiac Fever which has been traced to inhalation of droplets and vapors (aerosols) of improperly disinfected waters, and natural waters from fountains, cooling towers, and similar sources.<sup>4</sup> Because a cooling tower is a natural bacterial



**Figure 2.2** Schematic for a typical induced-draft cooling tower.

farm, it is important to maintain adequate disinfection and bacterial control in the tower water. *Legionella pneumonia* is considered a pathogenic bacterium which grows in protozoa and ciliated amoeba. It can also be resident in complex plumbing fixtures and even improperly disinfected hot tubs, and easily becomes airborne.

In the US, at one time, and still in several countries, hexavalent chromium was used as both a passivator (for preventing plant piping from corroding) and a bacterial inhibitor (because of its toxicity). In 1994, under the provisions of the Clean Air Act, the USEPA outlawed the use of hexavalent chromium in cooling tower waters because of the possibility that tower drift and other losses could create an air pollution hazard. Since that time, many cooling tower service companies have switched to phosphate as a principal cooling tower control chemical, and others have used antimony or other less toxic metals for tower corrosion control. Antimony is also a toxic compound, but not as toxic as hexavalent chromium ( $\text{Cr}^{6+}$ ). Expect the ground around the tower to be contaminated from droplet drift.

## 2.4 Boilers

Boilers are used for generating steam and hot water. They are an efficient way of generating usable energy from fossil fuels, natural gas, electricity, and nuclear fuels. Boilers have been described as a film of iron oxide used to transfer heat

into water. On a gross scale, that statement is true because boilers are steel constructed, and at high temperatures, the water can be highly corrosive unless it is treated to remove oxygen and to preserve the thin film of iron oxide that separates the water from the underlying steel.

There are special classes of boilers that can operate on seawater. These boilers are constructed of copper and brass alloys. Because of this construction, it is more important to protect them from corrosion because of the ease with which copper compounds corrode in an aggressive alkaline environment. While the operating water quality for both copper/brass boilers and steel boilers are generally the same, the chemical feeds tend to be slightly different. The steel boilers often use polyphosphates and catalyzed sodium sulfite and/or hydrazine as oxygen scavengers, while the copper/brass boilers often use hydroquinone as an oxygen scavenger, and copper-based boilers also need to control the addition of amines in the water because they can also be corrosive to the boiler. The higher the pressures in a boiler, the more necessary it becomes to maintain the dissolved oxygen (DO) levels in the low parts per billion ranges in order to prevent corrosion.

The water treatment requirements for a high-pressure boiler are much more restrictive than for lower pressure boilers. The American Society for Testing Materials (ASTM) and the American Society of Mechanical Engineers (ASME) have prepared guidelines for water quality parameters for boilers of various pressures (Table 2.1).<sup>5</sup>

**Table 2.1** American Society of Mechanical Engineers (ASME) guidelines for water tube boilers.

Drum pressure (psi)	Iron ( $\text{mg l}^{-1}$ )	Copper ( $\text{mg l}^{-1}$ )	Total hardness ( $\text{mg l}^{-1}$ )	Silica ( $\text{mg l}^{-1}$ )	Total alkalinity ( $\text{mg l}^{-1}$ as $\text{CaCO}_3$ )	Conductivity ( $\mu\Omega$ )
0–300	0.100	0.050	0.300	150	700	7000
301–450	0.050	0.025	0.300	90	600	6000
451–600	0.03	0.020	0.200	40	500	5000
Chemical				Maximum concentration (ppm)		
Sodium sulfite				$\text{Na}_2\text{SO}_3$	1.0	
Sodium chloride				$\text{NaCl}$	10.0	
Sodium phosphate				$\text{Na}_3\text{PO}_4$	25.0	
Sodium sulfate				$\text{Na}_2\text{SO}_4$	25.0	
Silica oxide				$\text{SiO}_2$	0.20	

One important reason to treat boiler water is to maintain the oxide coating on the inside of the boiler and prevent the formation of scales (calcium carbonate and silicates, and struvites [a magnesium, ammonia, and phosphate compound]), which can dramatically reduce the thermal efficiency of the boiler. Some marine boilers use a high-intensity magnetic field on the incoming water to prevent the formation of boiler scales. The magnetic treatment system is in use by the US Navy, but it is considered an unproven technology.<sup>6</sup> Another excellent source for boiler makeup water treatment is the Electric Power Research Institute *Boiler Water Treatment Guide*, TR107081, and NP-6377SL, Volumes 1 and 2.

Marine boilers tend to be a special case both from the standpoint of construction and operation. Marine boilers are generally brass and soft metals and are highly chloride tolerant. Seawater is used as the boiler working fluid, in contrast to steel and iron boilers where it is considered highly corrosive and is carefully regulated.

The amount of blowdown from a boiler is approximately 20% of the total volume of the boiler per day. Of the blowdown, surface blowdown is approximately 5%; scum blowdowns comprise about 1%; bottom blowdown (which may contain suspended solids) is about 10%; and the continuous blowdown represents about 4% of the total boiler volume per day. The boiler blowdown will be very hot, have little oxygen, be of high pH, and contain all the compounds mentioned above. The phosphates may be a significant component, and could provide a source for algal blooms if not adequately treated.

## 2.5 Iron and Steel Industry

A 1967 study by the US Department of the Interior looked at the water requirements of the iron and steel industry. The quantity of water used is dependent upon the steel-making process used, the quantity of recycled water, and other production factors. Gross water use in integrated steel plants ranged from 46.7 to 459 Cubic Meters per Tonne (Cu.M/MT) (11 200 to 110 000 gal/ton) of ingot steel, with a median of 137.8 CuM/MT (33 200 gal/ton), and in steel processing plants from 17.5 to 112 CuM/MT (4180 to 26 700 gal/ton with a median of 85 CuM/MT (20 400 gal/ton). Some of this difference in water use in steel plants can be attributed to variations in products and units, but even in some units, such as blast furnaces, that have virtually the same function, the range was notable. Gross water use in blast furnaces ranged from 22 to 129 CuM/MT (5220 to 31 000 gal/ton) of pig iron. In open-hearth furnaces the range was from 9.4 to 37 CuM/MT (2260 to 8810 gal/ton) of ingot steel. Several factors, more or less significant in all units of steel plants, account for these differences in water use.

Inasmuch as more than 95% of the gross water use in steel plants was for cooling, those factors that affect the amount of cooling water are by far the most important. Some factors that affect cooling-water requirements are age and condition of the plant, procedures of operation, and quality of cooling water.<sup>7</sup>

The effluent characteristics for the iron and steel industry are quite extensive. There are a number of organic and inorganic compounds in the wastewater. An Effluent Guidelines Development Document was produced by the USEPA in the mid-1970s and updated and revised in 2002. The characterizations are quite specific and exhaustive for the development of effluent guidelines. The sampling by USEPA included a number of priority pollutants and other metals. Expect to see oil, grease, some minor concentrations of organics, including phenolics, and a small quantity of related metal contaminants, including chromium, zinc, and miscellaneous heavy metals. The treatments are generally, first, for removal of metals, which will remove most metallic toxics, often followed by dissolved air flotation, and finally biological treatment before discharge.<sup>8</sup>

## 2.6 Mining Industries

Mining industries can use a large quantity of water. Depending upon the type of mining, the type of material mined, and the mining technique employed, the water used per ton of rock processes can range from a low of around 18.9 CuM (5000 gal), to over to 378.5 CuM (100 000 gal). The water contains relatively high levels of suspended solids, but in most cases the effluent from the mining process is generally sent to a tailings pond for settling. Consequently, the suspended solids in the effluent are relatively low, but may contain high quantities of dissolved minerals, and clay and other fines. The quantities of water discharged are largely dependent upon the weather because the mining operation is in the open.

Two principal exceptions to this include gold mining and coal mining. Sub-surface mines are very efficient water collectors, and significant problems have occurred with the drainage from abandoned coal mines, principally due to the oxidation of the sulfur compounds into sulfurous and sulfuric acids. In parts of Pennsylvania and West Virginia, where there are abandoned coal mines, drainage from these mines enters rivers and causes the pH to be low enough to inhibit aquatic life, and at one time, the pH of the Monogelia River near Morgantown, WV, was as low as pH 3.<sup>9</sup>

The water from coal mining may also contain quantities of radium and a number of dissolved metals and sulfates, which are present in the coal

seams. In parts of western Poland and eastern Germany where there are deep coal mines that pump water up to the surface, there is a concern for surface water quality deterioration due to chlorides, sulfates, metals, and radium. Radium is in the same part of the Periodic Table as calcium, and it can be incorporated into the body, ultimately finding its way into bones where the body generates blood cells. Exposure to radium is cumulative, and its presence in the body can create several types of cancers. However, because of the salt content in the mine water, it is often not practical to regenerate it with ion exchange. Alternative precipitation strategies have been used involving barium sulfate.

One of the greatest hazards associated with gold mining arises from the extraction and recovery system for low-grade ores. In the recovery process, sodium cyanide is sprayed on to the piles of extracted rock, which dissolves the gold. The gold-cyanide solution also contains a number of other heavy metals, and in 2000, a breach of a dam on a gold extraction process in Romania unleashed a heavy plume of cyanide-laced water into the Tisza River, killing fish and all aquatic life. Reportedly, the cyanide concentrations in the Tisza were between 30 and  $2\text{ mg l}^{-1}$  as it washed downstream.<sup>10</sup> According to the local biologists, cyanide levels greater than  $0.02\text{ mg l}^{-1}$  are harmful to aquatic life.

## 2.7 Fracking for Oil and Gas

Since 2000, there has been a tremendous boom in the number of natural gas wells drilled in the US and worldwide. The development of technologies associated with fracking and with horizontal wells has led to this boom. As a result, natural gas production has increased dramatically in the US and elsewhere. Fracking is not without its detractors and alarmists, as well as its boosters and promoters. In order to understand fracking, one needs to look at the use and development of horizontal wells. This technology, often referred to as “unconventional” gas exploration, has created an environmental and political stir throughout the US and Europe.<sup>11</sup>

Most geological formations are generally found in horizontal layers. Over thousands of years, plants and animals from previous geological ages have been compressed and heated underground to form natural gas and oil deposits. Drawing oil and gas from the ground is very expensive and often difficult.<sup>12</sup> One way in which extraction has been increased is through the use of horizontal wells.

Horizontal wells use the ability of the drill head to turn and produce a curved wellbore. The wellbore is curved to have a longer section in the energy-bearing (oil or gas) formation. Fracking is the overpressurization of the formation to form fractures for the oil and gas to flow to the collection well. The fractures are created by water pressures that are between 350 and 650 bar, and form splits in the rock formations. The fractures provide a shorter path for the oil and gas to release to the collection well. The fractures are held open by proppants, generally sand or ceramic pellets which are pumped into the fractures to hold them open. This type of well development can often increase the recovery of oil and gas by 55% or more over non-fracked wells, according to one manufacturer of proppants.<sup>13</sup>

In order to open fractures and increase the flow of oil and gas to the extraction wells, geologists use a variety of chemicals and proppants. Sand is the most common propellant used to pump into the wells to hold the fractures open, but all kinds of lubricants, chemicals, acids, and other compounds have been used.<sup>14</sup> Fracking uses a lot of water. In some cases, the volume can be as high as 26 500 CuM (7 000 000 gal.) per frack, and a well will need to be fracked or re-fracked several times over its life. About 10% of the fracking water is discharged from the well after the fracking is completed. It is this water that contains chemicals and is in need of treatment. On average, the median quantity of water used for fracking oil and gas wells was 15 275 CuM for oil wells and 19 425 CuM of water for gas wells. About 42% of the wells used less than 2600 CuM (2014 study). The highest average hydraulic fracturing water usage (10 000–236 620 m<sup>3</sup> per well) in watersheds across the United States generally correlated with shale-gas areas (versus coalbed methane, tight oil, or tight gas) where the greatest proportion of hydraulically fractured wells were horizontally drilled, reflecting that the natural reservoir properties influence water use, but the high water use is spatially varied, and seems to be highest where the rock formations are very tight, and shale formations.<sup>15</sup>

The wastewater generated by fracking is a witches' brew of chemicals, salts, and naturally occurring radioactive materials (NORM). The chemicals added include those shown in Table 2.2.

The flowback water (injected and then backflowing from the frack) and produced water (water in the formation which is associated with the gas or oil being recovered) generated by unconventional wells is difficult to characterize because it is dependent upon the sources and the formation, and the chemicals added. The USEPA has a *2015 Technical Development Document for Proposed Effluent Limitations Guidelines and Standards for Oil and Gas Extraction* EPA 821-R-15-003 (March 2015).

**Table 2.2** Common chemicals used in fracking.

Additive type	Main compound	Purpose
Dilute acid (15%)	Hydrochloric acid <sup>a)</sup>	Dissolved minerals/sand initiates cracks in rock
Biocide	Glutaraldehyde	Bacterial control
Corrosion inhibitor	N,n-dimethylformamide	Prevents corrosion
Breaker	Ammonium persulfate	Delays breakdown of gel polymers
Crosslinker	Borate salts	Maintains fluid viscosity at high temperature
Friction reducers	Polyacrylamide <sup>a)</sup> Potassium chloride Mineral oil	Minimize friction between the fluid and the pipe
Gel	Guar gum or hydroxyethylcellulose <sup>a)</sup>	Thickens water to suspend the sand
Iron control	Citric acid	Prevents precipitation of metal oxides
Oxygen scavenger	Ammonium bisulfite <sup>a)</sup>	Removes oxygen from fluid to reduce pipe corrosion
pH adjusters	Potassium or sodium carbonate	Maintains effectiveness of other compounds (e.g. crosslinker)
Propant	Silica quartz sand	Keeps fractures open
Scale inhibitor	Ethylene glycol	Reduces deposition on pipe
Surfactant	Isopropanol	Increases viscosity of fluid

a) Indicates degree of health hazard in concentrated form.

Source: Cornell University Report CRP 5072: *Hydraulic Fracturing – Effects on Water Quality* by Andrea Armudo and Sean Murphy, December 12, 2010.

The wastewater also contains a variety of metals and salts, including bromide, fluoride, nitrate, nitrite, phosphate, sulfate, sulfide, and a large number of cations, as shown in Table 2.3. Additionally, the waters may be highly saline (contain up to 43% sodium chloride) and often contain NORM, principally radium and daughter products. The levels of radium may be unacceptably high for direct discharge, and any treatment to remove the radioactive constituents will generate sludges which will need to be disposed of as hazardous wastes. Table 2.4 shows the typical constituents of NORM in selected waters.

The treatment of these waters is a relatively expensive process, and the wastes generated might contain enough radioactivity to preclude them from being placed in a conventional landfill.

**Table 2.3** Concentration of select metal constituents in unconventional drilling wastewater from the Marcellus Shale.

Parameter	Units	Range	Median	Number of data points	Number of detects
Aluminum	$\text{mg l}^{-1}$	1.7–6900	38	12	12
Arsenic	$\text{mg l}^{-1}$	ND–4.2	ND	12	6
Barium	$\text{mg l}^{-1}$	2.6–2000	13	14	14
Beryllium	$\text{mg l}^{-1}$	ND–0.018	ND	8	2
Boron	$\text{mg l}^{-1}$	ND–2.7	0.17	8	4
Cadmium	$\text{mg l}^{-1}$	ND–0.005	ND	8	1
Calcium	$\text{mg l}^{-1}$	150–15 000	1300	13	13
Chromium	$\text{mg l}^{-1}$	ND–11	0.010	12	8
Cobalt	$\text{mg l}^{-1}$	ND–1.8	ND	8	3
Copper	$\text{mg l}^{-1}$	ND–17	0.83	8	6
Iron	$\text{mg l}^{-1}$	4.2–18 000	86	12	12
Lead	$\text{mg l}^{-1}$	ND–8.0	0.35	12	10
Lithium	$\text{mg l}^{-1}$	ND–1.2	ND	8	1
Magnesium	$\text{mg l}^{-1}$	ND–3600	290	12	11
Manganese	$\text{mg l}^{-1}$	ND–350	4.3	12	11
Mercury	$\text{mg l}^{-1}$	ND–0.029	ND	8	2
Molybdenum	$\text{mg l}^{-1}$	—	0.10	1	1
Nickel	$\text{mg l}^{-1}$	ND–16	0.55	12	9
Potassium	$\text{mg l}^{-1}$	—	8800	4	4
Selenium	$\text{mg l}^{-1}$	ND–0.11	ND	8	3
Silver	$\text{mg l}^{-1}$	ND–0.010	ND	8	1
Sodium	$\text{mg l}^{-1}$	170–16 000	2900	12	12
Strontium	$\text{mg l}^{-1}$	1.8–1500	21	13	13
Zinc	$\text{mg l}^{-1}$	ND–38	2.1	12	10

Source: 55 DCN SGE00740. United States Office of Water (2015). *EPA-821-R-15-003 Technical Development Document for Proposed Effluent Limitations Guidelines and Standards for Oil and Gas Extraction*. Environmental Protection Agency, Washington, DC.

## 2.8 Petroleum Exploration

Conventional petroleum exploration is much less water intensive than the fracking alternative. In most cases, there are a few thousand gallons of water used to cool the drill bit, and remove drill cuttings. The water is recirculated through a mud tank of a few thousand gallons. The purpose of this tank is to allow fluids and drilling muds to be added to maintain the viscosity and density

**Table 2.4** Concentration of radionuclides in selected unconventional oil- and gas-produced water.

Parameter	Formation	Method(s)	Range (pCi l <sup>-1</sup> )	Median (pCi l <sup>-1</sup> )	Number of data points	Number of detects
Gross alpha	Marcellus	900.0	8.7–120 000	8700	74	74
Gross alpha	Niobrara	900.0	620–4000	1800	3	3
Gross beta	Marcellus	900.0	6.8–21 000	1600	73	72
Gross beta	Niobrara	900.0	250–1200	760	3	3
Radium-226	Marcellus	901.1 Mod., 903.0, 903.1, $\gamma$ -spectrometry	0.16–27 000	1700	103	101
Radium-226	Niobrara	901.1 Mod.	170–900	620	3	3
Radium-228	Marcellus	901.1, 903.0, 904.0, $\gamma$ -spectrometry	0–1900	470	94	92
Radium-228	Niobrara	901.1 Mod.	100–460	330	3	3

Source: United States Office of Water (2015). *EPA-821-R-15-003 Technical Development Document for Proposed Effluent Limitations Guidelines and Standards for Oil and Gas Extraction*. Environmental Protection Agency, Washington, DC.

of the drilling fluids. One of the major components of the drilling muds is barium sulfate, which is, because of its density, used to help keep the drill bore open and keep the drill head cool and lubricated.

With every well, there are at least one and probably two drill pits. These pits are generally 30–40 m long by 10 m wide and are scooped out of the earth and lined with a plastic liner. In some countries, the lining is omitted. The drill pit receives everything that is in the well, plus the cuttings, plus the oil, plus any spills, and anything else that is on the drilling platform. For wells, it is not uncommon to have several centimeters of heavy oil on the surface in a floating layer. If the pit is abandoned when the well is completed, it is left to contaminate the environment. If it is cleaned up, the oil is removed, the water is pumped through carbon or other treatment to remove oils, and discharged. The liner is removed and the pit is closed. If there is no liner, sometimes the pit is closed by adding specialized bacteria, and pumping the bacteria and the fluids in the drill pit until the oil concentration is well under 500 mg kg<sup>-1</sup>. Then it is run through a centrifuge and dewatered and disposed of in a non-hazardous landfill. The water is also treated to remove oils and discharged.

For most modern applications, any produced water from the well is pumped to the separation station along with the oil from the well. For most operations the amount of produced water is between 3 times and 10 times the amount of oil obtained from the well. The oil and water mixture is sent to a separation station where the two are separated, and the water is sent to a reinjection well

for disposal, and to help drive the oil in the formation toward a producing well and to maintain the formation pressure.

## 2.9 Petroleum Refining

Petroleum refining uses a lot of water. The total US refining capacity is estimated at about 15.5 billion barrels per year (McGraw Hill Financial). Depending upon the age and type of equipment, and the source of the crude oil, a typical

**Table 2.5** Typical values ( $\text{mg l}^{-1}$ ) for effluent characteristics from petroleum refinery discharges in the US and Canada.

Pollutant	Canadian study <sup>a)</sup> : average of 7 Ontario refineries	Average of 7 US refineries	138 US refineries, PCS data (1992) <sup>b)</sup>	
			Low	High
TSS	22	31	22.3	22.6
Chemical oxygen demand (COD)	49.2	85	93.1	93.1
Oil and grease	2.17	4.08	3.34	3.42
NH <sub>3</sub> (as N)	1.7	5.21	4.83	4.83
Sulfide	0.08	<0.03	0.044	0.052
Phenols (4AAP)	0.0110	0.047	0.038	0.040
Chrome, total	0.0068	0.028	0.0011	0.013
Lead	0.0041		0.004	0.006
Zinc	0.29	0.09	0.15	0.15
Benzene	0.0008	<0.005	0.0008	0.001
Toluene	0.0007	<0.004 (max)	<0.02	0.003
Naphthalene	0.0011	<0.003 (max)	—	—
Copper	0.0048	<0.012	0.0106	0.0112
Nickel	0.0034	<0.08	0.0159	0.0166
Arsenic	0.009	—	0.202	0.202
Cyanide	0.007	—	0.041	0.041
Selenium	0.005	—	0.145	0.145

Note: All values are expressed as milligrams per liter or  $\text{mg l}^{-1}$ .

- a) Source: *Best Available Treatment Technology for Ontario Petroleum Refining Sector*, August 1991.
- b) Source: US Environmental Protection Agency, Office of Water Engineering and Analysis Division (1996). *Preliminary Data Summary for the Petroleum Refining Category*. Publication Number EPA 821-R-96-015, Appendix 1 and 2. Low non-detects equal zero, high non-detects equal one-half detection limit.

refinery will use between 18 and 58 gallons of water per barrel of petroleum products produced. Another way of looking at the water use is that typical refineries will use between 0.43 and 1.4 barrels of water per barrel of oil produced.<sup>16</sup> The principal uses for water include: (i) steam generation; (ii) cooling; (iii) desalting (removing salt) from crude oil; (iv) generating hydrogen for sulfur removal; (v) equipment cleaning; and (vi) corrosion protection. Of the total quantity of water used, approximately 53% is used for cooling, and 42% is used for steam production. Further, approximately 38% of the water used is evaporated; 11% is vented as steam; 5% is consumed; 41% is discharged to surface waters; and approximately 5% is contained in sludges. In some cases, where water supplies are limited, industry and in particular refineries are using treated municipal wastewater as a source.

It should also be noted that refineries are designed to run on specific sources of crude oils, and that the individual types of crude can be substantially different. The salt content and the sulfur content of the crudes vary significantly, but there are other differences including the makeup of the asphalt, naphtha, paraffin, and other organic fractions of the petroleum. One source estimates that over 141 compounds in petroleum have been identified, but they only comprise about 44% of the compounds in petroleum.<sup>17</sup>

A 1996 study of US and Canadian refineries indicated the water quality for effluent data shown in Tables 2.5 and 2.6.<sup>18</sup> If a refinery discharges to a publicly owned treatment works (POTW), the discharge values are somewhat higher.

**Table 2.6** Summary of discharge data for refineries connected to a POTW.

Analytes ( $\text{mg l}^{-1}$ )	Maximum	Minimum	Mean
TSS	720	1	77
$\text{NH}_3\text{-N}$	86	9.7	16.48
Total cyanide	0.19	0.04	0.07
Phenols	190	<0.02	31.25
Total COD	2597	82	443
Oil and grease	326	1.05	41
Total chromium	2.18	0.36	1.24
Lead	<0.10	<0.06	<0.09
Zinc <sup>a)</sup>	0.99	0.13	0.58
Sulfide	13.1	<0.50	2.39
BOD <sup>a)</sup>	343	16.25	165
Total VOC <sup>a)</sup>	8.72	1.46	4.89
TDS	2160	130	1122
pH-SU	9.8	5.9	8.40

All values are in  $\text{mg l}^{-1}$ .

a) Indicates one dataset for one refinery in a 1996 survey.

It should be noted that there is a later study (2004) for Petroleum Effluent Guidelines, but that study relies on toxic release inventory data, and calculates the specific compounds and their releases rather than sampling the effluents and analyzing data for the compounds of interest. As such, it is considered less valuable in estimating effluent discharges.

## 2.10 Agricultural and Food Processing

Agricultural water use is quite variable. Crop size, climate, quantity of rainfall, type of crop, soil type, slope of the land, evapotranspiration potential, and method of application of the water to the crop are all variables that can greatly affect the water use for a particular crop or area. Irrigation supplements natural water demands in arid and semi-arid areas. In some areas, no irrigation is necessary for crops to flourish. According to some estimates, principally from California, irrigation is only about 80–90% effective in supplying crops with water. While the raising of livestock falls under the category of water use, it is very water intensive, and will be treated separately.

## 2.11 Crop Water Use

Perhaps the best independent statistics on water use and crops comes from [www.waterfootprint.org](http://www.waterfootprint.org). The data are collected under the auspices of UNESCO-IHE, and the University of Delft in the Netherlands. The main data page with the spreadsheets and data are located at <http://waterfootprint.org/en/resources/water-footprint-statistics>. Some of the data are extracted from that source and presented in Table 2.7. The data show total water use by type of crop, as it compares with water use for development of protein and fat.

The source publication by Mekonnen and Hoekstra (2010)<sup>19</sup> contains estimates of crop water use for blue, green, and gray water. The authors describe “blue water” as being derived from rainfall or surface waters; “green water” is that which is stored in the root zone of the soil and evaporated, transpired, or incorporated by plants and related agricultural, horticultural, and forestry products; “gray water” is the amount of fresh water required to assimilate pollutants to meet specific water quality standards. The grey water footprint also considers point-source pollution discharged to a freshwater resource directly or indirectly through runoff or leaching from the soil, impervious surfaces, or other diffuse sources.

Another specific source for water use is obtained from the USDA, classified on farm sizes and water use for western US irrigated land, type of irrigation,

**Table 2.7** 2010 crop production data and water use.

Crop Production for 2010 in the US			
Crop	Crop yield per irrigated acre	Inches of water applied per acre	Centimeters of water applied per hectare
Corn	174.8	10.74	74.78
Rice		27.39	190.69
Barley		13.93	96.98
Spring wheat	90.26	10.24	71.28
Winter wheat	52.06	9.30	64.73
Durum wheat	104.94	7.03	48.97
Sorghum		10.92	76.04
Oats		9.82	68.38
Peanuts		8.79	61.20
Barley	85.50	37.67	262.24
Barley, malt	83.76	87.39	608.42

Source: USDA ERS.

and crop value, but without regard to type of crop.<sup>20</sup> The State of California, Air Resources Board,<sup>21</sup> and The Pacific Institute have provided information on water use and irrigation in California.<sup>22</sup> In times of drought the public perception of water use is that certain crops, specifically almonds, have an unreasonably high water use compared with the remainder of the agricultural production of the state. The problem is that the figures are not specific enough per plant or per crop to measure the water use per crop acre. Lenntech<sup>23</sup> also has some good and clear data on water use by crop, and it is clear and simple to understand.

While crop irrigation water is not generally discharged as an effluent, the runoff will contain almost everything that is in the soils, plus a lot of fines from the soils. Only the excess, which is not evaporated or absorbed, will run off.

## 2.12 Vegetable and Fruit Processing

Using apples, oranges, and potatoes as an example, there are several different end products: sauces, canned, sliced, frozen, crushed, chopped, and as many varieties of those as one can imagine. The basic processes include cleaning, peeling, juicing, cooking, canning, or packaging, and where appropriate, freezing. Some fruits are peeled using a flash steam, others are parboiled, and still others use lye and caustic compounds to release the skins from the fruit.

**Table 2.8** Typical waste loadings for different types of fruit and vegetable processing.

Product	Water consumption (l MT <sup>-1</sup> )	Average BOD (kg kg <sup>-1</sup> )	TSS (kg kg <sup>-1</sup> )
<i>Apples</i>			
Juice	1880–3580	1.6–2.55	0.15–0.40
Other products	1380–14 800	3.4–10.1	0.35–1.05
Citrus	710–24 940	0.45–8.5	0.02–7.95
<i>Potatoes</i>			
Frozen	4090–15 510	4.45–36.95	5.1–45.5
Dehydrated	6530–12 010	7.75–15.2	3.8–12.15

Source: USEPA Effluent Guideline Development Document, for apple, citrus, and potato processing, March 1974.

Depending upon the process used, the wastes can be acidic or caustic or neutral. The things they will all have in common are pulp, and dissolved sugars, some acidity, and some of the peel or fruit covering. These all appear in the waste stream. According to a 1976 EPA study, the general range of effluent quality and water use applicable to the industry is shown in Table 2.8.

The principal caution in treating this type of waste is that cooked starches and food products that have been exposed to heat behave very differently in the laboratory from the raw products. Caution should be used in determining what the final product effluent should look like before pilot testing can be achieved.

## 2.13 Animal Farming and Concentrated Animal Feeding Operations

Raising animals requires much more water than raising crops. Hoard's Dairyman web blog provides some critical answers to the question of just how much water is required to raise animals.<sup>24</sup> Data from the Agronomy Department at the University of Texas has contra-indications regarding water use for crops. In an attempt to sort out the information, the USDA Economic Research Service also has limited data shown in Table 2.9.

There are many variables in dealing with agricultural use of water. As discussed above, land slope, crop type, weather, soil type, evapotranspiration, meteoric water, time of application of irrigation, and many other factors all play a part in crop water use computations. The US Geologic Survey Bulletin 1405 summarizes the agricultural and domestic and other types of water use in the US. Unfortunately, the publication does not break down the water use by the type of crop.

**Table 2.9** A comparison of water use by specific crop type vs. animal production.

	Liters per kilogram	Liters per kilocalorie	Liters per gram of protein	Liters per gram of fat
Sugar crops	197	0.69	0.0	0.0
Vegetables	322	1.34	26	154
Starchy roots	387	0.47	31	226
Fruits	962	2.09	180	348
Cereals	1644	0.51	21	112
Oil crops	2364	0.81	16	11
Pulses	4055	1.19	19	180
Nuts	9063	3.63	139	47
Milk	1020	1.82	31	33
Eggs	3265	2.29	29	33
Chicken meat	4325	3.00	34	43
Butter	5553	0.72	0.0	6.4
Pig meat	5988	2.15	57	23
Sheep/goat meat	8763	4.25	63	54
Bovine meat	15 415	10.19	112	153

Source: Mekonnen and Hoekstra (2010), <http://waterfootprint.org/en/water-footprint/product-water-footprint/water-footprint-crop-and-animal-products>.

Perhaps one of the most detailed and best sources is the Canadian Government's Agricultural Fact Sheets.<sup>25</sup> The information is quite specific and detailed, and careful inspection indicates general agreement with Table 2.9.

## 2.14 Livestock and Concentrated Animal Feeding Operations

Where one has livestock, mud and feces will inevitably follow. The fecal material is always rich in nitrogen and phosphorus and can contaminate the groundwater if not collected and handled properly. The more concentrated the animal population is within an area pasture, the more concentrated the wastes will be and the larger the likelihood that runoff and groundwater will be contaminated.

The USEPA has come up with some equivalences when considering the pollution potential from animals. The equivalence uses wastes generated by cattle as a basis for estimating waste generation from other types of livestock (see Table 2.10).

The figures in Table 2.11 are for minimal water use and do not consider the use of wash pens, a factor that can considerably add to water consumption.<sup>26</sup>

**Table 2.10** Water use on a dairy farm based on 160 acres and 2000 head of cattle.<sup>a)</sup>

Use type	No. of units	Gallons per unit	Gals. used per day	Purpose
Milk cows	2000	38.7	77 400	Drinking
Dry cows	400	17.3	6920	Drinking
Heifers, lbs				
1200	500	14.5	7250	Drinking
800	500	10.6	5300	Drinking
400	500	6.1	3050	Drinking
200	500	3.3	1650	Drinking
Bulk tank	4	60	240	Cleaning
Pipeline	3	250	750	Cleaning
Misc. equipment	3	30	90	Cleaning
Cow prep	2000	0.5	1000	Cleaning
Floor wash	3	150	450	Cleaning
Milk house floor	3	20	60	Cleaning
Total usage per day			104 160	
Average per cow drinking only			38.7	
Average per cow total dairy per day			52.1	

a) Raises own calves and heifers. Does not include water use for flush systems, wash pens, or extensive summer cooling.

**Table 2.11** Animal equivalents for pollution generation.

Animal type	Equivalent weight	Animal type	Equivalent weight
Cattle	1.0	Mature dairy cattle	0.7
Large swine (>20 kg)	0.25	Small swine (<20 kg)	0.10
1000 chickens	0.1	1000 turkeys	0.055
1000 ducks	0.005	Horses	0.5
Sheep or lambs	0.1		

Appendix V of the Water Footprint Report contains a complete database of the estimated blue, green, and gray water uses for livestock.<sup>27</sup>

One way of disposing of the nitrogen and phosphorus generated from animal manure is agronomic application of the manure. Of the total of the animal operations in the US, the vast majority have insufficient land for agronomic application.

The key to controlling pollution on all Concentrated Animal Feeding Operations (CAFOs) is manure management. In most cases, the manure will be a semi-solid, having over 20% total solids. Various management and cleaning operations can reduce that to less than 10% and make the manure flow like a liquid. At concentrations less than 12%, the manure is pumpable; at concentrations around 18% the manure is stackable, and can be managed in piles. If animal bedding is included, the concentration of solids in manure is often over 22%.<sup>28</sup>

The quantity of wastes generated by various animals is shown in Table 2.12. The density of the manure will be close to the weight of water. If bedding is included, the manure will be up to 80% of the weight of water, but the solids from the bedding will interfere with pumping operations unless cutter pumps are employed, and even then lines will plug. If pumping of these wastes is to be performed, use long-radius bends and elbows to transition the flows smoothly, avoiding areas where solids could build up.

Manure and byproducts associated with animal feeding operations have a high degree of volatile solids (VSs), chemical oxygen demand (COD), and potential for methane generation in an anaerobic digester. Table 2.13 indicates the digester potential for various products associated with animal wastes. There is a lot of variability in the data, and the amount of water used to help move the manure will greatly affect the results. The annual data can be used to estimate the quantity of waste material generated.<sup>29</sup>

**Table 2.12** Quantity of wastes generated by various animals in Concentrated Animal Feeding Operations (CAFOs).

Animal	Sub-classification	Manure generated – lb/yr per 1000 lb of animal mass
Swine	Grower finisher	29 380
	Farrow	12 220
	Farrow to finish	38 940
Poultry	All	25 550–31 025
Dairy	Lactating cow	30 478
	Heifer	24 090
	Calf	24 017
Beef and heifer	Steer, bulls, and calves	21 170
	Beef cows	22 995
	Heifer	24 090
Veal	All	22 265

**Table 2.13** Organic matter characteristics associated with digestion of CAFO wastes.

Substrate sampled	TS (% wb)	VS (% db)	COD:VS	COD converted to CH <sub>4</sub> (%)	Specific methane yield (l CH <sub>4</sub> /g VS)	Wet mass methane potential (m <sup>3</sup> CH <sub>4</sub> /1000 kg)
<i>Manures</i>						
Beef manure (outdoor pen)	15	82	1.2	17	0.084	10
Beef manure (covered pen)	17	82	1.1	23	0.10	14
Swine manure slurry	2.6	77	1.8	23	0.13	2.0
Dairy manure	12	84	1.2	55	0.24	23
Poultry litter	66	61	0.82	77	0.245	99
<i>Co-digestion byproducts</i>						
Wood shavings	92	99	0.19	33	0.067	61.5
Reed canary grass hay	84	93	0.93	92	0.12	94
Corn stover	80	93	1.0	44	0.18	130
Oat hulls	92	95	0.88	57	0.19	170
Sugar beet peel and pulp	18	92	1.15	54	0.23	38
Corn processing byproduct	9.4	54	3.0	84	0.26	13
Potato peel	9.1	96	0.64	100	0.27	23
Food scraps	29	95	1.3	57	0.29	79
Alfalfa silage	15	95	0.70	110	0.30	42
Slaughter facility sludge	9.1	94.5	1.5	102	0.60	52
Food grease	42	99	0.40	52	0.81	340

TS is total solids, VS is volatile solids, and wb and db are wet basis and dry basis respectively.

The principal pollutants derived from CAFO operations are biodegradable organics. Nitrogen, especially ammonia and total Kjeldahl nitrogen (TKN), potassium, phosphorus, and large quantities of COD and other volatile solids are all common. For poultry wastes, the COD can range up to 4500 mg l<sup>-1</sup>, and total suspended (non-filterable) solids (TSS) up to 2500 mg l<sup>-1</sup>, depending upon the amount of water used to dilute the wastes. Various types of wastes are extremely high in ammonia, TKN, and phosphorus. As such, even treated CAFO wastes have a high potential to cause algal blooms because of the phosphorus content. Denitrification and phosphorus removal will be required before direct discharge to rivers or lakes. In the US, Concentrated Animal Feeding Operations, dairy farms, and other high animal density operations have a “zero liquid discharge” requirement.

## 2.15 Slaughterhouse and Meat Packing and Processing Wastes

Slaughterhouse and meat packing wastes can be notoriously difficult to treat. The wastes can be characterized by distinct and compartmentalized operations. First is the kill floor; second is the de-hiding or skinning; and third is the cleanup. Each of these operations are separate.

The kill floor waste can contain some quantities of blood, although even in Kosher slaughterhouses, the blood is recovered and dried for its protein value. The blood has an incredibly high COD and nitrogen content. It is also very difficult to coagulate without first taking the pH down to less than pH 4 SU, and then carefully neutralizing and coagulating with a food grade polymer. In that manner, the coagulated blood recovered from the wastewater can be reprocessed and used for protein supplements to animal foods, where permitted.

A number of years ago, the USEPA presented a research paper wherein they were able to coagulate and precipitate blood in kill floor wastewaters by the addition of lignosulfonic acid (LSA) in an acid medium of pH 2–3. There was some indication that the LSA may also have to be dosed in stoichiometric quantities.<sup>30</sup> LSA addition has been demonstrated to remove 70–80% of the BOD from packinghouse and slaughter floor waste streams.

Alum often works as a coagulant, but it may cause other problems with the proposed re-use or recovery of the waste stream. Another treatment is to use high molecular weight organic polymers, available from chemical supply houses. The kill floor wastes also contain small quantities of skin, hair, and bones, and a quantity of sand and gravel, and whatever is in the animal's stomach at the time of the kill. With some separation, these wastes can be removed and recovered.

The hide and skinning operations are not particularly waste intensive, but there will be some wastes at the cleanup, and that will contain hair and some flesh.

The cleanup wastes are perhaps the greatest load. During the cleanup the washdown is conducted with hot water and detergent for grease removal, and then a clear water rinse followed by strong antibacterial disinfectant. Often the waste load from the cleanup cycle, usually conducted on the third shift, contain the greatest concentrations of grease and fats, and chlorides.

Many of the slaughterhouses use sodium chloride crystals as non-slip materials. This is common practice because the coatings applied to the surfaces to make them impermeable and easy to clean also make them slippery when coated with the grease associated with the trimming operations.

The grease and oil from the operation can be recovered and sent off for inedible rendering. (Rendering yields a yellow grease, white grease, bleachable fancy tallow, etc., as well as meat and bone meal and byproducts.) With proper care, and some handling, it is possible to collect the foam from a dissolved

air flotation plant on a meat packing plant, with solids approaching 20%, and fats, grease, and oils approaching 25%.<sup>31</sup> Additional processing of the waste can yield much higher production values. After treatment, the wastewater will have a FOG (fats, oil and grease) content of less than  $15 \text{ mg l}^{-1}$ , and TSS in the low  $20 \text{ mg l}^{-1}$  range. There is, however, still a substantial COD due to dissolved proteins and other compounds released from the blood, but the right chemical treatment can reduce the effluent COD substantially to levels compatible with municipal discharges. With biological treatment, the effluent can be treated to levels compatible with direct discharge to streams and rivers.

## 2.16 Dairy Wastes

Dairies are relatively clean operations as opposed to CAFOs. Dairies are highly sanitary and careful to deal with issues surrounding bacterial contamination of their products. Aside from cooling water, the largest dairy flows are associated with spills, processing wastes, and cleanup. Cleanup usually occurs on third shift, and bottle, container, and line washing represent the majority of the pollutant load. The exception might be in the cottage and other cheese processing, unless the dairy is reclaiming and drying whey. Cleanup also represents a part of the challenge to biological treatment because the quaternary amine bactericides and cleaning products often persist. The other characteristic is that the wastes are high in carbonaceous BOD and almost entirely deficient in nitrogen. There are a number of instances where a biological treatment system would not properly treat the wastes until a sufficient quantity of nitrogen had been added, generally far in excess of the quaternary amines. The ideal BOD : N : P ratio for biological uptake is approximately 100 : 5 : 1, but may be as high as 125 : 20 : 1.

## 2.17 Measuring Pollution

Pollution is measured by the product of concentration and flow. In the past 50 years, our ability to detect chemicals has grown remarkably. In 1970, the state of the art for metals detection was a concentration of between 1 and  $5 \text{ mg l}^{-1}$ , depending upon the sensitivity of the available atomic absorption unit. Commercial organic concentration measurement by gas chromatography was column dependent, and the routine levels of detection could be  $100 \text{ mg l}^{-1}$ , and possibly as low as  $10 \text{ mg l}^{-1}$  if pre-concentration equipment were used.

With the advent and incorporation of the computer into the laboratory equipment, analytical equipment became substantially more sophisticated, and the limits of detection increased over a 1000-fold. In today's market, it is not uncommon to detect and measure femtogram and picograms (parts

per quadrillionth, parts per trillionth) as opposed to micrograms (parts per million) which were measured in the 1970s.

The measurement ability of the laboratory is equipment-driven. Routine measurement of organic contaminants by gas chromatography/mass spectrography can detect and quantify many organic compounds in parts per billion concentrations (micrograms per liter).<sup>32</sup> The more sophisticated equipment can, with the latest equipment, measure nanograms and picograms (parts per billion and parts per trillion). Inductively coupled plasma arc with mass spectrography (ICP-MS) can routinely detect concentrations of some metals as low as  $0.05 \mu\text{g g}^{-1}$ .<sup>33</sup>

There are a number of “approved” analytical methods – those that have been accepted as standard techniques by the appropriate regulatory agencies (Table 2.14). Some of these methods are quite specialized, while others are

**Table 2.14** Common analytical methods for wastewater.

Analyte	Method	Analyte	Method
Aluminum	Flame ionization	Carbonate ( $\text{CO}_3$ )	Gravimetric/calculation
Antimony	Flame ionization	Cyanide (CN)	Colorimetric
Arsenic	Flame ionization	Fluoride (F)	Gravimetric
Calcium	Flame ionization	Hydronium ( $\text{OH}$ )	pH
Chromium	Flame ionization	Hypochlorite ( $\text{HClO}_2$ )	pH
Copper	Flame ionization	Hypochlorous ( $\text{ClO}_2$ )	pH
Hydrogen	pH	Nitrate ( $\text{NO}_3$ )	Colorimetric
Iron	Flame ionization	Nitrite ( $\text{NO}_2$ )	Colorimetric
Lead	Flame ionization	Sulfate ( $\text{SO}_4$ )	Colorimetric
Magnesium	Flame ionization	Sulfite (S)	Nephelometric
Manganese	Flame ionization	Sulfite (S)	Colorimetric (starch)
Mercury	Flame ionization	Other:	
Potassium	Flame ionization	Alkalinity	Colorimetric
Silica	Flame ionization	Total org. carbon	Gravimetric
Silver	Flame ionization	Dissolved $\text{O}_2$	Azide tit or probe
Sodium	Flame ionization	Org. nitrogen	Kjeldahl
Zinc	Flame ionization	Chem $\text{O}_2$ demand	Digestion/titration
Ammonia	Kjeldahl or Nesslerization	Biochemical $\text{O}_2$ demand	Difference in oxygen uptake
Bicarbonate ( $\text{HCO}_3$ )	Calculation		

relatively simple. The different governmental agencies often have different analytical protocols, depending upon state and country requirements. Before one can submit analytical information to a State or governmental agency for regulatory approval, it is best to have a sampling plan, an analytical plan, and a quality control plan.

## 2.18 The Sampling Plan

The sampling plan starts with an objective – generally the characterization of the discharge to or from a treatment system, or the characterization of a lake or river, or groundwater contamination. Common elements to the sampling plan must include: sampling equipment required; cleaning protocols before and after each sample to insure no cross-contamination; initial field measurements; type and number of containers to be used; and preservation techniques to be employed.<sup>34</sup> But each plan, while it may be generic in nature, must also address the specifics of the project, including the techniques to be used, and the equipment including pre-cleaned sample holding containers, individual container preservation methods, number of samples, sample storage and transportation conditions, and maximum allowable holding times. The sampling plan should also address personnel safety, the personal protective equipment to be used, and the level of training of the individual taking the sample.<sup>35</sup> Many individual States have their own sampling and analytical protocols.<sup>36</sup> Also, see the sample container information in the endnote.<sup>37</sup> It is a reference to sample container size, maximum sample holding time, and preservation method.

The sampling plan should also dictate the maximum holding times and conditions for transportation to the laboratory. Most sampling efforts are accompanied by large coolers full of ice for packing the samples for transport to the laboratory. Often the samples are shipped to a remote laboratory, and the travel times must be figured into the quantity of ice, as most of the samples, especially the samples with a biological component, must be stored at the temperature of melting ice, and when the laboratory receives the samples, the samples must be at the specified temperature, or the sampling and analysis is void.

The USEPA has its own list of 65 priority pollutants (toxic pollutants), which may have to be analyzed regardless of the source of contamination.<sup>38</sup> While the list is common to other countries, there are individual variances.<sup>39</sup> The analytical methodology for the toxic pollutants is specific and different from those used for soils.<sup>40</sup> Many of the water analysis methods are identical to those in *Standard Methods*.<sup>41</sup> Note that *Standard Methods* is not to be confused with USEPA Publication SW-846, which contains sampling and analytical protocols for solid wastes and contaminated soils, used in conjunction with the Resource Conservation Recovery Act.



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ENVIRONMENTAL MONITORING & LABORATORY ANALYSIS  
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PAGE: \_\_\_\_\_ OF \_\_\_\_\_

CLIENT NAME CLIENT ADDRESS/PHONE NUMBER/FAX NUMBER:				ANALYSIS REQUESTED									
				CONTAINER TYPE		PRESERVATION							
				PRESENTATION									
REPORT TO:	CC:	# of	L	P - PLASTIC	1 - HCl, 4°								
REQUESTED COMPLETION DATE:	PO #:	C O N T A I N E R S	A	A - AMBER GLASS	2 - H <sub>2</sub> SO <sub>4</sub> , 4°								
PROJECT NAME/STATE:		I	G - CLEAR GLASS	3 - HNO <sub>3</sub> , 4°									
PROJECT #:		D	V - VIAL	4 - LiCl, 4°									
DATE	TIME	MATRIX CODE*	O	S - STERILE	5 - NaOH/2Ac, 4°								
		C O M P	R	O - OTHER	6 - Na <sub>2</sub> SO <sub>3</sub> , 4°								
		G A B	SW - SURFACE WATER	7 - 4°									
			ST - STORM WATER										
			L - LIQUID										
			W - WATER										
			P - PRODUCT										
REMARKS/ADDITIONAL INFORMATION													
FOR LAB USE ONLY													
SAMPLED BY AND TITLE:		DATE/TIME:		RELINQUISHED BY:		DATE/TIME:		LAB #:					
RECEIVED BY:		DATE/TIME:		RELINQUISHED BY:		DATE/TIME:							
RECEIVED BY LAB:		DATE/TIME:		SAMPLE SHIPPED VIA:		COURIER		CLIENT	OTHER:	In-house location:			
SH:	Labeled Preserved	loc. Yes or No	Temperature:	UPS	FED-EX	Intact	Broken	Missing	Cooler #	Entered into LIMS:			
Please use Black Ink in inordinate form													

Figure 2.3 Chain of custody record. Source: Courtesy of Analytical Services, Inc.

The sampling plan moves on paperwork. Each sample must be labeled with the time and place, and the analyses required. There is also a master log for the analyses, which is transmitted to the laboratory to direct their operations. In general, each of the samples collected must have a label affixed to the sample, and it must be placed in a plastic bag (partially to protect the label, and partially to protect the sample from vapor contamination). A sample log form is shown in Figure 2.3. The purpose of the paperwork is to establish a “chain of custody.” The chain of custody is an evidential protocol that insures that (i) the sample integrity is valid, and (ii) no one else has tampered with nor interfered with the sample.

## 2.19 Analytical Methods and the Role of the Laboratory

Every measurement has some error associated with it. The error is dependent upon the method employed, the caution of the analyst’s technique, the interferences in the matrix, and the sensitivity of the equipment. Errors generally fall into the categories of systematic errors, instrument errors, proportional errors, calibration errors, method errors, interference errors, and blunders.<sup>42</sup> Part of the quality control procedures required include replicate analyses, and matrix spikes to ensure that the errors and outside influences have been minimized as far as practicable. The overall subject of errors is discussed further in Chapter 6.

Environmental contaminants that were invisible in previous times, or which were undetectable, are now measurable with high precision. Every time we analyze a sample, we are making a statement that the results are accurate within the error parameters, but we fail to state the parametric limits for the analyses. For example, the true value of a pollutant may be  $5.48 \text{ mg l}^{-1}$ . Buried in the description of the analytical method, one will find the error of the method. In this case, we will assume that the error is 10%. Then the laboratory is really telling us that the most probable value for the compound is  $5.48 \pm 0.548 \text{ mg l}^{-1}$ , and according to statistical theory, that has a 68% chance of being accurate. If we consider that we want a 99+% chance of accuracy, we must then expand our definition of error to include three times the error. In this case, it would be  $0.548 \times 3$  or  $1.664 \text{ mg l}^{-1}$ , giving  $5.48 \pm 1.664 \text{ mg l}^{-1}$  as the result of the analysis.

Many regulatory bodies rely upon a fixed number as an upper limit for regulatory compliance in discharges in both daily maximum and monthly average reporting of monitoring data. That fixed number has no leeway, unless the discharge permit specifies that it does. This has implications for both the process operations and for the analytical preparation and analysis.

The following tables illustrate some of the measurement and method errors associated with various types of environmental tests. The data on metals was obtained from the USEPA Analytical Methods; the data on BOD and COD (both types) is from the Hach Company.

There is a substantial caution required regarding certain types of popular analyses. For analyses of biochemical oxygen demand (BOD),<sup>43</sup> and total suspended solids or volatile solids, there are no primary standards, for the reason discussed in the endnote.<sup>44</sup> In many instances, the regulatory community, primarily for historical reasons, prefers the BOD test as its standard for measurement of oxygen uptake in an effluent. The BOD test is unreliable at low values of BOD, but, some regulatory agencies have issued discharge permits with BOD values of 2.5 or less (Tables 2.15–2.17).

**Table 2.15** Analytical method errors for common metals in water by ICP.

Element	Mean concentration ( $\text{mg l}^{-1}$ )	n	Representative standard deviation (RSD) (%)	Accuracy (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

Note: These performance values are independent of sample preparation because the laboratories analyzed portions of the same solutions and are provided for illustrative purposes only. Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

n, number of measurements.

**Table 2.16** Standard deviations for several types of BOD measurements.

Type of seed	Mean five-day BOD (mg l <sup>-1</sup> )	Standard deviation (mg l <sup>-1</sup> )
Settled fresh sewage	218	±11
Settled stale sewage	207	±8
River water (four sources)	224–242	±7–13
Activated sludge effluent	221	±13
Trickling filter effluent	225	±8

Note: Data taken from *Standard Methods*, 14th ed., p. 548, 1975.

**Table 2.17** Standard deviations for two types of COD measurements.

Precision of Mn III COD test				
Sample	Mn III COD (mg l <sup>-1</sup> )	Standard deviation (mg l <sup>-1</sup> )	Relative standard deviation (%)	Number of tests (n)
800 mg l <sup>-1</sup> COD	797	13	1.6	7
500 mg l <sup>-1</sup> COD + 500 mg l <sup>-1</sup> chloride	508	3	0.6	4
ASTM wastewater influent reference	1008	7	0.7	4
Wastewater influent	463	13	2.8	3

Dichromate COD precision and accuracy				
Sample	Dichromate COD (mg l <sup>-1</sup> )	Standard deviation (mg l <sup>-1</sup> )	Relative standard deviation (%)	Number of tests (n)
500 mg l <sup>-1</sup> COD	500 <sup>a)</sup>	1.7	0.3	3
500 mg l <sup>-1</sup> COD + 500 mg l <sup>-1</sup> chloride	508 <sup>a)</sup>	1.0	0.1	3
Wastewater influent	245 <sup>a)</sup>	6	2.4	5
Wastewater effluent	45 <sup>b)</sup>	4.7	2.6	5
Textile industry	176 <sup>a)</sup>	4.6	2.6	5
ASTM synthetic wastewater sample	1018 <sup>a)</sup>	14	1.3	3
Swimming pool	13 <sup>c)</sup>	0.6	4.6	3

Note: There is a difference in accepted analytical methods for COD, between the dichromate method, and the permanganate method. See the discussion by Hach (<https://www.hach.com/quick.search-download.search.jsa?keywords=COD>). Also see *The Science of Chemical Oxygen Demand*, Technical Information Series Booklet No. 9, by Wayne Boyles, Hach Chemical Company.

a) Hach High Range Dichromate COD Vial.

b) Hach Low Range Dichromate COD Vial.

c) Hach Ultra Low Range Dichromate COD Vial.

### 2.19.1 The Analytical Plan

Every laboratory should have an analytical plan that standardizes the handling of the samples, including storage protocols, sample handling and marking, analytical techniques to be used, standards for analyses, standards for reporting, detection limits for equipment, personnel safety, equipment operating procedures, and so on. The analytical plan is often a part of the quality assurance (QA) and quality control (QC) plan, and depending upon the regulatory agency in the local governmental body, a laboratory cannot be qualified to run data for submission to the government unless it has a reviewed and approved QA/QC plan.<sup>45</sup>

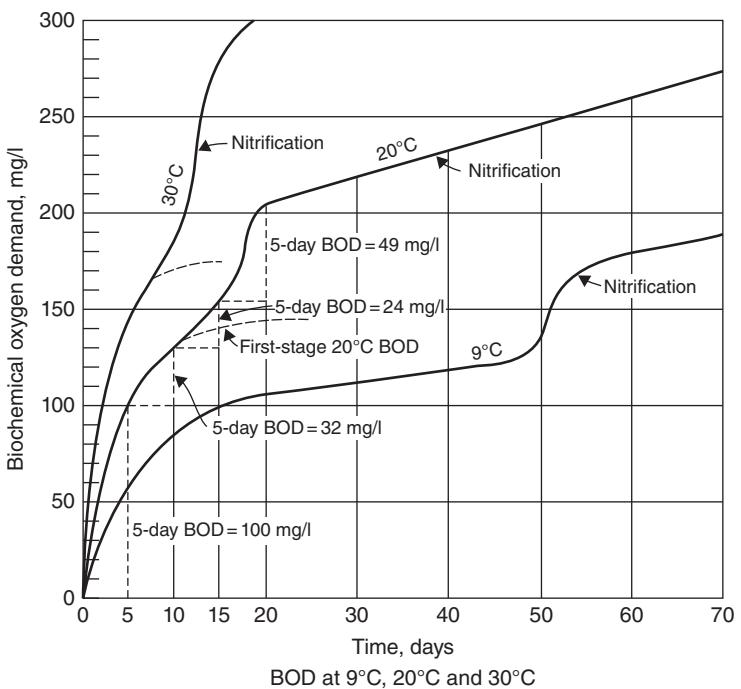
### 2.19.2 The Effects of Pollution on the Environment

Bacterial organisms are self-cannibalistic. In this sense, we are using the term microorganisms to include the bacteria and other microscopic organisms in the aquatic environment, as opposed to protists, water bugs, fish, and so on. These microorganisms have two distinct characteristics. They are comparable to young children at meal times – they have their food preferences, and will only eat their vegetables after some coaxing and or if they get hungry enough; and they are self-cannibalistic when their food disappears. These microorganisms in the environment are largely aerobic, but many are facultative and can perform chemical reduction reactions when oxygen levels are low. Because aerobic reactions are much faster, and more efficient for the organism, the aerobic pathway is preferable.

Facultative organisms can grow in aerobic and anaerobic conditions, and other principal classes of microbes include those that are obligate aerobes and obligate anaerobes. All of them have their place in treating wastewater and removing pollution.

When a waste (food) is introduced into a population, there is a slight delay until the organisms develop the enzymes needed to hydrolyze it so that it can be turned into food. The role of organisms in reducing organics is to gain energy for its own growth. If the wastes are not hydrolysable, they are not a food source for microorganisms in the aquatic environment. Aerobic growth is more efficient and faster – the growth rate of aerobes is about three times faster than anaerobes.

The immediate effect of the introduction of food into an aquatic environment is to cause a temporary drop in the dissolved oxygen levels in the stream, as there is often an immediate oxygen demand imposed by the waste. After some relatively short period, the microorganisms (bacteria, biota, etc.) in the stream will hydrolyze the waste, and start to digest it, aerobically if there is sufficient oxygen in the water, and co-metabolize it with nitrates, carbonates, phosphates, and sulfates. If the food is plentiful, the bacteria will grow at a very rapid rate, doubling every few hours. This is the log growth phase.



**Figure 2.4** Variation of BOD with temperature.

As the food (including oxygen) become more limited, the growth slows first to an endogenous respiration phase, and then into a log decline phase where the organisms are self-cannibalizing. The changes in oxygen levels in a receiving stream adversely affect the aquatic life, reducing the number of species and type of organisms. This is shown in Figure 2.4; the variety of species is the lighter line, and the darker line shows the number of species. When a stream becomes anaerobic, or anoxic, the higher organisms decline and disappear and the lower organisms multiply.

The recovery of the stream is due to the natural infusion of oxygen (surface and other re-aeration) as shown below. With the return of sustainable oxygen levels, the obligate anaerobic organisms die off, and the higher forms of aquatic life return.

### 2.19.3 Oxygen Depletion – Biochemical Oxygen Demand

The BOD test is based upon the Winkler Dissolved Oxygen Test. In it the concentration of oxygen is measured by titration of a manganous sulfate and alkaline sodium azide solution with dilute sulfuric acid in the presence of starch, which is added near the end-point of the titration. The Winkler test is generally

accurate to about  $0.000\,071\,3\text{ mg l}^{-1}$  of dissolved oxygen in natural systems, but the BOD test that involves a dilution and two oxygen determinations are accurate to about  $20\text{ mg l}^{-1}$  because of the handling errors, and so on.<sup>46</sup> Where there are a number of interferences present, modifications are available for the test. Advances in membrane and electrode technology have simplified the test procedures. Although the wet chemistry method is still the accepted reference standard, the use of DO probes has become so common that it is also accepted.

Below  $20\text{ mg l}^{-1}$  the BOD test is considered inaccurate. The accuracy and precision of the test decrease at low BOD levels. *Standard Methods* indicates that the test is highly variable. The typical range of variability for a known standard glucose–glutamic acid solution is  $198\text{ mg l}^{-1}$ . Inter-laboratory measurements reported in *Standard Methods* for 14 months and 421 triplicate samples indicated that the mean of the samples was  $204\text{ mg l}^{-1}$  with a standard deviation of  $10.4\text{ mg l}^{-1}$ .<sup>47</sup> The control limits for the sample are:  $\pm 30.5\text{ mg l}^{-1}$  (plus or minus approximately three standard deviations).

Despite some regulatory trends towards issuing permits with very low BOD numbers, the statistical reliability of very low values below  $20\text{ mg l}^{-1}$  does not exist. However, this has not stopped the regulatory community from regularly issuing permits with  $\text{BOD}_5$  discharge limit values of less than  $3\text{ mg l}^{-1}$  for extremely sensitive environments. At that point, one analyzes the effluent directly.

The BOD test is most often run for five days and less frequently for 20 days, but under research conditions, intermediate values are also run; however, the five-day test is the standard. The test version most often used for regulatory purposes requires that an aliquot of waste be placed in a BOD bottle<sup>48</sup> and sealed to prevent air intrusion. The measured oxygen depletion of the oxygen in the bottle after five days of incubation in a dark place at  $20^\circ\text{C}$  determines the  $\text{BOD}_5$  of a waste. The  $\text{BOD}_5$  is run with a nitrification inhibitor using a bacterial seed that is acclimatized to the waste being examined.

The BOD test is sensitive to time, temperature, nutrient, and waste acclimation. It comprises several portions: initial demand or depletion; carbonaceous demand; and nitrification demand.

The initial demand is measured when a dilute sample of the waste is added to the test bottle. It is the amount of oxygen depletion that occurs immediately upon sample addition. The carbonaceous demand occurs more slowly. It can be estimated by the following equation:

$$\text{BOD}_{(t)} = \text{BOD}_i(1 - e^{-kt})$$

where  $t$  is time in days,  $k$  is a determined constant, and  $\text{BOD}_i$  is the five-day BOD of the waste. The rate coefficient  $k$  can vary anywhere from 0.2 to 0.6, but is generally about 0.2.

The BOD is a measure of the rate of biological degradation of the material. It is primarily a measure of the carbonaceous demand, but that can be misleading.

The following illustrates the point of the variables and the difference in demand from nitrification. If the test is not corrected for nitrification, the waste will appear to exert a greater carbon demand than it actually does. The correction for nitrification is to add a small amount of ammonium chloride to the dilution water, in order to inhibit the nitrifiers from consuming oxygen. Otherwise, after about five days, most of the carbon is exhausted and nitrification begins, and the apparent BOD is higher than the actual carbonaceous demand.

Temperature plays a major role in biochemical reactions. The rate of biochemical reactions doubles for each  $10^{\circ}\text{C}$  rise in temperature up to about  $30\text{--}40^{\circ}\text{C}$ , at which point the bacteria are thermally inactivated, and most bacterial activity stops (see Figure 2.5).

The adjustment to the rate constant is:

$$k/k_0 = e^{C_t(T-T_0)}$$

where  $k_0$  is the rate coefficient at standard conditions,  $C_t$  is an adjustment coefficient, and  $T$  and  $T_0$  are measured in centigrade from a reference of  $20^{\circ}\text{C}$ .

The adjustment ratios for various temperatures and approximate values of  $k = k_0$  are shown in Table 2.18 and Figure 2.4.

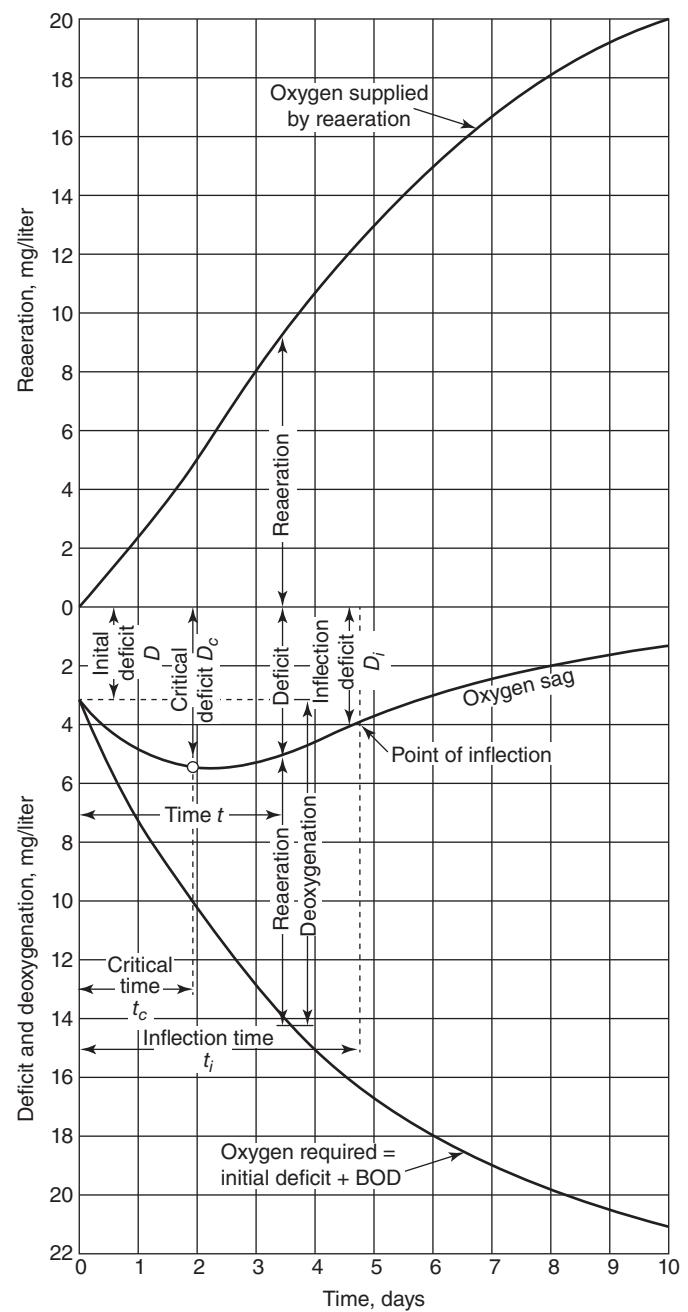
The Hach Company has developed a manometric test for the BOD that is, in many instances, similar to the Warburg respirometer. The Hach test uses amber glass bottles with plastic screw cap lids and magnetic stirrers in the bottles. The cap is connected to a piece of tubing, connecting it to a manometer which measures the change in pressure in the bottle. The manometer is calibrated in terms of  $\text{O}_2$  uptake and BOD. Inside the bottle is a stainless steel rod that has a cup containing potassium hydroxide (KOH). The bacteria in the amber bottle feed on the waste, which generates  $\text{CO}_2$  that is absorbed by the KOH. The practical advantage of the Hach system is that the manometer can provide a fairly rapid indication of any potential toxicity or shock-load problems, sometimes in time to allow the operator of the wastewater treatment plant to make adjustments to the system. The manometric BOD can also be used to estimate uptake coefficients and rate constants for wastewater.

#### 2.19.4 Oxygen Uptake in a Stream — The Oxygen Sag Equation

The discharge of an oxygen-depleting substance into a stream is not always harmful or permanently polluting. As we saw above, the discharge of a biodegradable substance into a stream stresses the oxygen levels. However, the stream re-aerates itself somewhat in proportion to the oxygen deficit.

The re-aeration is in proportion to oxygen transfer from the air, turbulence, and temperature. The basic rate of change in the oxygen deficit of a stream is given by the Streeter–Phelps equation (US Public Health Service Bulletin 146 (1925)). The deficit  $D$  is measured via the base formulation for the Oxygen Sag curve as follows:

$$\frac{dD}{dt} = kL_a - rD_a$$



**Figure 2.5** The oxygen sag curve illustrating oxygen depletion. Source: Fair and Geyer, *Elements of Water Supply and Wastewater Disposal*, John Wiley and Sons, 1963.

**Table 2.18** Variation of  $k_0$  with temperature.

$k_0$	$T - T_0$					
	-15	-10	-5	0	5	10
0.3	0.0111	0.0498	0.2231	1.0000	4.4817	7.3891
0.4	0.0025	0.0183	0.1353	1.0000	7.3891	7.3891
0.5	0.0006	0.0067	0.0821	1.0000	12.1825	7.3891
0.6	0.0000	0.0009	0.0302	1.0000	33.1155	7.3891

where  $D$  is a reference distance;  $D_a$  is the point of pollution or reference;  $k$  is the BOD oxidation constant;  $r$  is the rate of re-aeration;  $L_a$  is the first stage (carbonaceous) BOD or  $\text{BOD}_5$ .

$$D = \frac{kL_a(e^{-kt} - e^{-rt})}{(r - k)} + D_a e^{-rt}$$

When the equation is re-written, the points of minimum oxygen concentration and inflection are found by the following equations:

$$f = r/k$$

$$D_c = (L_a e^{-kt})/f \quad \text{and} \quad t_c = [1/(k(f - 1))] \ln \{f[1 - (f - 1)(D_a/L_a)]\}$$

where  $D_c$  is the time to the critical oxygen level and  $t_c$  is the distance to the critical oxygen level.

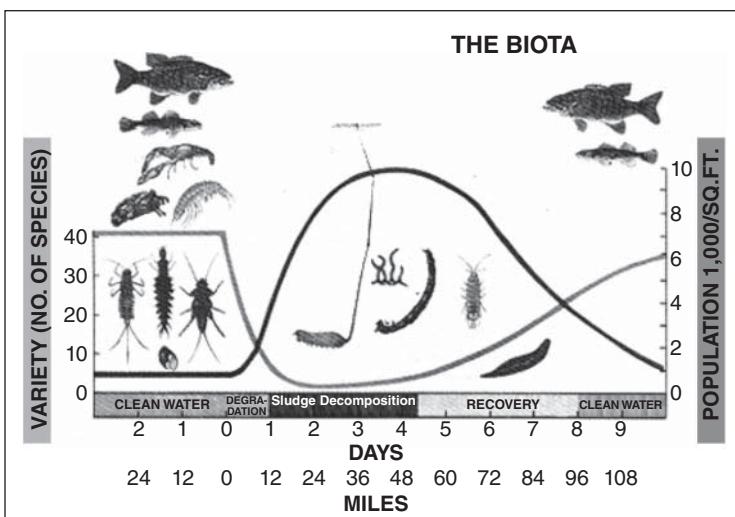
The relationships are shown in Figure 2.5.

### 2.19.5 Biology of Polluted Water

The change in oxygen levels in the stream leads to changes in the aquatic environment. Many of these changes are reversible, but some are not. The changes occur not only to the chemistry but also to the biology and ecology of the stream.

As the oxygen levels start to drop, species begin to disappear. Certain species such as trout and game fish require a minimum dissolved oxygen content around  $5 \text{ mg l}^{-1}$ . If the oxygen content falls below the critical level, the fish cannot traverse the region, and migration for spawning is effectively eliminated.

As the oxygen content falls further and drops toward zero, the biota and the plants change. Benthic deposits develop in the stream and some metals begin to precipitate while others are reduced. The nitrates are reduced to ammonia (causing toxicity) and then further to nitrogen gas. When the nitrates are gone, the phosphates and the sulfates reduce next. By this time the Oxidation Reduction Potential (ORP) is in the negative range, on the order of  $-100 \text{ mV}$  or less,



**Figure 2.6** Variation of aquatic species with contaminated water.

the river is a reducing environment, sulfates are reduced to  $\text{H}_2\text{S}$ , and dissolved metals are precipitated. The river water turns dark gray to black. The release of  $\text{H}_2\text{S}$  and some excess  $\text{NH}_3$  is continuous, causing the “rotten egg” odor associated with anaerobic conditions.

The river is essentially “dead” until the facultative and anaerobic bacteria have consumed their food and start to die off. Surface reaeration continues, and when the demand for oxygen is reduced, the stream oxygen content starts to rise to the point where it can begin to supply enough oxygen to the river or until entering streams carrying dissolved oxygen have sufficient dilution to change the anaerobic conditions. At that point, the river can start to recover, but the ecology has changed, perhaps permanently (Figure 2.6).

## 2.19.6 Nitrogen

There are several principal forms of nitrogen which are important in the water environment. Nitrate, or  $\text{NO}_3^-$ ; nitrite or  $\text{NO}_2^-$ ; organically bound (often proteinaceous) nitrogen, and ammonia or  $\text{NH}_3$ . The atmosphere is approximately 79% nitrogen ( $\text{N}_2$ ) gas, but it is not a strong factor in evaluating water pollution.<sup>49</sup> Nitrite is only a very minor factor because it is an intermediate on the oxidation path between ammonia and nitrate.  $\text{NO}_2^-$  is, in moderate concentrations, a toxin to aquatic life, but fortunately its presence and persistence are extremely low, generally less than  $0.2 \text{ mg l}^{-1}$  under most circumstances. Nitrate, on the other hand can exceed  $20\text{--}50 \text{ mg l}^{-1}$  levels from natural and manmade sources. Nitrate is a special problem in drinking water because it may cause methemoglobinemia, or blue baby syndrome, which is fatal to

infants. Accordingly, the USEPA, the WHO, and many other environmental health agencies have limited the maximum concentration in drinking water to under  $20\text{ mg l}^{-1}$ , and in the US to under  $10\text{ mg l}^{-1}$ .

### 2.19.7 Phosphorus

Phosphorus is an important nutrient for algae growth and also for bacterial growth. As will be discussed later, the approximate concentration of elements in many bacteria is 125 : 20 : 1, as carbon : nitrogen : phosphorus. Nitrogen is not a limiting factor as noted above. In order to eliminate algal blooms from ponds, lakes and rivers, phosphorus is the selected control parameter. The EPA water quality criteria state that phosphates should not exceed  $0.008$  and  $0.047\text{ mg l}^{-1}$  for discharge into lakes and reservoirs, and between  $0.128$  and  $0.01\text{ mg l}^{-1}$  for rivers and streams depending upon the ecoregion and localized factors.<sup>50</sup> The earlier guidance from EPA was  $0.05\text{ mg l}^{-1}$  for streams discharging into a lake or reservoir,  $0.025\text{ mg l}^{-1}$  for total P concentration within a lake or reservoir, and  $0.1\text{ mg l}^{-1}$  for flowing streams. Surface waters maintained at between  $0.008$  and  $0.047\text{ mg l}^{-1}$  P tend to remain uncontaminated by algal blooms.<sup>51</sup> In Florida, for example, the presence of algal blooms was limited when the phosphate concentration was less than  $30\text{ }\mu\text{g l}^{-1}$ .<sup>52</sup>

Algal blooms create several undesirable consequences in rivers and lakes. During daylight hours, the algae produce oxygen, and the dissolved oxygen concentration in the water body rises and can approach saturation levels; but at night the algae continue to respire and consume the oxygen they put back into the water. The extreme variation in oxygen levels is adverse to the survival of the higher forms of aquatic life, and fish are often the first casualties.

Algae also can impart a taste and odor to the water which is persistent and difficult to remove. The various types of algae can produce a variety of tastes and odors including: earthy (geosmin); musty (isopropylmethoxypyrazine and isobutylmethoxypyrazine); turpentine or oily (methyl tertiary butyl ether); fishy or rancid (2,4-Heptadienal, decadienal, octanal) and others. Many of these compounds are detectable (taste or smell) at concentrations of  $50\text{ }\mu\text{g l}^{-1}$  or less. Their removal requires oxidation or carbon adsorption, and a combination of hydrogen peroxide and UV light can be effective in removing or destroying some of the taste- and odor-causing compounds.<sup>53</sup> Cyanobacteria can also cause the formation of cyanotoxins, and many countries have established limits of  $1\text{ }\mu\text{g l}^{-1}$  on cyanotoxins in water. Another side-effect of algal blooms can often be the formation of “red tides” due to fertilization of seawater, and there are many reports of domesticated animals and livestock dying after drinking from ponds or rivers where there was a substantial algal bloom. The suspected cause is believed to be an alkaloid toxin produced by the algae.<sup>54</sup>

When algal blooms occur, the algae take up the phosphorus and incorporate it into their structure. But, when cold weather comes, and the algae die off, they often sink to the bottom of a pond where they decay and re-release the

phosphorus back into the water column, and the cycle starts all over again. One of the few successful techniques for removing algae from the water column is to precipitate it with iron or aluminum salts (ferric chloride, or aluminum sulfate) or precipitate it with calcium (lime) to form calcium phosphate. The success of these techniques is often marginal and may be temporary, lasting a few years at most. The ultimate solution may be dredging the lake or pond, or biological treatment with the harvesting of algae or bacteria that take up and hold phosphorus.<sup>55</sup>

## Notes

- 1 A voluntary discharge can be one where an operator decides that it is too difficult to recapture and recycle the wash water used in cleaning, or it can be an off-specification batch of chemicals, or a drained tank where the contents are sewered rather than captured and recycled. In short, anything that is discharged to the process sewer which probably should not be, fits the description.
- 2 The background on this was that the union plant (now closed) had developed a set of bad housekeeping practices and attitudes. At one meeting we were told that the name "Environmental Control Department" implied that it was our job to control the messes and pollution made by the operations group. We sought and received permission from the plant manager to fill in the holes in the curbing around that portion of the plant so that it was watertight. We then went in and poured quick-set cement into the existing sewers to seal them. The instantaneous result was to remove the ability of the operators to dump wastes and off-spec materials to the drains. The housekeeping in the area immediately improved and there were no further problems, except for the moaning of the operators when they found out that they had to change their work habits and operate the plant in an environmentally friendly manner rather than in the sloppy manner to which they were accustomed.
- 3 A good reference on air conditioning and the principal practices for cooling towers can be found here: [http://www.google.com/url?url=www.emsd.gov.hk/emsd/e\\_download/pee/wcacsCoP\\_Part\\_1.pdf&rct=j&q=&esrc=s&sa=U&ved=0CC8QFjAAahUKEwiIj\\_L\\_JLIAhUDlx4KHZU6AAM&usg=AFQjCNFPi6kkYE\\_svYdmqX17-Kta4ZmMeQ](http://www.google.com/url?url=www.emsd.gov.hk/emsd/e_download/pee/wcacsCoP_Part_1.pdf&rct=j&q=&esrc=s&sa=U&ved=0CC8QFjAAahUKEwiIj_L_JLIAhUDlx4KHZU6AAM&usg=AFQjCNFPi6kkYE_svYdmqX17-Kta4ZmMeQ). It is a three-part work that contains the theory and practice of cooling systems. The link is only for Part 1, but the other two parts can be accessed from the first.
- 4 *Legionella* bacteria cause Legionnaire's disease, which was first discovered in the Philadelphia area Veterans' Administration Hospital in the 1970s. The bacterial often grows in protozoa and other aquatic organisms, which shelter it from high temperatures and many disinfection chemicals. For more

information see: <http://www.cdc.gov/legionella/clinicians/disease-specifics.html>.

- 5 ASME also has the following phosphate treatment guidelines for boilers below 600 psig:

Hydroxide alkalinity	100–600 ppm
Phosphate	30–50 ppm
Silica	200 – (0.25 × boiler pressure)
Total dissolved solids	2000–3000 ppm

- 6 See: *The Coast Guard Engineer's Digest*, vol. 31, No. 253, Spring 1993, for details on magnetic treatment system test results; *Naval Engineers Evaluate Magnetic Boiler Feedwater Treatment as an alternative to Chemicals* by CDR Gregory J. MacGarva, Naval Engineering (G-ENE); NTIS: *ETP Fluid Conditioning Systems, NTIS Report- Hibben, AD-757887, Magnetic Treatment of Water*. See also: *Standard Specification for Boiler Compounds and Water Treating Chemicals*, Institutional Water Treatment Program, by Kent W. Smothers, Mark D. Brooks, and Chuck Curtiss.
- 7 *Water Requirements of the Iron and Steel Industry*, US Geological Survey Paper 1330-H (available on the Internet).
- 8 *Development Document for Final Effluent Limitations Guidelines and Standards for the Iron and Steel Manufacturing Point Source Category*, April 2002, USEPA, available on their website.
- 9 [http://pa.water.usgs.gov/reports/wrir\\_98-4258.pdf](http://pa.water.usgs.gov/reports/wrir_98-4258.pdf): a 1997 study.
- 10 <http://www.theguardian.com/world/2000/feb/14/1>.
- 11 At the time of writing, most of the EU and the UK rely upon natural gas imported from the states of the former Soviet Union. In turbulent political times, the energy supply from those states can be curtailed on the supply side, to influence public opinion and international relations. The EU and the UK each have over 100 years supply of natural gas available to them, but Green campaigners and other regulatory issues have limited the consideration of the utilization of shale gas supplies. See Inogate's mapping of gas pipelines at <http://www.mappery.com/map-of/Europe-Proposed-Natural-Gas-Pipelines-Map>.
- 12 A short example will suffice. Take a sponge and place it in a pan, then fill the remaining area of the pan with sand. Then pour oil into the sponge and the pan until the sponge is saturated. Using a straw, try to extract the oil from the sponge and the pan. This is a reasonably accurate analogy of the process of oil extraction. Sometimes the sponge and the oil may be in a confined layer that allows for easy extraction. Many other times, the oil has to be extracted by a jack pump – a pump with a long rod that pumps the oil from the bottom of the well, lifting it to the surface. If you succeed in extracting some of the oil from your pan, how do you get the remainder, and what is the recovery percentage? These are the issues of reservoir engineering.

- 13 Source: Fairmont Sanitrol on their website comparing propants to slickwater,  
[http://fmsa.com/Production/?gclid=CjwKEAiA9uaxBRDYr4\\_hrtC3tW8SJAD6UU8GhbLa3VwGP29cjUZeDnqnTw1RyQEE58Ya0hD\\_U4ByRoCqB7w\\_wcB](http://fmsa.com/Production/?gclid=CjwKEAiA9uaxBRDYr4_hrtC3tW8SJAD6UU8GhbLa3VwGP29cjUZeDnqnTw1RyQEE58Ya0hD_U4ByRoCqB7w_wcB).
- 14 See *Data Regarding Hydraulic Fracturing Distributions and Treatment Fluids, Additives, Propants, and Water Volumes Applied to Wells Drilled in the United States from 1947 through 2010*, available on the USGS website.
- 15 *Hydraulic fracturing water use variability in the United States and potential environmental implications*, Tanya J. Gallegos, Brian A. Varela, Seth S. Haines, and Mark A. Engle, AGU Water Resources Research Study.
- 16 *Optimization of Water Usage at Petroleum Refineries*, by C.H. Guernsey & Co., presented at the Water/Energy Sustainability Forum, Salt Lake City, UT, September 15, 2009.
- 17 [http://petrowiki.org/Crude\\_oil\\_characterization](http://petrowiki.org/Crude_oil_characterization).
- 18 *Preliminary Data Summary for the Petroleum Refining Category* USEPA Publication number EPA 821-R-96-015 (1996 Study).
- 19 Mekonnen and Hoekstra. (2010). The green, blue, and grey water footprint of crops and derived crop products. <http://waterfootprint.org/en/water-footprint/product-water-footprint/water-footprint-crop-and-animal-products>.
- 20 <http://www.ers.usda.gov/topics/farm-practices-management/irrigation-water-use.aspx>; <http://www.globalagriculture.org/report-topics/water.html>; <http://pubs.usgs.gov/circ/1405/pdf/circ1405.pdf>.
- 21 [www.arb.ca.gov/fuels/lcfs/workgroups/lcfssustain/hanson.pdf](http://www.arb.ca.gov/fuels/lcfs/workgroups/lcfssustain/hanson.pdf).
- 22 [http://www.pge.com/includes/docs/pdfs/shared/edusafety/training/pec/water/blaine-hanson\\_water\\_forum\\_complete.pdf](http://www.pge.com/includes/docs/pdfs/shared/edusafety/training/pec/water/blaine-hanson_water_forum_complete.pdf).
- 23 <http://www.lenntech.com/water-food-agriculture.htm>.
- 24 [http://www.hoards.com/blog\\_water-bottleneck-on-farm](http://www.hoards.com/blog_water-bottleneck-on-farm).
- 25 [www.omafra.gov.on.ca/english/engineer/facts/07-023.htm](http://www.omafra.gov.on.ca/english/engineer/facts/07-023.htm).
- 26 [http://www.hoards.com/E\\_crops/cf5](http://www.hoards.com/E_crops/cf5).
- 27 Appendix V, <http://waterfootprint.org/media/downloads/Report-48-WaterFootprint-AnimalProducts-Vol2.pdf>.
- 28 EPA Development Document for CAFOs, page 6–1.
- 29 Oklahoma Cooperative Extension Service, *BAE 1762 Methane Production Potential of Waste Materials*.
- 30 See *Removal of Protein and Fat using Lignosulfonic Acid from Meat Slaughtering and Packing Wastes*, by T.R. Foltz, Jr., K.M. Ries, and J.W. Lee, Jr., found at: <http://infohouse.p2ric.org/ref/19/18649.pdf>.
- 31 Animal fats are often rendered. Aluminum salts used for coagulation can interfere with the rendering process. Iron salts do not have the same problem but stain the rendered product and make it less usable.
- 32 [http://image.sciencenet.cn/olddata/kexue.com.cn/bbs/upload/15147ICP\\_or\\_AA.pdf](http://image.sciencenet.cn/olddata/kexue.com.cn/bbs/upload/15147ICP_or_AA.pdf).

- 33 <http://www.eag.com/documents/icp-oes-ms-detection-limit-guidance-BR023.pdf>.
- 34 In a number of instances, samples are to be preserved with reagent grade nitric or hydrochloric acids in each sample container. It is often preferable to have pre-cleaned sample containers with the preservative already applied. These pre-cleaned containers (bottles and jars) can be ordered from a laboratory supply house.
- 35 The sampling plan should specify the type of clothing, the level of protection and equipment, and by reference, if the location is sufficiently hazardous, there are US and EU protocols regarding the use of some types of personal protective equipment, especially if respiratory protection is required. For the US operations, the applicable standard is OSHA 1910.132, and it includes a requirement for training where PPE is to be worn. See the following requirements: [https://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=9777](https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9777).
- 36 For example: <http://www.in.gov/idem/files/performpresanalychemdata.pdf>, and the reference page for Florida Department of Environmental Protection: <http://www.dep.state.fl.us/water/sas/qa/index.htm>. The Florida requirements are quite complete and thorough, as are the Indiana plans. They are a bit different but reflect the approaches of individual states.
- 37 <http://asi-lab.com/resources/containers-preservations-holding-times>.
- 38 The list of toxic pollutants can be found here: <http://www.gpo.gov/fdsys/pkg/CFR-2014-title40-vol29/xml/CFR-2014-title40-vol29-sec401-15.xml>.
- 39 For the list of EU priority pollutants (substances) see: [http://ec.europa.eu/environment/water/water-framework/priority\\_substances.htm](http://ec.europa.eu/environment/water/water-framework/priority_substances.htm).
- 40 <http://www2.epa.gov/cwa-methods>.
- 41 *Standard Methods* is a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). The full title is *Standard Methods for the Examination of Water and Wastewater*. As such, it is a standard reference work for most analytical laboratories.
- 42 *Errors in Chemical Analyses, Lecture 1 (notes)*: <http://memo.cgu.edu.tw/hsiu-po/Analytical%20Chem/Lecture%201.pdf> and <http://unicorn.ps.uci.edu/M3LC/lectures/LectureWeek1.pdf>.
- 43 BOD is measured by oxygen depletion in a 300 ml closed bottle using acclimated nutrient seed. There are many ways of creating errors in the BOD test, not least of which is using non-acclimated seed materials.
- 44 The standard for biochemical oxygen demand and total suspended solids measurements are highly variable. The two compounds used to measure BOD standard are glutamic acid and glutamine, which should give a value of around 200–204 mg l<sup>-1</sup> plus or minus 15%, and the variability of BOD is due to the ability and acclimatization of the bacteria in the seed water to the material for the substrate. There is no accepted standard for TSS or volatile suspended

- solids (VSS). The variability in these measurements is of the order of 15%. The reason for the variability of the TSS/VSS measurements is that the tests rely upon a 0.45 µm filter, and research has shown that there are a number of solids in wastewater which are less than that size. To that end, the International Water Association modeling group recommends that the insoluble fraction in wastewater is that which is greater than 0.2 µm. [http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2008\\_11\\_25\\_methods\\_method\\_biological\\_1684-bio.pdf](http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2008_11_25_methods_method_biological_1684-bio.pdf).
- 45 See the QA/QC Plan guidance from the State of Indiana for an example: <http://www.in.gov/idem/nps/3383.htm> [http://www.floridahealth.gov/environmental-health/onsite-sewage/research/\\_documents/final319qapp.pdf](http://www.floridahealth.gov/environmental-health/onsite-sewage/research/_documents/final319qapp.pdf), and [http://www.dep.state.fl.us/labs/docs/lab\\_qualitymanual.pdf](http://www.dep.state.fl.us/labs/docs/lab_qualitymanual.pdf).
- 46 The test is accurate to about 0.05 ml of O<sub>2</sub> per l, which is equivalent to 0.00007143 mg. See the following reference: [http://www.ioos.noaa.gov/qartod/dissolved\\_oxygen/codispot1988\\_oxygenprotocol\\_a.pdf](http://www.ioos.noaa.gov/qartod/dissolved_oxygen/codispot1988_oxygenprotocol_a.pdf).
- 47 APHA, AWWA & WEF, *Standard Methods*, 19th ed., p. 5–3.
- 48 The BOD bottle is a narrow-mouth bottle with a ground glass stopper and a funnel rim around the ground glass seal. Before the bottle is put into the incubator, water is added to the funnel neck around the top of the bottle and the top wrapped with foil or plastic wrap to prevent seal water evaporation. The samples are then incubated in the dark for five days at 20°C. The oxygen deficit is measured and the depletion used to compute the BOD.
- 49 Many forms of bacteria such as cyanobacteria (blue-green algae) can fix nitrogen from the air and convert it to inorganic compounds which are usable by plants.
- 50 <https://www.epa.gov/nutrient-policy-data/ecoregional-nutrient-criteria-rivers-streams>.
- 51 <http://www.water.ncsu.edu/watershedss/info/phos.html>.
- 52 *Relating Algal Bloom Frequencies to Phosphorus Concentrations in Lake Okeechobee*, William W. Walker, Jr. and Karl E. Havens. <http://www.wwwalker.net/pdf/chlaokee.pdf>.
- 53 <http://www.waterrf.org/publicreportlibrary/91169.pdf>.
- 54 <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.473.6171&rep=rep1&type=pdf>, and [http://www.trojanuv.com/resources/trojanuv/casestudies/Taste\\_and\\_Odor\\_Fact\\_Sheet\\_RevSep05.pdf](http://www.trojanuv.com/resources/trojanuv/casestudies/Taste_and_Odor_Fact_Sheet_RevSep05.pdf).
- 55 <http://www.ecy.wa.gov/programs/wq/plants/algae/lakes/LakeRestoration.html>.

## 3

### Groundwater and its Treatment

The challenges of groundwater treatment often pose special problems for the water treatment professional, because of the lack of fundamental understanding of the issues of hydraulics associated with the collection and manipulation of groundwater. In this brief chapter, we will attempt to highlight some of the challenges and solutions associated with groundwater treatment. This chapter is not really treatment per se, but the hydraulics required to make the treatment viable.

As briefly discussed in Chapter 1, there are a number of factors that can influence the quality of the groundwater. They are:

1. The characteristics of the aquifer and its geology, including the chemical composition of the rock from which the groundwater is drawn.
2. The aquifer pore and grain size, porosity, storage coefficient, fractures, organic materials in the soil, clays, and soil structure and profile.
3. The movement and age of the water in the aquifer.
4. The source and quality of the water that enters the aquifer. There isn't really much one can do about this because much of the aquifer water will be hundreds of years old, and be derived from great distances away from the point of withdrawal.
5. The number and kinds of aquifers and aquiclude. The structure may be simple or extremely complex, and interconnected, or separated. In some instances, water in the same aquifer, when separated by an aquiclude, may move in different directions.
6. Mixing of groundwaters with other sources.
7. Anthropogenic factors such as surficial contamination or infiltration from various sources.

Any and all of these factors can influence the movement of contaminants in the groundwater.

### 3.1 Hydraulics of Groundwater

As briefly discussed in Chapter 1, Darcy's law governs the flow of groundwater. Darcy's law is expressed as:

$$Q = KiA$$

where  $Q$  is the quantity, usually in gallons, liters, or cubic meters;  $A$  is the area of the cross-section of the aquifer;  $i$  is the hydraulic gradient or the slope of the hydraulic grade line, usually expressed as a dimensionless number;  $K$  is the permeability coefficient, and has the dimensions of velocity, generally measured in centimeters per second, or feet per year.

There are a number of alternative formulations for the Darcy equation. The following

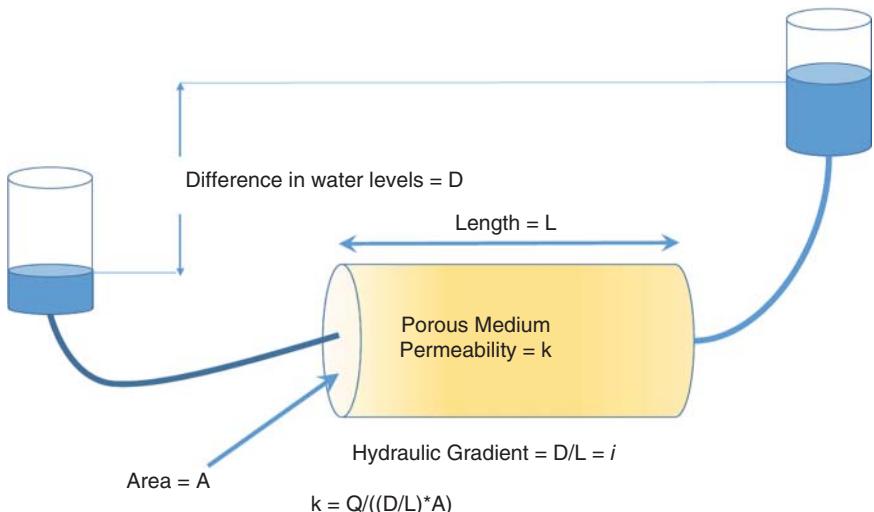
Alternate formulations for Darcy's Law include

$$V = Ki \text{ and } Q = \frac{AK(D)}{\mu L},$$

where the variables in Figure 3.1 are applicable and  $\mu$  is the dynamic viscosity of the fluid. Dynamic viscosity is defined as the product of kinematic viscosity and density. Figure 3.1 will help illustrate the concepts.

When one looks at flow of water in an aquifer, the equations are modified slightly by substitution.

$$Q = KbI$$



**Figure 3.1** Darcy's law – determining permeability.

**Table 3.1** Hydraulic conductivity of various soils.

Soil type	Range of conductivity in $\text{cm s}^{-1}$
Fine to coarse gravel	$10^6$ – $10^3$
Fine to coarse sand	$10^4$ – $10^{-1}$
Silt loess	$10$ – $10^{-3}$
Silt loam	$10^2$ – $10^{-2}$
Glacial till	$10^2$ – $10^{-6}$
Marine clays	$10^{-3}$ – $10^{-6}$
Shale	$10^{-3}$ – $10^{-7}$
Limestone – unfractured	$1$ – $10^{-4}$
Sandstone	$10$ – $10^{-2}$
Fractured rock – limestone and igneous	$10$ – $10^{-2}$

Source: Data taken from *Groundwater and Wells*, 2nd ed. (1986) by Johnson Filtration Systems, Inc., St. Paul, MN.

where  $Q$  is the flow,  $K$  is the average conductivity of the aquifer,  $b$  is the thickness of the aquifer, and  $I$  is the hydraulic gradient. This is exactly equivalent to the equation above.

The range of  $K$  for various soils is shown in Table 3.1. The values for conductivity in metric terms are  $1 \text{ m}^3$  of water per day at  $15.5^\circ\text{C}$ .

Thies (1935), one of the early groundwater investigators, proposed another modification of the formula,<sup>1</sup> substituting  $T$  as the transmissivity of the vertical section through which the water flows, giving the formula

$$Q = TIw$$

where  $w$  is the width of the vertical section, and  $I$  is the hydraulic gradient.

But for an aquifer, the water flows through the pores in the rock and sand and gravel, but we measure the bulk flow. The porosity of the rock is expressed as  $h$ , and the velocity of the water in the porous medium is calculated by:

$$Q = VA = \frac{KA(\delta h)}{L},$$

where  $\delta h$  is the difference in head between two points,  $h_2$  and  $h_1$ . Then,

$$V = \frac{K(h_2 - h_1)}{L}/\eta$$

where  $V$  is velocity. In the US ( $7.48 \text{ gallons/ft}$  as opposed to the Imperial gallons which are 20% larger) system of units, the hydraulic conductivity  $K$  has units of gallons per day per square foot and the volume needs to be converted to cubic feet. The velocity term is obtained by dividing the equation above by  $7.48 \eta$  rather than  $\eta$ , to get velocity in terms of feet per day.

**Table 3.2** Selected porosities and specific yields for common soil types.

Soil type	Porosity %	Specific yield %
Clay	45–55	1–10
Sand	25–40	10–30
Gravel	25–40	15–30
Sand and gravel mix	10–35	15–25
Sandstone	5–30	15–25
Shale	0–10	0.5–5
Limestone <sup>a)</sup>	0–10	0.5–5

- a) Limestone and unfractured crystalline rocks have very low specific yields, but limestone, and in particular weathered limestone, often has solution cavities and unusually high connectivity and porosity, often making it look more like Swiss cheese than solid rock. Therefore the porosity and specific yields may be proportionally larger.

Source: Data taken from *Groundwater and Wells*, 2nd ed. (1986) by Johnson Filtration Systems, Inc., St. Paul, MN.

The porosity of an aquifer depends upon grain sizes. The volume of water an aquifer or portion of an aquifer will hold does not necessarily indicate how much water the aquifer will yield when pumped. When a porous medium is gravity-drained, it will yield only a fraction of its total volume, due to surface tension of the liquid and other factors. This is known as the “specific yield” of the aquifer, and it is important in dewatering a region, and in trying to remove gross contamination of an aquifer. The following table shows some of the porosity and specific yields of representative types of formations. For confined aquifers, the specific yield cannot be determined because they are not drained during pumping, and any water released from storage is primarily due to the compression of the aquifer (Table 3.2).

## 3.2 Soil Particles and Surface Areas

Soil particles have a small size and a large surface area per unit of volume. Imagine a cube 1 m on a side. The area is six square meters. Now, chop that cube into eight equal pieces, each cube is 0.5 m on a side. Each smaller cube has one face area of 0.25 square meters, but the total surface area of each individual cube is 1.5 square meters, and since there are 8 of them, the total surface area is 12 m<sup>2</sup>. Dividing each of those cubes again, we now have 64 cubes, each 0.25 m on a side with a surface area of  $6 \times 0.25^2 = 0.375$  m<sup>2</sup>. So now the total surface area of

all the cubes =  $0.375 \times 64 = 24 \text{ m}^2$ . As our cubes become smaller and smaller, the surface area grows.

But many particles are not cube shaped but are round or semi-spherical. In a 1 mm cube we can put one sphere of 1 mm diameter. That has a surface area of approximately  $3.14 \text{ mm}^2$ . If we use a smaller sphere of 0.04 mm diameter, and assume cubic packing, the number of particles that can pack into our 1 mm cube is  $1.7 \times 10^7$  particles, and the total surface area is approximately  $850 \text{ m}^2$ . The approximate total volume of the particles is  $0.57 \text{ mm}^3$ , which is not significantly different, but slightly larger, than the original  $0.524 \text{ mm}^3$  volume of the original 1 mm sphere. Because many particles in nature have naturally occurring negative electrical surface charges, and will tend to hold contaminants on the surface, it is much more difficult to decontaminate a fine-grained soil than it is to decontaminate a coarse soil. The method of adsorption may be much more important than absorption for contaminated soils, just because there is so much more area in the fine-grained soil.

### 3.3 Well Hydraulics

There are three types of well in current use for monitoring groundwater – Types I, II, and III. The wells are shown in Figure 3.2. The Type I well is used for most common monitoring well installations. The annular space between the borehole and the well piping is commonly sealed with soil from the borehole to prevent surface contamination from entering the borehole and contaminating the well. The effectiveness of this type of well seal is only as good as the surrounding soils. If there is a porous or inadequate well seal, it will allow surface water to enter the groundwater at the point of the well and contaminate it.

The Type II well is the well is cased, and the annulus between the casing and the borehole is filled with cement and/or a cement–bentonite clay mixture to prevent the well from acting as a vertical conduit to move contaminants from a higher to a lower zone, and to prevent intrusion of surface water into the well. There is an additional seal at the top of the sand pack/bottom of the grout seal to further reduce the possibility of surface water intrusion.

In situations where there is significant contamination in one formation, and it is necessary to sample the formation beneath the contaminated zone, a different type of well is used. This Type III well is fully cased through the contaminated zone. The top borehole is larger and is filled as shown in Figure 3.2. When the well is completed, a second well is drilled through the bottom of the first well. The upper well is completed and bottom-sealed through the contaminated zone, and the well is carefully drilled to make sure that there is no contamination pathway through the contaminated zone.

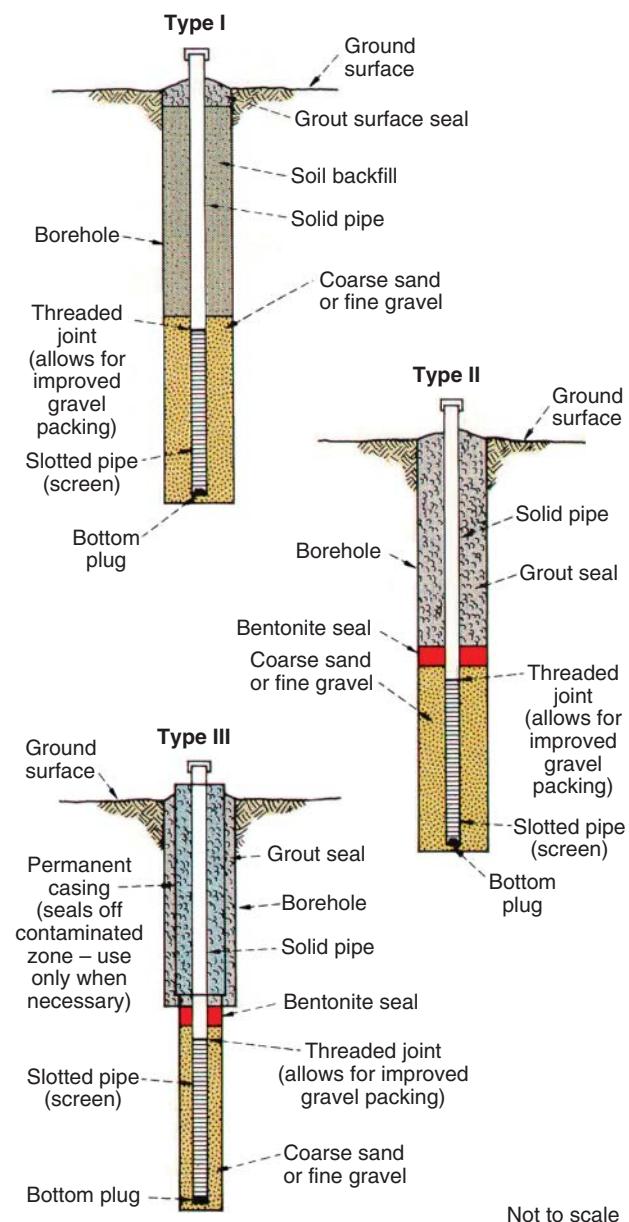


Figure 3.2 Common types of monitoring wells.

### 3.4 Well Packing and Screens

Finishing a well in an aquifer requires a well screen and some well (sand) packing unless it is completed in fractured rock. The packing is generally graded and screened sand, selected to keep the surrounding soils from being washed into the well: a sort of pre-filter. The packing is kept from the well interior by a section of screen. The screen slot size is generally selected based upon the size of the sand packing and/or the soil if it is not sand-packed, but in some instances, we have seen large diameter groundwater monitoring wells (in Hungary) with welded ladder steps for entry, and the openings for the sand pack were cut with an acetylene torch.

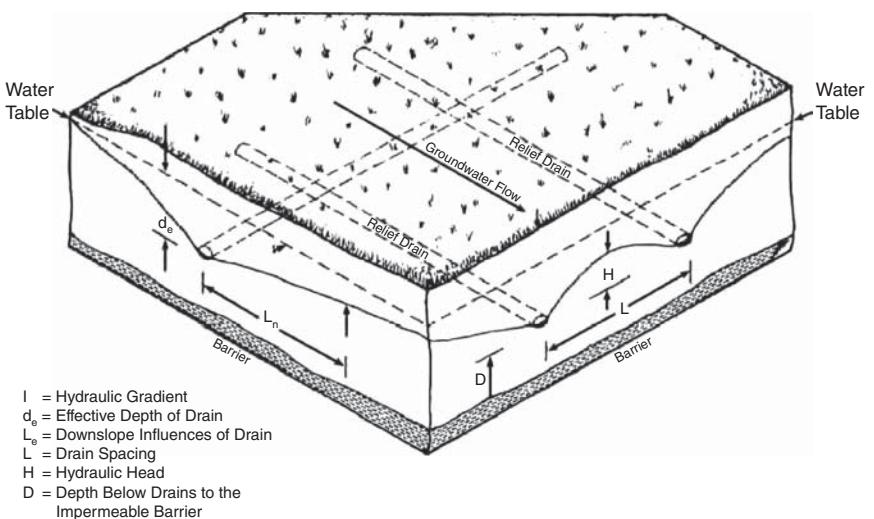
Well screens are selected by the geologist/well driller based on the size of the soils in the surrounding medium, and the well screens are selected based upon the width of the slots and the open area of the screen. Most monitoring wells are constructed of PVC, and the slots in the screens are plunge cut with a small thin saw with a width between 1 and 0.25 mm (0.394" to 0.01"). The screens can also be constructed from brass and stainless steel, and the wire is often drawn into triangular shapes and welded to the screen.<sup>2</sup>

The amount of open area in the screen system is important for pumping the well, and for when the well is used as an injection well to deliver gases or liquids into a treatment zone. When PVC piping is used in remediation of hydrocarbons, it is critical to select a well screen opening large enough to account for the action of the hydrocarbon on the PVC, which can cause it to swell and seal off the openings in the screen.

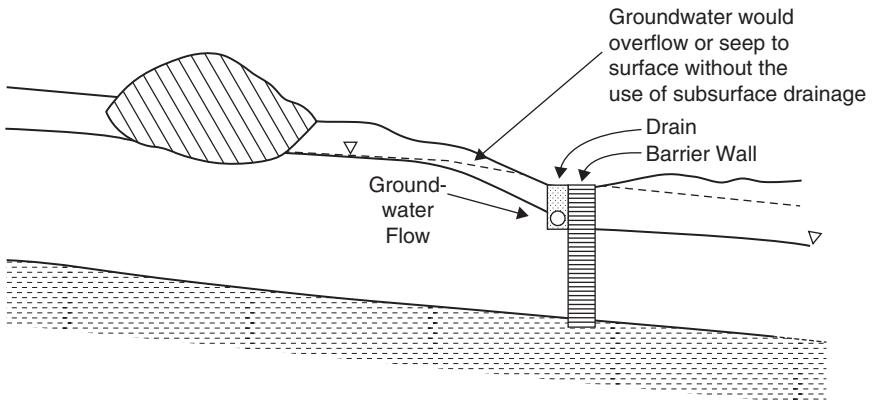
### 3.5 Trenches

Drainage trenches are often used to control the movement of near-surface groundwater. Figure 3.3 illustrates this point, as the groundwater is being drained by the trench and drain system shown. The purpose of the trenches is to lower the groundwater, which flows into the trench by gravity and is conveyed to the collection point where it is removed. Trench systems, like sewers, are usually surrounded by a gravel-packed bed both for support of the trench and for prevention of soil infiltration.

Trenches can employ well screens, but that is relatively rare. Most often, a trench is gravity-drained to a sump, and not under vacuum from a pump. Many trenches are built with perforated pipe, and have a relatively large open area with respect to the diameter of the trench piping, sometimes 25% or more of the pipe area per unit of length. Depending upon the service, some trenches come with their own gravel pack and an outside envelope of filter fabric to reduce the possibility of silt and soil accumulation in the trench. Other techniques include excavating a trench, lining it with filter fabric and gravel, and bedding the pipe



**Figure 3.3** Typical trench utilization for dewatering.



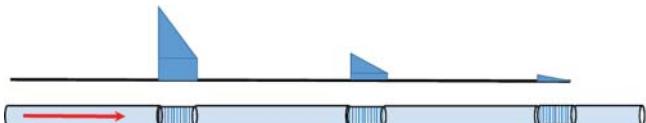
**Figure 3.4** Movement of groundwater contamination.

in the gravel. The filter fabric is then used to cover the top of the gravel bed, surrounding the drainage pipe in an envelope.

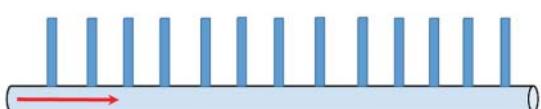
Trenches can be one-sided or two-sided. A one-sided trench has a vertical barrier installed as shown in Figure 3.4. This increases preferential collection from one area of the trench, but will not eliminate flow from the other side of the barrier, or flow coming around the ends of the barrier.

When a trench is used as an infiltration point to convey liquid or gas into the trench, the characteristic of the trench is substantially different. Injecting gas

Discharge pattern for a pipe using sections of well screen



Discharge pattern for a pipe using spaced orifices



Height of figure represents proportional flow from pipe

**Figure 3.5** Flow profiles for properly and improperly designed injection wells and trenches.

into a trench? Yes, as a newer remediation technique, but it is usually done by horizontal well (see Figure 3.5).

The idea behind an infiltration trench is to deliver chemicals into the groundwater in a controlled manner over a spatially controlled area. This may require pumping, or at least attention to the size of the opening and head losses through which the liquid or gas is flowing. The principal difference between a delivery trench and a horizontal well is the type of construction technique and the depth, length, and diameter of the trench versus the well.

For injecting liquid into the ground one has to consider the head losses through a nozzle or an orifice as the control point. First, recognize that simply installing a length of well screen is a self-defeating procedure because the open area of the well screen will be so large that it will take a disproportionate share of the flow, flooding the immediate area around the screen, and starving the far end of the pipe. That works in both directions, for collection and distribution. What is needed is a series of uniformly spaced holes as shown below.

The challenge is to balance the open areas (orifices) and the effect of those orifices on flow rate and hydraulic losses, to get a uniform distribution of the flow. By controlling the size and spacing of the open areas, one can insure uniform flow in water and/or gas distribution and collection.

This problem is encountered in filter gallery piping beneath the filter media. There is a need for underdrain piping which distributes backwashing water uniformly so that the filter can be cleaned.

The most effective type of distribution system is one that is tailored to the piping system.

### 3.5.1 Orifices and Pipe Losses

The formula for energy losses through a nozzle or orifice plate is the same, just the coefficient of discharge is different.

$$q = C_d A_o [2gh]^{0.5}$$

where  $C_d$  is the discharge coefficient,  $A_o$  is the area of the orifice and  $2gh$  is the acceleration of gravity times the hydraulic head. All of it has to be in the same appropriate units. The coefficient of discharge is between 0.59 and 0.61 for most orifice plates, depending upon the Reynolds number for the fluid system. Michael Duchene and Edward A. McBean reported the head loss coefficients for a number of different piping systems as equal to 0.6 to 0.66 depending upon the depth of burial and the depth of flow in the distribution piping. They principally experimented on piping systems with four openings around the pipe.<sup>3</sup> They also accounted for differences in hydraulic head for the various openings due to their location on the pipe.

The ideal situation is to design the distribution system so that the flow and the losses at the end of the pipe are zero. One way of designing the system would be to analyze the pipe at each perforation. If the flow in the pipe is  $Q$  and each orifice takes  $q$  out of the pipe flow, then the flow in the pipe after the first orifice opening is  $Q-q$ , which provides a new velocity  $V_{q1}$  in the pipe between the first and second openings, and a new set of friction losses for that length. Similarly, the flow after the second perforation is  $Q-2q$ , and the velocity for the next section is  $V_{q2}$ . Accurate calculation of the piping losses would require  $n+1$  different frictional calculations for head loss and friction in the length of the perforated pipe. That is just unrealistic and extremely cumbersome.

An old article in a textbook from the 1960s provides a good answer.<sup>4</sup> In that, they suggested that with a pipe of constant diameter, the head losses through the nozzle were approximately equal to the friction losses, equal to about a third of the frictional flow in the pipe. Put in scientific terms, the friction head or  $h_f$  is equal to the value shown below:

$$H_f = (KQ_0^2/L^2)^* (l - l^2/L + l^3/L^2)$$

where  $K$  is the hydraulic coefficient equivalent to the head losses in the total length of the pipe at full flow conditions;  $L$  is the length of the pipe;  $l$  is the fractional length of the pipe where the losses are occurring; and  $Q_0$  is the total flow in the pipe at maximum conditions. Remember that you will need to have the total head on the inside of the pipe greater than the pressure on the outside of the pipe.

Another solution technique is to perform an analysis across the orifice. In a simple case we have  $q_n = CA_o[2gh]^{0.5}$ , where the value of  $C$  is 0.60, the value of the large pipe flow is  $Q$  and the individual orifice value is  $q$ , and the hydraulic head differential between the inside of the pipe and immediately outside the pipe is  $h_d$ , which accounts for the submergence of the pipe. If you set the nozzle

losses greater than the pressure head against the pipe plus the pipe friction, the design works.

**Example** In a 2" ID (5.08 cm ID) pipe, 300 ft (91.5 m) long, it is desired to distribute 100 gallons min<sup>-1</sup> (378.5 l min<sup>-1</sup>) through it uniformly over its length using 30 nozzles or orifices. Find the size of the nozzles or orifices.

The first task is to decide the coefficient of nozzle losses with respect to the material above. We have chosen 0.6 as a conservative value, which is acceptable.

Next, calculate the head losses in the length of pipe due to friction. For this we employed standard tables, which gave us: 8.59 pounds per square inch per hundred feet of pipe. That is equivalent to 19.48 ft (6.05 m) of frictional head resistance.

If the pipe is submerged 3 ft (0.9 m) under the water, the total head loss is then  $19.48 + 3 = 22.48$  ft of head (6.85 m of head).

Each nozzle or orifice should discharge about 3.33 gallons per m (12.60 l/m).

The nozzle size should be  $A = \frac{q}{0.6 * \sqrt{2gh}}$

In the proper units,  $q = 7.426 \times 10^{-3}$  cubic feet per second,  $g = 32.18 \text{ ft s}^{-2}$  and  $h = 22.48$  ft. Then  $A$  is  $3.25 \times 10^{-4}$  square feet or 0.0469 square inches ( $0.3021 \text{ cm}^2$ ). That translates to a hole of approximately 0.2443 in. or 0.6203 cm, which has a drill size of  $D = 0.246"$ .

### 3.6 Compressible Flow

Compressible flow occurs in air and other gases. The formula for nozzle flow must account for a few more variables, such as the initial and final states and temperatures. As the air crosses the orifice it changes temperature, decreasing sharply as it expands from the nozzle. In order to prevent the formation from plugging into an ice flow, one must account for the change in temperature across the orifice, and preferentially keep the gas temperature above freezing to avoid ice formation.

The equations for compressible gas flow across a nozzle are a bit different. For this we need to introduce an entirely new set of terms. The formulas given above are applicable only for incompressible flows. They are modified by introducing the expansion factor to account for the compressibility of gases.

$$\dot{m} = \rho_1 Q = CYA_2 \sqrt{2\rho_1(P_1 - P_2)}$$

$Y$  is 1.0 for incompressible fluids and it can be calculated for compressible gases.<sup>5</sup>

### 3.6.1 Calculation of Expansion Factor

The expansion factor  $Y$ , which allows for the change in the density of an ideal gas as it expands isentropically, is given by:

$$Y = \sqrt{r^{2/k} \left( \frac{k}{k-1} \right) \left( \frac{1 - r^{(k-1)/k}}{1 - r} \right) \left( \frac{1 - \beta^4}{1 - \beta^4 r^{2/k}} \right)}$$

For values of  $\beta$  (ratio of orifice diameters) of less than 0.25,  $\beta^4$  approaches 0, and the last bracketed term in the above equation approaches 1. Thus, for the large majority of orifice plate installations:

$$Y = \sqrt{r^{2/k} \left( \frac{k}{k-1} \right) \left( \frac{1 - r^{(k-1)/k}}{1 - r} \right)}$$

where  $Y$  is the dimensionless expansion factor;  $r = P_2/P_1$  (absolute pressures); and  $k$  is the dimensionless specific heat ratio ( $C_p/C_v$ ), but for air it is 1.4 which is good enough for most cases, unless one has a really heavy vapor concentration in the gas.<sup>6</sup>

Substituting the equation into the mass flow rate equation and making a few substitutions using the Gas Law, we get:

$$Q_1 = CA_2 \sqrt{\frac{2ZRT_1}{Mw} \left( \frac{k}{k-1} \right) \left[ \left( \frac{P_2}{P_1} \right)^{\frac{2}{k}} - \left( \frac{P_2}{P_1} \right)^{\frac{k+1}{k}} \right]}$$

and the final equation for the non-choked (i.e. subsonic) flow of ideal gases through an orifice for values of  $\beta$  less than 0.25, where:

$k$  = specific heat ratio  $C_p/C_v$ , dimensionless

$M$  = mass flow rate at any section,  $\text{kg s}^{-1}$

$Q_1$  = upstream real gas flow rate,  $\text{m}^3 \text{s}^{-1}$

$C$  = orifice flow coefficient, dimensionless

$A_2$  = cross-sectional area of the orifice hole,  $\text{m}^2$

$P_1$  = upstream gas pressure, Pa with dimensions of  $\text{kg}/(\text{m s}^2)$

$P_2$  = downstream pressure, Pa with dimensions of  $\text{kg}/(\text{m s}^2)$

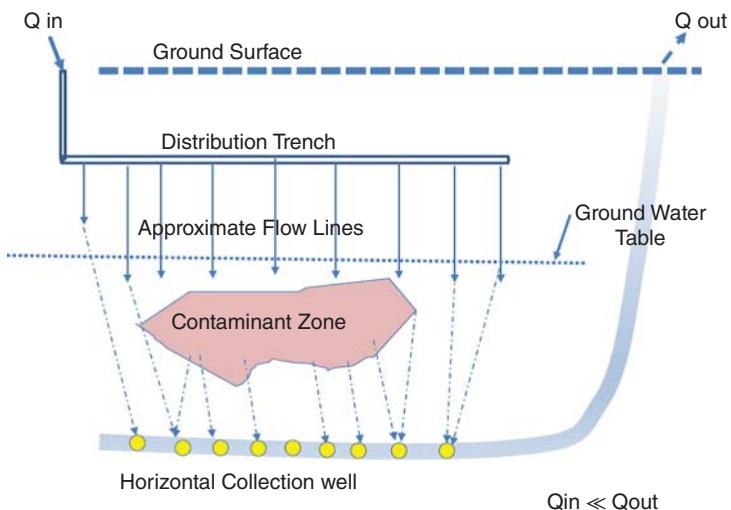
$Mw$  = the gas molecular mass,  $\text{kg/mol}$  (also known as the molecular weight)

$R$  = the Universal Gas Law Constant =  $8.3145 \text{ J}/(\text{mol K})$

$T_1$  = absolute upstream gas temperature, K

$Z$  = the gas compressibility factor at  $P_1$  and  $T_1$  and, dimensionless – but most of the time it is equal to 1.0 for air at environmental temperatures generally encountered.

A final check of the velocity of the gas through the orifice is required, as it should not exceed the speed of sound (approximately  $340 \text{ m s}^{-1}$ ), and it should also be checked for temperature on the lower pressure side to insure that the gas vapor will remain above freezing. (If there is sufficient water vapor in the air, one would have to correct for density of the gas.)



**Figure 3.6** Horizontal well and distribution trench for subsurface cleanup.

The entire set of equations is easily arranged on an Excel spreadsheet, and the total orifice size and pressure drop and gas flow can be calculated. Then, using the same data, select a drill size and a spacing which is suitable to the length of the pipe, number of orifices, and the pressure drop.

Because the open area of even a fine well screen is very much larger than a pre-drilled or punctured hole in the pipe, even a short distance of screen can substantially distort the injection or collection patterns used in the horizontal well. Figure 3.6 illustrates the potential uses of horizontal wells and trench. In the figure, the trench is being used to apply nutrients to speed degradation, the horizontal well is beneath the contaminated zone, and the objective is to apply the nutrient chemicals evenly and collect the degradation products evenly. This is a three-dimensional problem shown in a two-dimensional drawing, so the flow patterns are imperfect. A critical hydraulic analysis is required to insure that the liquids are evenly distributed and collected in the well and trench. In all cases the Darcy theories hold and the water moves in response to differences in head.

### 3.6.2 Groundwater Hydraulics

According to the National Ground Water Association, approximately 26% of the freshwater used in the US is from groundwater sources, and that figure amounts to about 79.6 billion gallons<sup>7</sup> ( $301.19 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ ). Most if not all of the groundwater is withdrawn using wells.

In the material above we saw how Darcy's law is applied to flow through a porous medium. Where wells are utilized, the water withdrawal creates a cone

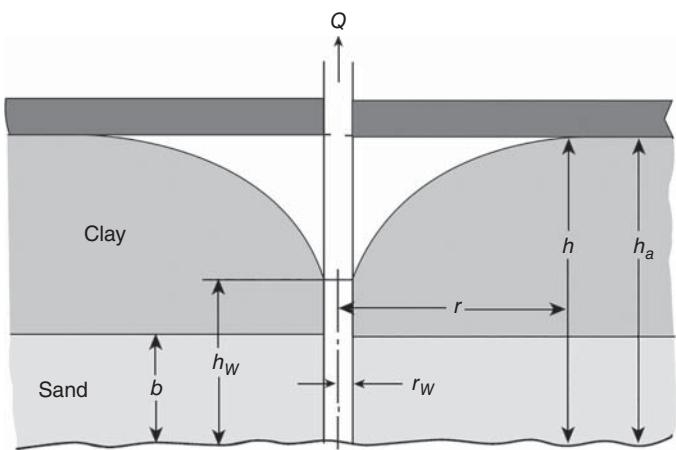


Figure 3.7 Groundwater well hydraulics.

of depression in the aquifer which is generally circular but can be elongated if the overall flow of groundwater is strong enough. In examining the flow of groundwater, the principles of superposition are applicable. The equations and formulation for a groundwater well are shown below. The presence of one or more wells can be modeled by the use of superposition. One cautionary note: the use of vertical wells may not be effective in cleaning up a dense aqueous or non-aqueous plume that is moving across a well field. Many authors have found that well spacing is critical in assuring capture of this type of plume (see Figure 3.7):

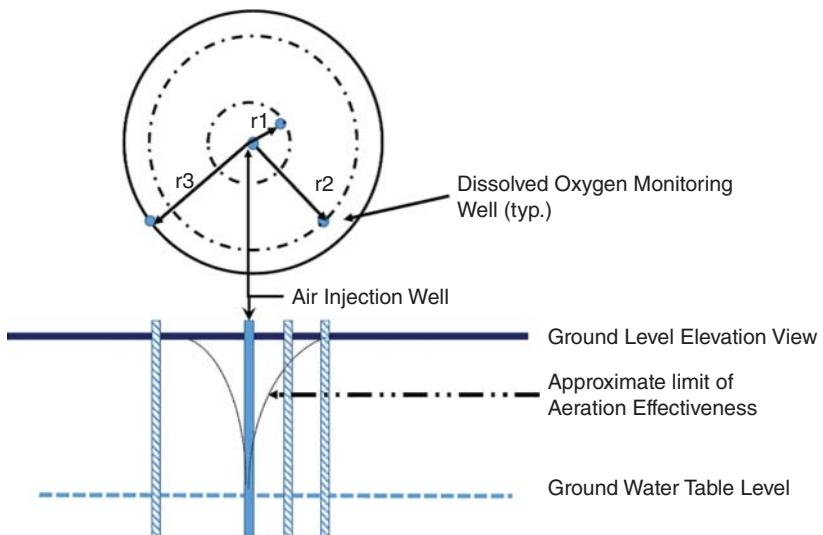
$$Q = Z\pi r b K \frac{dh}{dr}$$

$$h - h_w = \frac{Q}{2\pi K b} \ln \frac{r}{r_w} \quad \text{or} \quad h - h_w = \frac{Q}{2\pi T} \ln \frac{r}{r_w}$$

where  $r_w$  is the radius of the well,  $K$  is the coefficient of permeability,  $h_w$  is the height of water in the well being pumped,  $h_a$  is the hydraulic head at non-pumping conditions,  $b$  is the thickness of the aquifer, and  $Q$  is the pumping rate.

Before we leave the topic of groundwater hydraulics, it is also important to mention the effect of injection wells. Injection wells have been used to distribute treatment liquids to contaminated sites, and have also been used to help volatilize and strip compounds from water by injecting air beneath the contaminated underground plumes and capturing the air and the contaminants above the contaminant zones.

The effective radius of the cone of influence is proportional to the expansion of the bubble as it rises through the liquid, the soil porosity and density, the rate



**Figure 3.8** Plan and elevation views for determining effectiveness of an air injection well for stripping volatiles.

of the airflow, and the depth of introduction below the fluid surface. At the current time, the best way of determining the efficiency and diameter of the cone of influence of an injection well is to determine its radius of influence under field conditions, by setting a screened well at or below the depth of concern, and blowing in air under controlled conditions. Measure the pressure of the air, and the amount of air. Determine the effective radius of the injection well by measuring the increase in dissolved oxygen (DO) concentration in water at various distances from the well (see Figure 3.8). Note that you may have to drill other wells in order to make these measurements, and be sure to measure the background DO and contaminant concentrations before you start the test. You will also need to measure the surface elevations and the depth of the liquid in the wells to the nearest millimeter, as well as the change in DO and contaminant levels over time.

### 3.7 Groundwater Treatment

Lots of contaminants can render groundwater marginal or unusable. In the US alone, according to the National Groundwater Association, approximately 44% of the US population relies on groundwater sources for drinking – either directly or indirectly – and more than 13 million US households that are occupied year-round have private wells.<sup>8</sup> Earlier we discussed the importance

of quality water with respect to the Primary and Secondary Drinking Water Standards. The most common contaminants in groundwater are calcium, magnesium, manganese, iron, sulfur compounds, nitrates, and many organic chemicals. The inorganic compounds tend to be from natural sources. The organic chemicals are most often from man-made sources. Some of the most pernicious organic compounds are perchloroethylene, from dry cleaning operations, and BTEX (benzene, toluene, ethyl benzene, and xylene) from leaking underground petroleum storage tanks and their dispenser piping. Other common sources of organic contamination can arise from landfills, septic systems, agricultural application of pesticides, and improper disposal of solvents used in degreasing, and even improper disposal or leaking chemicals at a lawn and garden center, to name but a few.

The US Geological Survey lists a number of common contaminants found in groundwater.<sup>9</sup> We have endeavored to provide some qualitative guidance for the treatment and removal of some of those contaminants in Table 3.3. The table illustrates a number of treatment regimens for most of the common contaminants, along with references where applicable. The table attempts to present groundwater treatment systems that are both usable and practical; however, what may be practical in a large system will not be practical for a small system, and vice versa.

In most instances, groundwater has good bacterial quality, especially when drawn from deep aquifers. The shallow aquifers are more susceptible to contamination from surface sources, and each case and each well is individual, and needs an assessment and analysis for quality, quantity, and contaminants compared with the needs for the process or intended user.

In most instances, there will be a group of contaminants in groundwater because the water has picked them up from the geological formations that contain the water. Compounds like iron ( $\text{Fe}^{2+}$ ),  $\text{CaCO}_3$ , and  $\text{Ca}(\text{HCO}_3)_2$  are often found in groundwater, especially where the foundation geology is limestone-based. For small systems, cation exchange resins may be satisfactory to remove the compounds, replacing the cations with sodium ( $\text{Na}^+$ ). The same source on a larger scale might use chemical precipitation and softening to accomplish the removals.

Sulfur in groundwater is generally associated with either  $\text{SO}_4^{2-}$ , or  $\text{SO}_3^{2-}$ , or  $\text{H}_2\text{S}$ . The common salts are calcium, sodium, phosphate, and magnesium, although when combined with hydrogen, sulfur makes a strong acid as in  $\text{H}_2\text{SO}_4$ .  $\text{MgSO}_4$  in moderate quantities is associated with causing diarrhea in humans, and calcium sulfate and calcium phosphate are fundamental to the structure of bones in the human body. Hydrogen sulfide can be removed by aeration, but the sulfates can only be removed by anion exchange or by lime softening which precipitates the  $\text{CaSO}_4$  at about  $1600 \text{ mg l}^{-1}$ .

**Table 3.3** Frequently occurring natural compounds in water and their treatment.

Chemical or element	Significance	Concentration ranges	Type of treatment most commonly employed	USEPA Drinking Water Standard concentrations
Aluminum	Precipitation, some minor health effects	0.3–6 µg l <sup>-1</sup>	Chemical precipitation or ion exchange	50–200 mg l <sup>-1</sup> (National Health Guidelines)
Ammonia	Taste, odor, health effects	0.1–100 µg l <sup>-1</sup>	Remove by aeration	Preferable concentrations less than 10 mg l <sup>-1</sup>
Antimony	Toxicity, decreased longevity	<1 µg l <sup>-1</sup>	Ion exchange	0.006 mg l <sup>-1</sup>
Arsenic	Carcinogenic, toxic cumulative poison	0.01–8 µg l <sup>-1</sup>	Ion exchange, co-precipitation on iron	0.01 mg l <sup>-1</sup>
Barium	Hypertension, gastrointestinal problems	5–220 µg l <sup>-1</sup>	Chemical precipitation (sulfate) or ion exchange	2 mg l <sup>-1</sup>
Beryllium	Possible carcinogen, chronic toxicity, lung and liver damage	<1 µg l <sup>-1</sup>	Ion exchange	No standard
Cadmium	Replaces zinc in bones, high blood pressure, toxic, liver and kidney damage	<1 µg l <sup>-1</sup>	Ion exchange	0.005 mg l <sup>-1</sup>
Calcium	Can cause deposits and scaling. Little harm to drink except in high concentrations	0.02–95.3 µg l <sup>-1</sup>	Softening (ion exchange) or chemical precipitation	No standard but less than 50 mg l <sup>-1</sup> generally accepted as "soft" water
Chloride	Taste at high levels, corrosion to plumbing systems	1.3–68.2 µg l <sup>-1</sup>	Not really treated at these levels. Treatment by ion exchange over 250 µg l <sup>-1</sup>	250 mg l <sup>-1</sup>
Chromium	Cr <sup>3+</sup> is nutritional element Cr <sup>6+</sup> is carcinogenic and toxic			0.1 mg l <sup>-1</sup> total
Copper	Taste impermeant, internal distress		Ion exchange/carbon adsorption	At Cu levels above 1.3 mg l <sup>-1</sup> treatment is mandated

(Continued)

**Table 3.3** (Continued)

Chemical or element	Significance	Concentration ranges	Type of treatment most commonly employed	USEPA Drinking Water Standard concentrations
Cyanide	Toxic to blood, spleen and brain		Chlorination	0.2 mg l <sup>-1</sup>
Fluoride	Decreases tooth decay but can impact bones	0.1–1.1 mg l <sup>-1</sup>	Calcium chemical precipitation, or ion exchange	2 mg l <sup>-1</sup>
Hardness	Increases scale formation and decreases effectiveness of soaps	0.1–500 mg l <sup>-1</sup> as CaCO <sub>3</sub> equivalent	Ion exchange and chemical precipitation	No set goal but <30 mg l <sup>-1</sup> is easily achievable
Iron	Degrades taste, causes red staining on fixtures	0.01–10 mg l <sup>-1</sup>	Aeration plus chemical precipitation or ion exchange	0.3 mg l <sup>-1</sup>
Lead	Delays mental development, cumulative toxin, affects blood	0.001–2 µg l <sup>-1</sup>	Chemical precipitation and/or ion exchange	Treatment if above 0.015 mg l <sup>-1</sup> , goal is zero
Manganese	Causes brown stains, can be toxic to plants in high concentrations	0.01–10 mg l <sup>-1</sup>	Chemical precipitation/ion exchange	0.05 mg l <sup>-1</sup>
Mercury	Acute and chronic toxicity, affects nervous system and kidneys. Extremely toxic and can turn teeth and nails blue	0.0001–0.3 µg l <sup>-1</sup>	Sulfide precipitation or ion exchange	0.002 mg l <sup>-1</sup>
Nickel	Lifetime exposure can cause heart and liver damage	0.001–3 mg l <sup>-1</sup>	Ion exchange	No standard
Nitrate nitrogen	Can cause "blue baby" syndrome in newborns, can reduce oxygen carrying capacity of blood	0.01–100 mg l <sup>-1</sup>	Denitrification or ion exchange	10 mg l <sup>-1</sup>

Total nitrogen	Nitrate breaks down to nitrite. Same as nitrate	$0.01\text{--}100 \text{ mg l}^{-1}$	Biological treatment or ion exchange	$1 \text{ mg l}^{-1}$ as nitrite
Selenium	High doses can cause livestock problems, can be toxic			$0.05 \text{ mg l}^{-1}$
Silver	Toxic, will color skin (blue), affects mucus membranes, eyes, etc.	$<1 \mu\text{g l}^{-1}$	Ion exchange, chloride precipitation	No standard
Sodium	Risk to those on low sodium diets, and can affect taste	$0.2\text{--}80 \text{ mg l}^{-1}$	Ion exchange	$250 \text{ mg l}^{-1}$ is often objectionable. $50 \text{ mg l}^{-1}$ is acceptable. No standard
Sulfate	Causes scaling on heat exchangers, has a laxative effect on humans	$0.01\text{--}40 \text{ mg l}^{-1}$	Chemical precipitation or ion exchange	$250 \text{ mg l}^{-1}$
Thallium	High doses damage liver, kidneys and brain. Also a toxic poison	$<1 \mu\text{g l}^{-1}$	Ion exchange	$0.002 \text{ mg l}^{-1}$
Zinc	Toxic to plants at high levels, minimal damage to humans	$1\text{--}35 \text{ mg l}^{-1}$	Chemical precipitation, ion exchange	$5 \text{ mg l}^{-1}$
Color	Objectionable appearance	$0\text{--}50$ color units	Chemical coagulation, filtration or carbon adsorption, also oxidation	15 color units
Turbidity	"Dirt in the water" – gives a cloudy appearance			
pH	Low pH water tastes acetic. High pH water is "slippery"	$6.1\text{--}7.9 \text{ SU}$ (standard units)	Neutralization for high pH, acidification for low pH. pH 7 is neutral	pH 6.5 to pH 8.5
Plasticizers	Can accumulate in fatty tissues and affect nervous system, and can cause cancers	$0.001\text{--}3 \mu\text{g l}^{-1}$	Carbon adsorption	Varies widely depending upon plasticizer. Goal is generally zero

(Continued)

**Table 3.3** (Continued)

Chemical or element	Significance	Concentration ranges	Type of treatment most commonly employed	USEPA Drinking Water Standard concentrations
Pesticides	Many different types of poisoning reactions depending on specific type of exposure	0.001–5 µg l <sup>-1</sup>	Carbon absorption	Goal for most is zero or less than 0.005 mg l <sup>-1</sup> depending upon the compound
Gasoline and oils	Taste and odor problems, plus possible digestive and carcinogenic effects	0.1–15 mg l <sup>-1</sup>	Aeration (stripping) and carbon absorption	Benzene 0.005 mg l <sup>-1</sup> Xylenes – total 10 mg l <sup>-1</sup> Toluene – 1 mg l <sup>-1</sup> Ethylbenzene 0.7 mg l <sup>-1</sup>
Volatile organic chemicals/pesticides	Can be nuisance or can, if chlorinated, be a powerful carcinogen	1–3 µg l <sup>-1</sup>	Aeration and carbon absorption	Requirements vary from 0.001–0.1 mg l <sup>-1</sup> depending on compound
Coliform bacteria	Direct indication of fecal contamination either by animals or humans	1–10 MPN (MPN is most probably number)	Chlorination/oxidation or other disinfection and filtration	Goal is zero
Odors	Odors are aesthetically unpleasant and may indicate other types of contamination	0.1 to 5 Standard Odor Units	Aeration, disinfection by chlorine	No standard but very low (oxidation), not necessarily preferable

Note: The Drinking Water Standards include primary and secondary standards as well as guidelines. Not all substances have guidelines or standards because of their rarity in drinking waters. Pesticides are the general exception. Many pesticides not shown in the table have primary standards of 0.001 mg l<sup>-1</sup> or less, with the goal of the regulations to reduce the concentrations to zero. The level of permitted quantities in the drinking water depends upon the chemistry of the compound. EU and WHO drinking water standard values are generally higher.

Source: USEPA *Primary and Secondary Drinking Water Standards; Quality of Water from Domestic Wells in Principal Aquifers of the United States 1991–2004*, USGS Publication number SIR2008-5227 (<https://pubs.usgs.gov/sir/2008/5227/includes/sir2008-5227.pdf>).

## Notes

- 1 Thies (1935). *The Theis Equation: Evaluation of Storage, Transmissivity and Automated Fitting of Pump Test Data*. Kansas Geological Society and the Department of Interior. See <http://www.kgs.ku.edu/Publications/Bulletins/GW3/>
- 2 See <http://JohnsonScreens.com> for their catalog. For example, the Johnson Screen catalog indicates that a 4" diameter well screen has between 11 and 11.6 square inches of open area per square foot of screen. The size of the open area would be so great that the liquid and/or gas would be dispersed within the first few feet of screen. By comparison, a horizontal well may have less than 0.2 square inches of open area per foot of pipe. Johnson Well Screen catalog: <http://www.johnsonscreens.com/sites/default/files/8/715/Stainless%20Steel%20Well%20Screens%20and%20Accessories%20-%20North%20America.pdf>.
- 3 Michael Duchene and Edward A. McBean, Water Resources Bulletin, Vol. 28, No. 3, June 1992, American Water Resources Association.
- 4 *Water Supply and Wastewater Disposal*, by G.M. Fair and G.C. Geyer, John Wiley and Sons, pp. 686–689.
- 5 See: [http://nvlpubs.nist.gov/nistpubs/jres/9/jresv9n1p61\\_a2b.pdf](http://nvlpubs.nist.gov/nistpubs/jres/9/jresv9n1p61_a2b.pdf), a paper from 1929 to 1932 by the National Bureau of Standards.
- 6 Alternatively, one can obtain  $C_v$  and  $C_p$  from the Internet on sites such as: [http://www.engineeringtoolbox.com/spesific-heat-capacity-gases-d\\_159.html](http://www.engineeringtoolbox.com/spesific-heat-capacity-gases-d_159.html).
- 7 *Estimated Use of Water in the United States in 2005*, US Geological Survey Circular 1344, October 2009.
- 8 <http://www.ngwa.org/fundamentals/use/pages/groundwater-facts.aspx>.
- 9 <http://water.usgs.gov/edu/groundwater-contaminants.html>.

## 4

# Statistics of Measurements

*Consistency is more important than accuracy!*

R. Sobel, Allied Chemical

*Facts are stubborn things, but statistics are more pliable.*

Mark Twain (1835–1910)

*The further you get from the way the numbers were obtained, the more absolute they become.*

J. S. Lagarias, Resources Research, Inc., Reston, VA

## 4.1 Introduction to Statistical Measurements: Background

This chapter was developed from a problem involving permitting on industrial wastewater discharge in the United States. The importance of the material was subsequently confirmed in conversation with friends in Europe, who, while working under a very different permit system, have similar problems.

Most, if not all, industrial discharges are required to have a permit that tells them how much pollution they can discharge within a specific time limit. In the United States, the permits generally have a daily maximum and a monthly average for a number of pollutants. The pollutants are expressed in mass limits, kilograms per day, for most pollutants except pH, and some biomonitoring parameters. In the majority of cases, in the US permits, the monthly average discharge limit is one-half of the daily maximum limit.

The US permit system has some peculiarities in that the discharge limits are taken as absolute numbers and the enforcement is uneven. In many instances, industries are held to a tight standard, whereas municipal permit violations are often overlooked or totally ignored. The regulatory agencies have a tendency to charge large fines and criminal penalties against industries but not against municipalities. There are a few instances where municipal workers have been fined or jailed but those are few and principally where there was a deliberate

attempt to falsify data or operate the treatment plant in deliberate violation of regulations.<sup>1,2</sup>

In many instances, industries, and occasionally municipalities, are restricted to the amount of water they can take from a lake or a river or groundwater and are also limited on the amount of water they can discharge, as well as the quantity of pollutants they discharge. Because flows are not carefully or accurately measured, most industries have only a vague idea of what they discharge and report to the regulatory agency with respect to their permit limits.

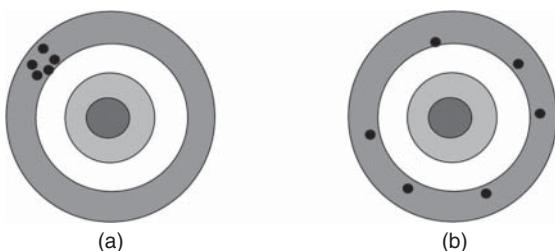
In previous chapters, we have seen how inaccuracies in sampling and flow measurement can produce errors. The regulatory community views the permit limits as absolute limits rather than the estimates they should be. Consequently, if an industry exceeds the daily maximum or the monthly average value in their permit, they become liable to heavy fines.

The European Union and the United Kingdom use a metering system. The discharger pays for every kilogram of the pollution discharged. The environmental agency sets a rate for discharge. If the user discharges quantities above their permit limit, the rate goes up and it costs the user more to discharge until the next period.

## 4.2 Significant Figures

The advent of the electronic calculator and computer has enabled everyone to compute numbers with many significant figures. However, the tendency to report anything beyond about three significant figures in an environmental permit is totally unwarranted and downright foolish. In most cases, the use of two significant figures is adequate. The use of additional figures gives a false sense of confidence regarding the accuracy of the discharge and the corresponding position within the permit. As will be shown below, the accuracy is just not that good to warrant more than three figures at most.

In Figure 4.1, the target is the bull's-eye. The target on the left shows high precision or repeatability but poor accuracy. The target on the right has high accuracy but poor precision. It is similar to the statistician who went out hunting ducks. After several hours in the blind, one duck flew overhead. The



**Figure 4.1** Precision versus accuracy. (a) High precision, low accuracy and (b) high accuracy, low precision.

statistician fired one shot leading the duck by 20 m. He overcorrected and fired the second shot 20 m behind the duck. To this day, he will claim that on the average, the duck is dead.

### 4.3 Probable Error

The concept of probable error comes to us from the surveying community, as a way to estimate the accuracy of placement of a survey pin or the length of a line. The probable error in a measurement is composed of individual independent functions  $f_1 \dots f_n$  and the measurement  $M$  is composed of the functions as follows<sup>3</sup>:

$$M = f_1(x) + f_2(x) + f_3(x) + \dots + f_n(x)$$

The error  $e$  in  $M$  is given as

$$e^2 = (e_1 \frac{dx}{df_1})^2 + (e_2 \frac{dx}{df_2})^2 + \dots$$

where  $e_1, e_2, \dots$  are the errors in measurement of the individual parameters.

The approach for error estimation can be used in all types of environmental measurements, including air measurement and solid and hazardous waste estimates.

Consider the following problem set as an example of how the estimation of errors works. You are operating a chemical plant with a cooling tower and a fly ash pit. The flow is large but the suspended solids levels are low.

You have permit that is issued in mass units – that is, kilograms per day. The flowmeter is a 0.3048 M (1 ft) Parshall flume with a discharge equation of

$$Q (\text{M}^3 \text{ s}^{-1}) = 0.6909H^{1.522}$$

$\text{M}^3$  is in Cubic Meters =  $59\ 667H^{1.522} \text{ M}^3 \text{ day}^{-1}$  at a flowmeter depth of 0.42 M (16.14 in.)  $Q = 59\ 667 \times (0.42)^{1.522} = 15\ 940 \text{ M}^3 \text{ day}^{-1} = 10^6 \text{ gallons day}^{-1}$ .

The average discharge of suspended solids in the effluent is  $10 \text{ mg l}^{-1}$  and the published accuracy for the test<sup>4</sup> according to standard methods is 15%. Because of the waves in the discharge channel, we cannot make reliable measurements of the level in the flume with an accuracy of greater than 0.01 M.

The daily average discharge permit limit is  $165 \text{ kg day}^{-1}$  as set by the regulatory agency.

The average suspended solids discharge is

$$\text{Mass} = 0.01 \text{ kg M}^{-3} \times 15\ 940 \text{ M}^3 \text{ day}^{-1} = 159.4 \text{ kg day}^{-1}$$

Therefore, how accurate is the measurement? In reality, one or two significant figures would be sufficient.

Currently, you are within permit limits, but how much room do you have within the limits of accuracy?

Since the Mass is  $C \times Q$ , the error is given by the following:

$Q$  is dependent on  $H$ , and the error in  $H = 0.01$ , error in  $e_c = 0.15 \times 10 = 1.5 \text{ mg l}^{-1} = 0.0015 \text{ kg M}^{-3}$

In addition,  $d_{\text{Mass}}/dC = 53693H^{1.522}$ , which is 15 940 and  $d_{\text{Mass}}/dH = 1.522 \times 59667H^{0.522}$ , which is 57 742 and

$$\begin{aligned} e^2 &= (e_c \times d_{\text{Mass}}/dC)^2 + (e_H \times d_{\text{Mass}}/dH)^2 \\ &= [0.0015 \times 15940]^2 + [0.01 \times 0.01 \times 57742]^2 \\ &= 23.91^2 + 5.78^2 \\ &= 571.68 + 33.37 = 271977 = 605 \\ e &= (605)^{0.5} = 24.6 \text{ kg day}^{-1} \end{aligned}$$

Now, if the discharge is 159 kg day $^{-1}$ , and applying a single error range to the discharge value, we could be above or below our permit because of uncontrolled variables. At a 95% confidence interval (two times the probable error), our true value could be between:

$$\text{Lower level: } 159 - 2 \times 24.6 = 109.8 \text{ kg day}^{-1}$$

$$\text{Upper level: } 0.159 + 2 \times 24.6 = 208 \text{ kg day}^{-1}$$

which tells us that a single set of measurements is insufficient to determine permit compliance. The use of suspended solids is just an example. Each parameter has a measurement uncertainty associated with the flow and with the laboratory analysis.

In an enforcement situation or in permit negotiations, we need to be as accurate as possible. Permit non-compliance can result in significant violations.

Clearly, we need to repeat the measurements to increase our confidence in our measured values, to reduce the error.

## 4.4 Repeat Measurements

When you have a large degree of uncertainty in measurements, the only way to reduce them are either to repeat the measurements a number of times or to improve the accuracy of your instruments. As the latter is often not possible without great expense, it is cheaper to replicate the measurements.

The error, for a constant process, can be reduced by increasing the number of measurements. The magnitude of the error decreases by the error divided by the square root of the number of repeat measurements or

$$\text{Error}_{\text{repeat measurements}} = e_{\text{Mass}}/\sqrt{n}$$

In the case above, if we want to have the error in measurement equal to no more than 5 kg day $^{-1}$ : Error<sub>repeat measurements</sub> = 5, =  $24.6/\sqrt{n}$  and  $n = 24.6^2/25$  or

about 24 sets of measurements for total suspended (non-filterable) solids (TSS) and flow to reduce the probable error to  $5 \text{ kg day}^{-1}$ .

There are two cautionary notes: (i) one will have to consider the additional workload on the laboratory for performing the additional analysis to reduce the level of uncertainty and (ii) if the number of repeat measurements required to give a satisfactory level of confidence about the discharge is large, there may be justification for renegotiating and relaxing the discharge permit limits to a more sensible and allowable limit under a different set of assumptions.<sup>5</sup>

## 4.5 Net Process Measurements

Many environmental permits are formulated on the basis of net discharges or

$$D = I - O$$

where  $I$  is the inflow and  $O$  is the outflow for a process.

The error in  $D$  for this case is given by the variances: variances are equivalent to  $e^2$ .

$$\text{Var}_D = \text{Var}(I) + \text{Var}(O) - 2 \text{ covariance}(I, O)$$

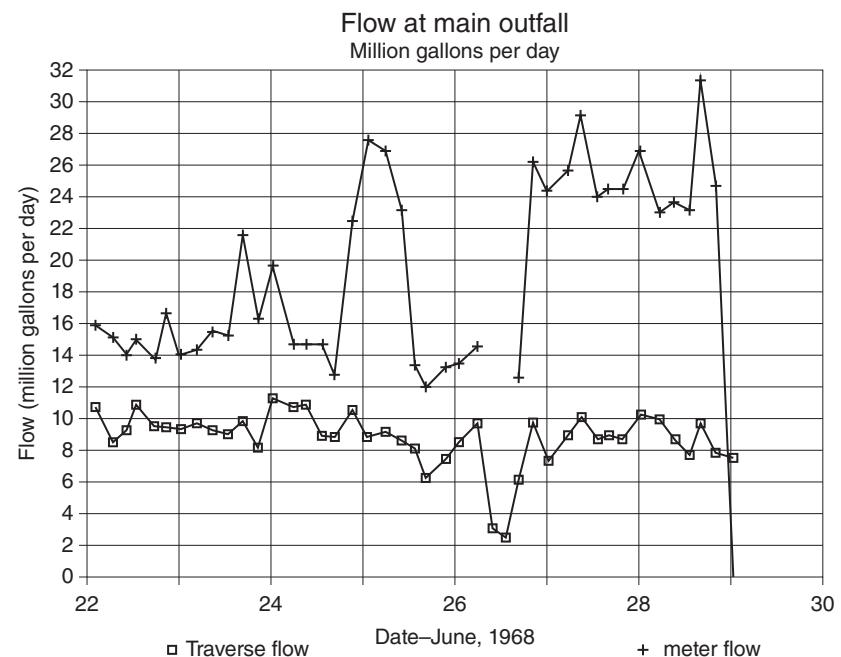
If the two measurements are truly independent, the covariance will be zero.

### 4.5.1 Calibration

Increased accuracy starts with accurate flow measurement and open-channel flow theory and measurement. The accuracy of a badly installed weir is  $\pm 10\%$ .<sup>6</sup> The improper flow conditions can materially change that figure. The improper installation of a Parshall or other flume or weir that results in rapid or shooting flow through the throat can result in significantly under measurement of the flow. Even electronic flowmeters are accurate to about 2% of what is being measured.

If you need a reliable calibration measurement, consider using tracer fluids such as fluorescein dyes or measurable concentrations of a salt added to the flow channel at a known or constant rate over the period of your calibration.<sup>7</sup>

One also needs to observe and pay attention to the downstream conditions. Figure 4.2 illustrates what can happen when downstream conditions are ignored. In this instance, a Parshall flume with an 8' or 2.43 M throat width was measuring the flow from a paper mill in South Georgia. The flume discharged directly into the wet well of a pumping station. The pump high water levels were incorrectly set, allowing water to back up and flood the throat and the channel of the Parshall flume. The resulting flow metering figures were extremely high, and the plant was using much less water than it had thought



**Figure 4.2** Wastewater flows from a paper mill with solid deposition and flooding problems.  
Source: Global Environmental Operations, Inc.

it was using. The inaccuracies in the flow caused problems for their treatment system as well.

The upper set of data points was obtained from the flume gauge in the pump house. The lower set of figures was obtained by performing a set of traverses with a highly accurate current meter.

### 4.5.2 How to Measure Your Flow Accurately

In a hydraulics laboratory, there is often a large-scale weighing tank where weight measurements can be used to measure flows accurately. Although that is not practical for the field, there are a number of ways to determine flows accurately in the field.

#### 4.5.2.1 Gurley Current Meter

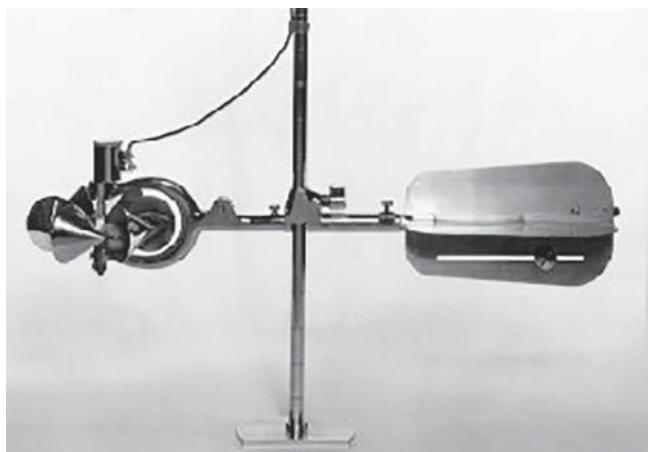
The Gurley current meter, also known as the Gurley-Price current meter is the accepted industrial standard for water flow measurement. Its accuracy is 2% of the true values, a figure which is in line with other instruments suitable for field or laboratory measurement. The Gurley current meter comes in two sizes, the

Pygmy meter and the larger Gurley-Price meter. The designs are similar except for the size of the units. Both employ six conical buckets on a frame, which is supported by top and bottom pins. When submerged, the buckets wheel freely in response to the flow. The meters are capable of measuring water velocity from 0.2 to 25 ft s<sup>-1</sup> (0.061–7.62 m s<sup>-1</sup>). They are primarily used for relatively clean water, where there are no lumpy solids, or fibers that could attach themselves to the meter and wrap around the pinions.

Figure 4.3 is a Picture of the Price-type current meter with a wading rod used to measure flows at a constant depth in an open channel.

The Hach Company manufactures an electronic flowmeter with (2%) accuracy over the range of 0.5–20 ft s<sup>-1</sup> (0.15–6 M s<sup>-1</sup>). It has no moving parts but relies on electromagnetic measurement where moving conductive fluids cut a magnetic field generated within the sensor. The principal limitation on the device is the conductivity of the fluid.<sup>8</sup>

Ultrasonic Doppler and electromagnetic flow measurement techniques are being successfully used in a variety of closed and open conduits. Both types of flowmeters rely upon the placement of the sensor or transmitter-receiver pair to provide an average velocity along a specific path on a conduit's cross section. The flow measurements can be quite accurate, as long as the fluid is non-aerated (does not contain bubbles) and it is of a relatively uniform consistency. Measurement of flow rates for emulsions or mixed fluids presents a special problem, as with the electromagnetic flowmeter, the emulsion may contain non-conductive fluids, which will not register, and the sonic velocity of emulsions and mixed fluids<sup>9</sup> may be inconsistent making ultrasonic measurement applications less reliable.



**Figure 4.3** Gurley-Price current meter. Source: *Water Measurement Manual*, US Bureau of Reclamation.

A velocity measurement system for a “large” circular or rectangular conduit should have at least two crossing paths for ultrasonic flowmeters. Otherwise, if the velocity profile in the conduit is skewed, the flow measurement across the diameter may miss the areas of highest flows. An electronic flowmeter’s published accuracy is between 2% and 6% based on the electronics of the system.

Pitot tubes can also be employed to measure velocity. The most common is the p-type pitot tube. The pitot tube is most commonly used for air velocity measurements, but it can also be used to measure water velocity. The pitot tube relies on the formula for velocity head with a two pipe measuring system (Figure 4.4).

The formula for pressure measurement is

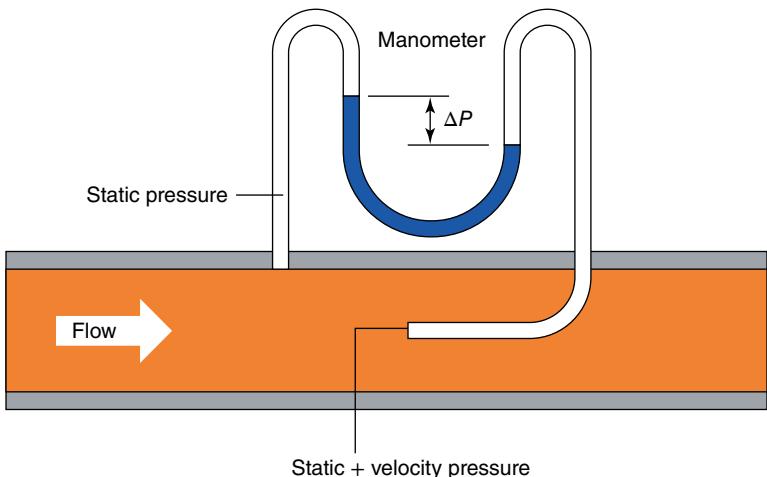
$$V = \sqrt{2(P_t - P_s)/\rho}$$

where  $V$  = velocity,  $P_t$  = total pressure,  $P_s$  = static pressure, and  $\rho$  = fluid density.

Other types of accurate flow measurement devices are discussed in the US Bureau of Reclamation’s publication: *Water Measurement Manual*, which is available on-line at <https://www.usbr.gov/tsc/techreferences/mands/wmm/index.htm>.

The manual is an excellent reference and should be a part of every environmental engineer’s technical library. The manual is free in download form, but there is a charge if a paper copy is required.

In order to obtain accurate flow measurements, it is important to make a weighted traverse of the flow. In open channels with regular or irregular shapes,



**Figure 4.4** P-Type pitot tube often used in closed conduits and for air velocity measurements. Source: Drawing courtesy of [www.spiraxsarco.com](http://www.spiraxsarco.com).

the traverse should be based on equal area segments of the cross section of the conduit. In rivers and rectangular channels where there is a relatively straight section upstream of the flow measurement point, the flow measurements are often made at the 0.2 and 0.6 fractions of the cross-sectional depth, and the flow is computed on a weighted area-velocity method. The use of the 0.2 and 0.6 depth measurements is not a firm rule. For initial flow measurements, one should always use several points in developing the vertical flow profile for that conveyance section.

Depending on the dimensions of the channel, or conduit, it will be necessary to profile both horizontally and vertically in order to obtain accurate flow measurements. Depending on the width of a rectangular channel, a minimum of four sets of vertical profiles should be used. For larger channels, over 16 ft (5 m) in top width, it may be necessary to use 8–10 sets of vertical profile measurements for accuracy.

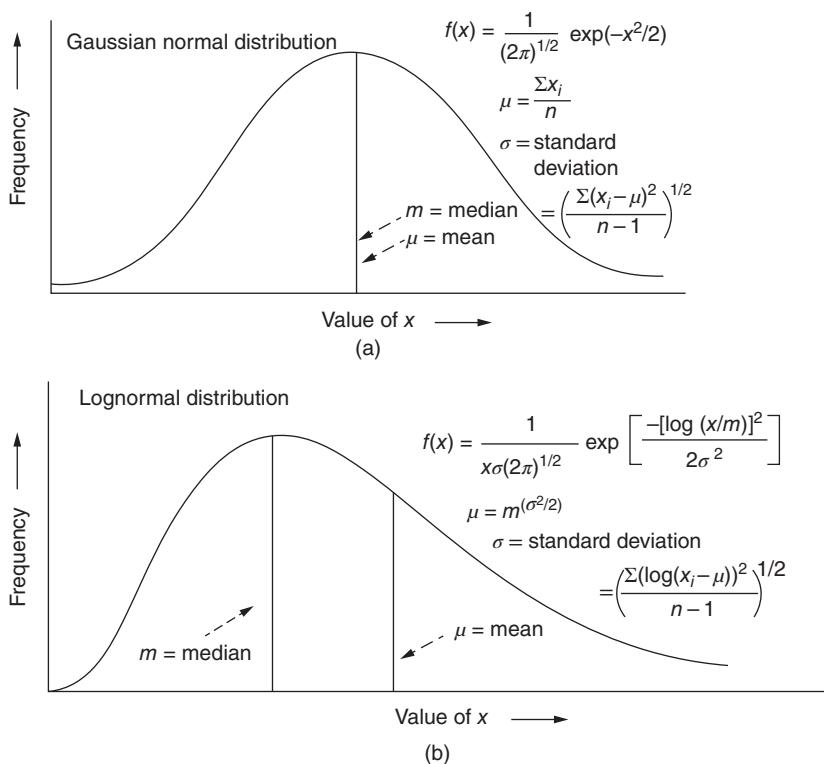
## 4.6 Statistical Distributions for Environmental Events

There are a many ways an effluent treatment system can fail. Failure is equivalent to permit exceedances. Most often, these will be caused by mechanical equipment failure, human error, spills, and poor maintenance. These errors lead to unplanned outages and system failures. Weather-related events that can also cause upsets and incidents – because the plant got flooded, or the rainfall was higher than the sewer system could take, etc.

When most of the regulatory agencies started to establish the permit system, the most common method of setting the limits for monthly average and daily maximum values were based on the standard Gaussian distribution or the Student's t-distribution. However, those are only a few of the several different distributions that can be used to analyze discharge statistics. Some of the more popular distributions include (i) lognormal distributions, (ii) 2 and 3 parameter Weibull distributions, (iii) mixed Weibull distributions (with 2, 3, or 4 subpopulations), (iv) gamma distributions, (v) logistic distributions, (vi) log-logistic distribution, and (vii) Gumbel distributions.<sup>10</sup> Two of the most popular distributions used in the analysis of environmental events, and especially effluent discharges, are the lognormal distribution and the Weibull distribution.<sup>11</sup>

Gaussian-type statistical distributions should not be applied to effluent statistics because (i) the fit is poor and (ii) there is no allowance for unplanned or extreme events that can increase discharge quantities above permit limits.<sup>12</sup> Spills, line breaks, process upsets, and other plant operations can cause these events.

Each distribution has both a probability density function and a cumulative density function – the probability density function curve for Gaussian distributions is the normal bell-shaped curve we are used to seeing and is balanced



**Figure 4.5** (a) Gaussian frequency distribution. (b) Lognormal frequency distribution.  
Source: Both figures courtesy of *Statistical Distributions* by N.A.J. Hastings and J.B. Peacock, John Wiley Publishers, Halstead Press, 1975.

above and below the mean. The Weibull distribution has a longer right tail indicating higher probability for extreme values.

The Weibull and the Gaussian distributions are shown in Figure 4.5a,b.

#### 4.6.1 Weibull Distributions

The Weibull distribution is most commonly used in prediction of failures for motors, parts, lamps, and other failure events. The Weibull distribution can have three parameters,  $x$  (number of observations),  $\lambda$  (a shape parameter), and  $\alpha$  (a location parameter), which moves the starting point of the distribution curve off the zero point. The  $\alpha$  parameter can be positive or negative as required. The  $\lambda$  shape parameter dictates the slope of the curve when plotted on log-probability paper, and at values less than 1 produces a curve that is exponential; when  $\lambda$  is above 1, the curve begins to look like the standard distribution curve for Gaussian statistics. The differences Weibull and lognormal distribution functions

can be minimal when the Weibull shape parameter  $\lambda = 3.44$ , where the Weibull approaches the lognormal distribution function.

	Weibull	Lognormal
Function	$F(x; \lambda, \beta) = \frac{\beta}{\alpha} \left( \frac{x - \lambda}{\alpha} \right)^{-(\beta-1)} \exp \left( - \left( \frac{x - \lambda}{\alpha} \right)^\beta \right)$ <p>When <math>\lambda = 0</math> and <math>\alpha = 1</math>, the equation becomes a two-parameter Weibull distribution or</p> $f(x) = \gamma x^{(\gamma-1)} \exp(-x^\gamma)$ $x \geq 0, \lambda > 0$	$Y = \ln X$ $\frac{1}{x\sigma\sqrt{2\pi}} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}}$
Mean $\mu$	$= \lambda + \alpha \Gamma \left( \frac{1}{\beta} + 1 \right)$ <p>where <math>\Gamma(\alpha) = \int_0^\infty e^{-x} x^{\alpha-1} dx</math></p> <p>Or <math>(\beta - 1)!</math></p>	$e^{\left( \mu + \frac{\sigma^2}{2} \right)}$
Standard deviation $\sigma$	$\sigma = \alpha \sqrt{\left\{ \Gamma \left( \frac{2}{\beta} + 1 \right) - \Gamma \left( \frac{1}{\beta} + 1 \right)^2 \right\}}$	$e^{\mu + \frac{1}{2}} \sigma^2 \sqrt{e^{\mu + \frac{1}{2}} \sigma^2 - 1}$
Cumulative distribution function	$F(x) = 1 - e^{-(x^\gamma)}$	$\frac{1}{2} + \frac{1}{2} \operatorname{erf} \left[ \frac{\ln x - \mu}{\sqrt{2}\sigma} \right]$ <p>where <math>\operatorname{erf}</math> is the error function:</p> $\operatorname{erf}(x) = \frac{2}{\pi} \int_0^x e^{-t^2} dt$

The procedure for preparing a curve fitting on a three-parameter Weibull distribution is described in two publications: (i) <http://Wikipedia.org> and (ii) *Life Data Analysis Reference* by <http://Reliasoft.com>.<sup>13</sup> The easiest way of preparing a Weibull plot is to use Log-probability plots and determine the parameters graphically.

## 4.7 Black Swans and Data Analysis

### 4.7.1 Black Swans

A “Black Swan”<sup>14</sup> is an unanticipated extreme event that was not recognized until after it occurred. The topic of Black Swans has been explored by Nassim

Nicholas Taleb in his book, *The Black Swan*. One of his theses is that we tend to apply statistics, especially Gaussian Normal and Student's t-statistics to systems where they are not applicable.

Natural but extreme events do occur. Hurricanes and other weather-related events can be "black swans." Manmade events such as the Deepwater Horizons Gulf of Mexico explosion, fire, and oil spill, the Torrey Canyon shipwreck, and the Exxon Valdez spill can also be "black swans." Statistically, these events are often well beyond the ranges predicted by Gaussian distributions.

#### 4.7.2 Data Analysis

Weibull and lognormal statistics make physical sense because they better model the likelihood of extreme events. Any city or industry has an almost unlimited potential to create a large discharge of contaminants to a waterway. For cities, it is often when the treatment plant is upset, or the illegal dumping to the sanitary sewer. Firefighting operations can contaminate storm sewers. Industries occasionally spill or dump things to the sanitary sewer or treatment plant and cause a major treatment plant upset. We know that those do happen.

#### 4.7.3 Outliers

In our analysis of environmental data, we often disregard outliers because they do not fit our correlation efforts. When we do not understand the situation that caused an outlier, we have no basis to discard it in our analysis. We also assume that our data as "absolute" because we do not understand how, and under what conditions, they were obtained.

Correlation and scientific consensus is not proof of causation or lack of causation. If a large number of scientists say that gravity causes things to fall upward, that does not make it so, nor does it make upward gravity a law!

In the same manner, absence of the high values for discharges does not mean that the events that could cause the high discharges just have not shown up *yet!* Probability is not risk, and we need insights into the possible errors that could occur in measurements and in the real-world events that could lead us to our own "Black Swans."

Anyone who says, "That couldn't happen here because it hasn't happened before, and I've been involved with this plant for X (a number generally over 20) years!" – *is someone who is whistling past the graveyard*. Just because it has not happened before does not give guarantee of non-occurrence in future.

When we use and develop models for our statistical work, do we really understand the limits and errors of the model, or are we like one of my students who said, "Don't bother me with the theory – just show me where to plug the numbers into the right formula, and I'll get you an answer!" But, is it the correct answer?

## Notes

- 1 There are several classifications and types of permits in the United States. The two most common types of permits that can affect an industrial discharger are Pretreatment Permits and Direct Discharge Permits. Both have numerical limits.
- 2 Quoting from the USEPA's website: "A person who Negligently or Knowingly Discharges a pollutant from a point source into a water of the United States without a NPDES or 404 Permit or in violation of a permit Statute: 33 U.S.C. 1319 (c) (1) and (c) (2) [*is subject to the following penalties*]: Penalty: Negligent Violations: 1 year and/or \$2,500–25,000 per day; Subsequent convictions 2 years and/or \$50,000 per day. Knowing Violations: 3 years and/or \$5,000–50,000 per day; Subsequent convictions 6 years and/or \$100,000 per day. Relevant Regulations: 40 C.F.R. 122."
- 3 See "Measurement Uncertainties in the pollutant discharge permit system," by David Russell and James J. Tiede, *Chemical Engineering*, October 6, 1978.
- 4 See Standard Methods for the Examination of Water and Wastewater under Solids. Published by APHA, ASCE, and WEF.
- 5 At one plant, the old Allied Chemical Works, in South Point, OH, the once through cooling water flows were between 415 000 and 360 000 M<sup>3</sup> day<sup>-1</sup>. The initial permit was badly drawn, and a statistical analysis indicated that the plant would have had to collect and analyze more than 80 sets of influent and effluent samples per day in order to verify compliance with the permit conditions. On that basis, the NPDES permit for the plant was redrawn to reflect a different set of assumptions regarding the statistical distribution used in computing the daily average and daily maximum permit limits.
- 6 Information based on experience and with a conversation with Dr. Don Bloodgood, Eminent Professor at Purdue University regarding the statistics of measurement and the work of an unidentified graduate student's Master of Science thesis.
- 7 A very good reference on weirs and calibration is found in <http://www.suncam.com/courses/100222-04.html>. By Dr. Harlan H Bengston, PE. The course is quite detailed and the SunCam Price is \$90.00 as of 2016, but the course material can be downloaded and printed for free.
- 8 I had the opportunity to use a Hach Flowmeter (at that time manufactured by Marsh-McBirney) on a paper mill wastewater survey. The device was easy to use and worked well where the fluid was conductive. We found out that the waste stream from tall oil production was nonconductive, and the current meter could not measure the velocities.
- 9 Mixed fluids are those that contain two identifiable phases.
- 10 *Systems Analysis Reference*, by ReliaSoft Corporation, [www.reliasoft.com](http://www.reliasoft.com)
- 11 "Frequency distributions of secondary and tertiary effluent parameters," by Fitzpatrick, J.A., Swanson, C. L., and Pipes, W.O., *Proceedings of Purdue*

- University 31st Industrial Waste Conference*, 1976; and, "Now you see it . . ." by Russell, D.L., and Tiede, J.J., *Proceedings of the Purdue University 33rd Industrial Waste Conference*, pp. 211–217. Both articles are available from Purdue Library Archives on-line.
- 12 The Allied Chemical South Point Works was built as a Defense Works Plant during WWII and had a once-through cooling water system that pulled water directly from the Ohio River. When the river suspended solid level was high, the difference between the influent- and effluent-suspended solid values exceeded a net negative 150 000 kg day<sup>-1</sup> because of the silt and mud in the river being deposited in the pipes and cooling coils in the plant. After the solid levels in the Ohio River declined to their more normal levels, the plant would discharge approximately 50 000 kg day<sup>-1</sup> of suspended solids for several days as the deposited solids washed out of the piping. The 1970s era discharge permit for the plant was 600 kg day<sup>-1</sup>, net increase. As a result, of improperly applied statistics in the writing of the permit, the plant was exceeding discharge permit limitations, and accumulating potential civil and criminal violations for those events. The permit did not consider the suspended solids removed from the discharge during high suspended solids levels from the intake; it only considered the permit exceedance. The permit was successfully renegotiated to a different statistical basis, which allowed the plant to operate within the permit, even when the Ohio River discharges were high, but the process of renegotiation required approximately six months. The other items that could have created a massive discharge of suspended solids included a failure of a dike on a fly ash storage pond, and heavy rainfall runoff from unvegetated areas in the shipping yards.
- 13 [http://reliawiki.com/index.php/Life\\_Data\\_Analysis\\_Reference\\_Book](http://reliawiki.com/index.php/Life_Data_Analysis_Reference_Book) and [https://en.wikipedia.org/wiki/Weibull\\_distribution](https://en.wikipedia.org/wiki/Weibull_distribution).
- 14 *The Black Swan: The Impact of the Highly Improbable*, by Nassim Nicholas Taleb, published by Random House.

# 5

## The Flow of Water and Wastewater

*No man ever steps in the same river twice, for it's not the same river and he's not the same man.*

Heraclitus

In most instances, the flow of water and wastewater is marginally understood. Everyone knows that water and sewage flow downhill, but the fundamental questions remain. How much is flowing? And how fast is it flowing? Without understanding some of the limitations on our ability to measure flow, we can only poorly establish the quantity of pollution we are measuring. It is safe to say that over many years of practice, many mistakes have been made in flow measurement that led to system underdesign or overdesign.

The discharge of a substance is measured by multiplying the quantity and concentration and summing it over time. If either are substantially mischaracterized, the result can be catastrophic, in either direction.

Most wastewater is conveyed in circular pipes, rectangular channels, triangular channels (gutters along the roadside curb), and frequently in channels, ditches, and swales. The principles of measurement and flow are the same in all of these, but special cases exist, and we will examine some of the basics of those cases as well as of the normal cases to develop a better understanding of the many ways in which flow measurement can go wrong, and how to avoid those errors.

### 5.1 Statistical Basis for Error Estimation

Everything we measure has some implicit error. Even with laser measurements, there is still some uncertainty, but it is smaller than it has ever been before. Consider a room that you are in, reading this book. Measure the dimensions of the room using a ruler or meter stick, and compute the volume. Now repeat the same measurements and volume calculations using a laser measuring device.

In each measurement there is some inherent error. For example, the ruler stick may be accurate to the nearest 1 mm, or 1/16th of an inch. If you are using a pencil to mark the location for the next measurement, how thick is the point of the pencil and how carefully are you lining up the end of the stick to the same point on the pencil mark?

If you are measuring a 20 ft room and the 1 ft ruler you are using is off by 1/16th of an inch, the uncertainty in your measurement, assuming you were careful with alignment, will be 20/16 of an inch, or 1 1/4 inches. If you use a meter stick that is off by 1 mm, your measurement could be off by up to 6 mm. These are systematic errors in your measurement and will bias your results. If we have a laser-measuring tool,<sup>1</sup> the stated uncertainty in the measurement is around 1.59 mm, and is better than either the 1 m rod, or the foot-long ruler. Moreover, there are no systematic errors in the measurement. The increased accuracy in measurement comes at a cost, and while laser measurement is highly accurate, it may not be worthwhile if a ruler is available and the measurement is not that critical, and the laser measuring tool may not be worth the price.

In dealing with discharge permits and compliance issues, accuracy is important. The point is that in the US and in some other countries, a permit limit is an absolute. If the permitted discharge value is 300, and the measured discharge is 299, the plant is within its permit limits and fines are avoided. However, if the plant discharge is 300.5 or even 300.1, the plant is not in compliance and fines may be imposed. This is true for water pollution and air pollution calculations.

The problem is that, given our limits on measurement accuracy, the real value could be anywhere between 330 and 270 with reasonable certainty, and that 300.5 and 299 are still the same number when accuracy of measurement is considered. Therefore, it is often best to have a permit strategy that incorporates not only the limits of accuracy, but also the type of distribution. We will discuss that a bit later. The first task is to understand flow measurement.

## 5.2 Open Channel Hydraulics

Most environmental measurements are made in open channels. An open channel is one, regardless of shape, with a free liquid surface at the top of the channel. The channel can be round, square, egg-shaped, or oval, but the basic requirement is that the channel has a free space at the top of the channel. If this basic condition is violated, one no longer has open channel flow, and would be in the realm of pressurized flow, where different sets of conditions and equations apply.

The *hydraulic radius* is defined as area of the flow/wetted perimeter for all conveyances, regardless of whether they are open- or closed-top. The hydraulic radius is denoted by  $R_h$ .

For any discharge, the flow  $Q$  is the product of the velocity  $V$  times the area of the liquid  $A$ . In open channels there are a number of flow regimens which can make measurement relatively easy or quite difficult and unreliable. There are also definite and easy relationships between the depth of flow and the discharge. Where the flow is passing through a defined shape at a "relatively low velocity," it is possible to measure the flow within 3–5% accuracy or better by measuring the depth alone.

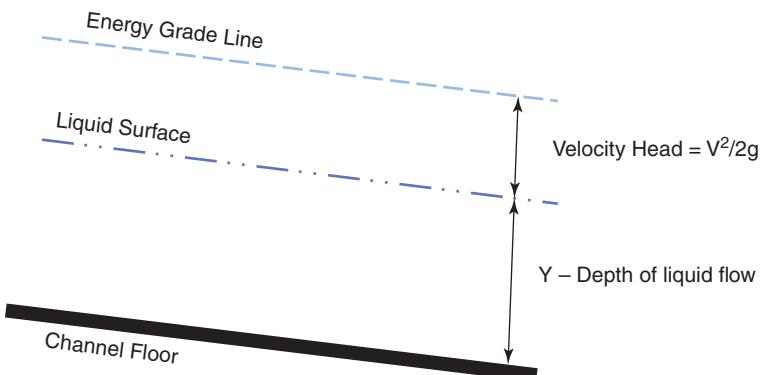
In an open channel there are a number of flow regimens that can occur, and some of them make determination of flow by measurement of the depth extremely difficult. These conditions are encountered when the flow–depth relationship has a large change in discharge for a very small change in depth, or where the flow is accelerating or decelerating rapidly.

The basic equation in flow measurement is the same as used in closed conduit measurement: the Bernoulli equation, where the head measured between two points, 1 and 2, is equal to:

$$E = (Z_1 - Z_2) + \alpha \left( \frac{V^2_1 - V^2_2}{2g} \right) + \left( \frac{p_1 - p_2}{\gamma} \right)$$

where  $E$  is the hydraulic head or elevation of the theoretical energy grade line;  $Z$  is the elevation of the channel bottom above a fixed datum;  $\alpha$  is a velocity and momentum coefficient (usually less than 1.10) for the velocity term;  $V$  is the velocity of the fluid;  $g$  is the acceleration due to gravity;  $p$  is the pressure head; and  $\gamma$  is the weight of the fluid.

For open channel flow, the flow is by gravity and not pressurized. The hydraulic grade line  $h$  is generally the same height as the water surface, or depth of flow. This is because there is essentially no pressure, causing the pressure term to go to zero, and the depth is designated by  $y$ . The difference in the energy grade line and the hydraulic grade line is due to the energy from the velocity head. This is illustrated in Figure 5.1.



**Figure 5.1** Energy and hydraulic relationships for open channel flow.

In open channel flow there are two more depths one should be interested in and understand. These are the *critical depth* and *normal depth*. The depths are related to the flow in a channel, but are deterministic in the sense that behavior of the liquid at any point is dependent upon its relationship to the critical or normal depth.

Most open channel applications are *turbulent flow*. Although it is highly unlikely that laminar flow (Reynolds number under 2000) will be encountered, if the fluid is viscous, non-water based, or contains extremely high levels of emulsified oils and other solids, then that may in fact be the case. If the channel or sewer has a distinct oil layer, that is a two-phase flow regime, and it is often appropriate to ignore the viscous layer unless there is clear evidence that the oil or viscous fluid has influenced the flow regimen. If so, then two-phase analysis may be appropriate. Paper plant sewers may be particularly susceptible to this type of flow from tall oil sewers.

The Bernoulli equation and the Manning equation are used to define flow in open channels.

The flow in any channel is defined by the Manning formula:

$$V = \frac{1}{K} R^{2/3} S^{1/2}$$

In the above formula  $K$  is defined in both metric and Imperial units.  $K$  in Imperial units is  $n/1.486$ , and in metric units,  $n/1$ .  $R$  is the hydraulic radius, which is the wetted area divided by the wetted perimeter, or  $R = A/P$ .  $S$  is the slope of the floor of the channel (measured in m per m or ft/ft, and is dimensionless); it is usually positive but can be negative. This leaves  $n$ , which is a surface roughness coefficient for the channel. The roughness of the channel is a tabular value which is used for estimation and design (see Table 5.1).

The result of all of this is to give us the depth of normal flow in a channel or conveyance  $D_N$ . Conventional nomenclature often uses the letter  $y$  instead of  $D_N$  for normal depth.

One of the most common locations where open channel flow is encountered is in a sewer or circular conveyance. Circular sewers are the most common case of open channel flow in piping, both in municipal and in industrial applications, but sewers can be egg-shaped and have a variety of other shapes as well.

The depth of flow in a circular sewer is a function of the flow. When the pipe is flowing full, the hydraulic radius  $R$  is equal to the area divided by the wetted perimeter  $\frac{\pi D^2}{4\pi D} = D/4$ , which resolves to  $D/4$ . If the pipe is less than full, the computation becomes slightly more difficult, and the chart in Figure 5.2 is helpful in computing values of flow  $Q$  and  $n$  for the pipe.

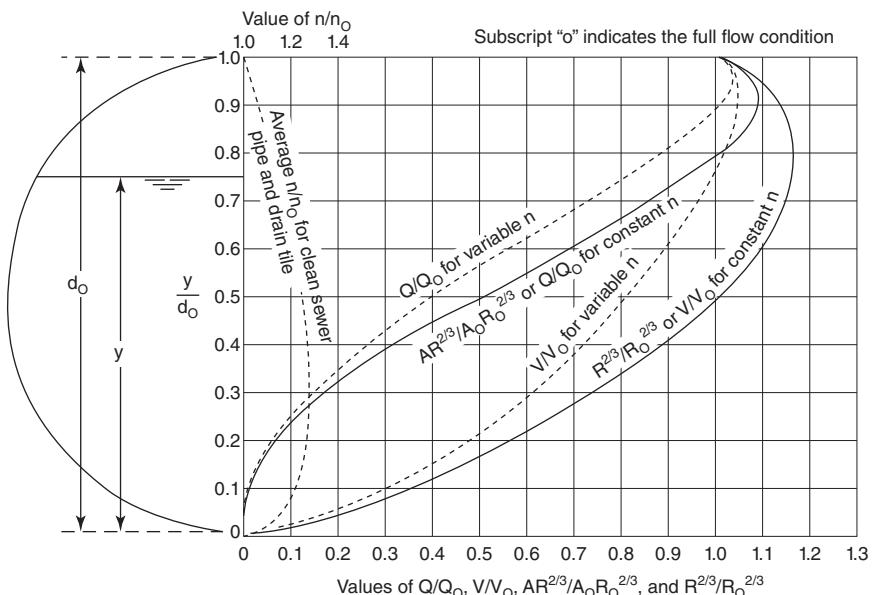
For other channel shapes, Table 5.2 will aid in the computation of the hydraulic radius and wetted perimeter.

Given the slope of a channel and the approximate roughness estimated from Table 5.1, one can estimate the approximate discharge within about 10–15% by computing the area and wetted perimeter, and Manning equation.

**Table 5.1** Typical values for coefficient of  $n$  in the Manning equation.

Channel material	Low value of $n$ for smooth channels	High value of $n$ for rough channels
Earth	0.020	0.04 with partial blockage
Vegetation	0.05 (low vegetation)	0.05–0.10 for very high vegetation
Meandering stream	1.0 for minor meandering	1.3 for severe meandering
Metal-brass	0.009	0.013
Cast iron	0.010 coated	0.016 uncoated
Corrugated metal pipe	0.017	0.030
Cement	0.010 (smooth)	0.015 (rough mortar)
Clay sewers	0.011	0.018 (with manholes and open joints)
Stone	0.023 (rubble and rip rap)	0.036
Cut rock	0.025 (smooth channel)	0.050 (jagged and irregular)

Source: Values taken from *Open Channel Hydraulics* by V.T. Chow, McGraw Hill Engineering Series (1959); the book has been reprinted in pdf: <http://heidarpour.iut.ac.ir/sites/heidarpour.iut.ac.ir/files/u32/open-chow.pdf>.



**Figure 5.2** Flow characteristics in a circular sewer. Source: Figure is in the public domain but was developed by Thomas R. Camp, "Design of Circular Sewers to Facilitate Flow," originally published in *Sewage Works Journal*, 1946, Vol. 18, No. 3. The *Sewage Works Journal* has been renamed as the *Journal of the Water Environment Federation*.

**Table 5.2** Hydraulic properties of various cross-sections used in calculation of flows.

Section	Area A	Wetted perimeter P	Hydraulic radius R	Top width T	Hydraulic depth D
 Rectangle	$b y$	$b + 2y$	$\frac{by}{b + 2y}$	$b$	$y$
 Trapezoid	$(b + zy)y$	$b + 2y\sqrt{1+z^2}$	$\frac{(b+zy)y}{b+2y\sqrt{1+z^2}}$	$b + 2zy$	$\frac{(b+zy)y}{b+2zy}$
 Triangle	$zy^2$	$2y\sqrt{1+z^2}$	$\frac{zy}{2\sqrt{1+z^2}}$	$2zy$	$\frac{1}{2}y$
 Circle	$\frac{1}{8}(\theta - \sin \theta)d_0^2$	$\frac{1}{2}\theta d_0$	$\frac{1}{4}\left(1 - \frac{\sin \theta}{\theta}\right)d_0$	$\frac{(\sin \frac{1}{4}\theta)d_0}{2\sqrt{y(d_0-y)}}$	$\frac{1}{8}\left(\frac{\theta - \sin \theta}{\sin \frac{1}{2}\theta}\right)d_0$
 Parabola	$\frac{2}{3}T y$	$T + \frac{8}{3}\frac{y^{2*}}{T}$	$\frac{2}{3}\frac{T^2y^*}{T^2 + 8y^2}$	$\frac{3A}{2y}$	$\frac{2}{3}y$
 Round-cornered Rectangle ( $y > r$ )	$\left(\frac{\pi}{2} - 2\right)r^2 + (b + 2r)y$	$(\pi - 2)r + b + 2y$	$\frac{(\pi/2 - 2)r^2 + (b + 2r)y}{(\pi - 2)r + b + 2y}$	$b + 2r$	$\frac{(\pi/2 - 2)r^2}{b + 2r} + y$
 Round-bottomed Triangle	$\frac{T^2}{4z}\frac{r^2}{z}(1 - z\cot^{-1}z)$	$\frac{T}{z}\frac{\sqrt{1+z^2}-2r}{z} \times (1 - z\cot^{-1}z)$	$\frac{A}{P}$	$2[z(y-r) + r\sqrt{1+z^2}]$	$\frac{A}{T}$

\*Satisfactory approximation for the interval  $0 < x \leq 1$ , where  $x = 4y/T$ . When  $x > 1$ , use the exact expression  $P = (T/2)[(\sqrt{1+x^2} + 1/x)n(x + \sqrt{1+x^2})]$ .

**Nomenclature:** In open channels, the letter  $D$  and  $d$  are used to denote diameter.  $Y_N$ ,  $Y_O$ , and  $Y_C$  are used to denote the depth of flow in the channel or pipe. At full pipe,  $Y_O = D$ .

**Example 5.1** A 50 cm sewer with a slope of 0.001 is flowing at about 65% full. What is the discharge if the sewer is concrete,  $n = 0.013$ ?

$$\begin{aligned} R_{\text{full pipe}} &= D/4 = 0.5/4 = 0.125 V_{\text{full pipe}} \\ &= (1/0.013)(0.125^{2/3})(0.001^{0.5}) = 0.6081 \end{aligned}$$

$$\begin{aligned} \text{Area} - \pi/4 \times 0.52 &= 0.1963 \text{ m}^2, Q_{\text{full}} = 0.1963 \times 0.6081 \\ &= 0.0931 \text{ m}^3 \text{ sec}^{-1}. \end{aligned}$$

From the chart above,  $Q/Q_{\text{full}} = 0.78 \times 0.0931 = 0.0726 \text{ m}^3 \text{ sec}^{-1}$ .

**Example 5.2** There is flow in a grass-lined natural channel with a top width of approximately 15 ft and an overall depth of 10 ft. The slope you have determined from topographic mapping is 0.004 m/m over the entire length of the channel. You measured the water depth at a footbridge and found it to be 5 ft. What is the flow in the channel?

Because we don't know a lot about the channel and its geometry, we will make some rough calculations which we can refine by hydraulic survey of the channel. But, since that is a lot of work, and we need a number, how can we calculate the approximate flow?

First: Look at the channel shape, which in this case can be approximated by a parabola. We know the width and depth of the parabola. Looking at Table 5.2 on hydraulic sections, we can get the following data.

Top width = 15 ft, overall depth = 10 ft.

First we have to find the top width at the 5 ft section.

The general equation is  $y = C X^2$ , so at  $X = 7.5$ ,  $X^2 = 56.25$ , and since  $y = 10$ ,  $C = 10/56.25 = 0.1778$ , or  $y = 0.1778X^2$ , so when  $Y = 5$ ,  $X = \sqrt{5/0.1778} = X = 5.3$  for  $\frac{1}{2}$  of the stream or 10.606 for the full width of the stream. So  $T = 10.606$  ft.

Then:

$$\begin{aligned} \text{The area } A &= (2/3) T \times y = 2/3 \times 10.606 \times 5 \\ &= 35.333 \text{ square feet} \end{aligned}$$

$$\begin{aligned} \text{The wetted perimeter} &= T + 8y^2/3T = 10.606 + 8 \times 25/(3 \times 10.606) \\ &= 16.892 \end{aligned}$$

Top width at the 5 ft depth =  $3A/2y = 3 \times 35.333/(2 \times 5) = 10.599$ , which is approximately the same as the value we calculated: 10.606

$$\begin{aligned} \text{Hydraulic radius} &= (2T^2y)/(3T^2 + 8y^2) \\ &= (2 \times 10.6^2 \times 5)/(3 \times 10.6^2 + 8 \times 5^2) = 2.0893 \end{aligned}$$

$$\text{Hydraulic depth} = 2y/3 = 5 \times 2/3 = 3.333$$

Finally, we get the  $n$  value from Table 5.1 for grass-lined channels.

$$V = 1.486/n \times R^{2/3}S^{1/2} = 1.486/0.05 \times 2.0893^{2/3} \times 0.004^{1/2}$$

$$= 3.06 \text{ ft s}^{-1}$$

$$\begin{aligned}\text{Discharge} &= Q = V \times A = 3.06 \times 35.333 \\ &= 108 \text{ cubic feet per second} = 3.071 \text{ m}^3 \text{ s}^{-1}\end{aligned}$$

Table 5.2 gives the calculation parameters for a variety of conveyance shapes.

### Example 5.3 Free Fall Method

You have a 20 cm diameter pipe flowing part full, and the discharge drops approximately 2 m into a pond. Using only a carpenter's square, estimate the discharge from the pipe.

#### Solution:

Start by measuring the depth of flow in the pipe, which in this case is 15 cm.

Then by holding or aligning the long side of the carpenter's square in parallel to the water surface of the pipe, with the short leg of the square pointing downward, determine the distance and the fall of the intersection of the water surface with the vertical and horizontal legs of the square.

By using the fall of the liquid and the formulae for Newtonian physics,  $s = \frac{1}{2}gt^2$ .

We estimate that at the 12' (30.54 cm) spot the flow has dropped approximately 25" (63.5 cm).

Then:

$$63.5 = 0.5 \times 980 t^2 \text{ giving } t = 0.36 \text{ s.}$$

The velocity is

$$v = 30.54/0.36 = 84.8 \text{ cm s}^{-1} = 2.78 \text{ ft s}^{-1}.$$

Since the liquid is flowing at 15 cm in a 20 cm pipe, we can calculate the area of the liquid as:<sup>2</sup>

$$\begin{aligned}h &= 2r - y = 20 - 15 = 5 \\ \theta &= 2 \arccos[(r - h)/r] = 2 \arccos((10 - 5)/10) \\ &= 2 \arccos(5/10) = 1.04072 \text{ rad} \\ A &= \pi r^2 - r^2(\theta - \sin\theta)/2 = 3.1416 \\ &\quad \times 10^2 - 10^2(1.04072 - \sin(1.04072))/2 \\ &= 314.16 - 9.059 = 305.1 \text{ cm}^2\end{aligned}$$

And the discharge =  $305.1 \times 84.33 = \text{cm}^3 \text{ s}^{-1} = 0.02573 \text{ m}^3 \text{ s}^{-1}$  or  $408 \text{ gal min}^{-1}$

It is always a good idea to make a capacity check in the units with which you are most familiar, so going to hydraulic tables, and getting the flow in a 20 cm pipe (approximately 8") the flow at 408 gal min<sup>-1</sup> is around 3 ft s<sup>-1</sup>, so the system checks with common sense.

### 5.3 Froude Number

In every free-flowing fluid in a conveyance, the relationship between the inertial force of the fluid and gravity is expressed by the Froude Number, or  $N_F$ :

$$N_F = \frac{V}{\sqrt{gL}}$$

where  $V$  is the velocity, and  $L$  is a characteristic length. For open channels, the characteristic length is taken as equal to the normal depth of flow  $y_N$ .  $y_N$  is the depth of flow of the fluid in a plane normal to the direction of the flow, or

$$N_F = V / \sqrt{gy_N}$$

When  $N_F$  is equal to 1, the flow is critical, and the gravity forces balance the momentum forces. When the flow is in a critical state, there is only one relationship between depth and flow. It is the principle upon which almost all open channel flow measuring devices operate. If  $N_F$  is less than 1, the flow is considered tranquil; but if  $N_F$  is greater than 1, the flow is rapid or shooting, and flow measurement becomes significantly more difficult because the flow can dramatically increase or decrease for a very small, and almost often immeasurable change in the depth of flow.

Most open channel flowmeters work because of the definitive relationship between depth and discharge that occurs at critical flow.

In any channel of any shape there is a relationship between the channel slope and the normal flow. That is given by the Manning formula, shown in the first section. The normal depth ( $d_n$ ) for the channel may be above or below the critical depth. The critical depth ( $y_c$ ) is the depth at which gravity and friction forces balance and  $N_F = 1$ .

Applying the Froude number when  $N_F = 1$  yields the formula for critical depth  $y_c$ :

$$y_c = V^2/g$$

Applying the Manning equation yields:

$$y_c = 1/n^2 \times 1/g \times R^4 / 3 \times S$$

When there is a rectangular channel, one can make substitutions to express  $A/P$  as a function of  $y$ , and when one makes the substitution of  $Q = V \times A$ , the

overall function is:

$$y_c = \frac{Q^2 S}{g n^2 A^{\frac{2}{3}} P^{\frac{4}{3}}}$$

It is possible to combine the above equation much more as a function of the channel geometry and simplify the geometry so that  $y_c$  is a function of channel slope  $S$  and  $Q^2$ .

For any one value of  $Q$ , there is one and only one value of  $d_c$ . This is why critical flow measurement devices work. This includes all types of flowmeters from Parshall flumes to Cutthroat flumes to Palmer-Bowlus flumes, and all types of weirs.

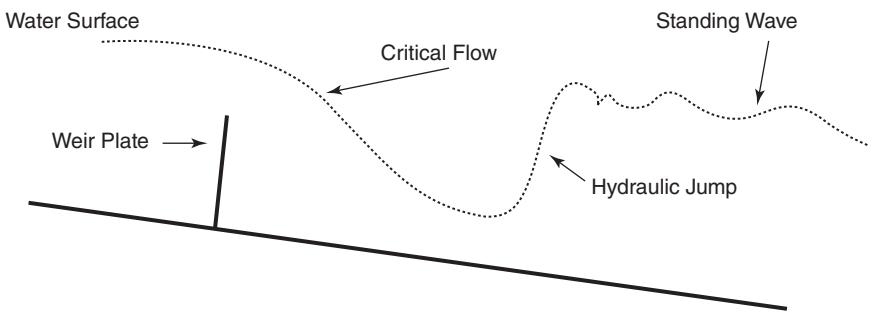
The flow in any open channel may be above or below the critical flow. The slope of the channel is classified as mild, critical, horizontal, steep, or adverse (see Figure 5.3).

The behavior of the liquid in a channel is determined by the slope, channel roughness, and the flow. The depth of flow in the channel at any one point in time may be calculated and the flow depth at almost any other point predicted if one includes a consideration of the depth of the critical flow in the computations. As the liquid moves down the channel, it will either increase or decrease in depth with distance, sometimes approaching the flow level in an asymptotic fashion.

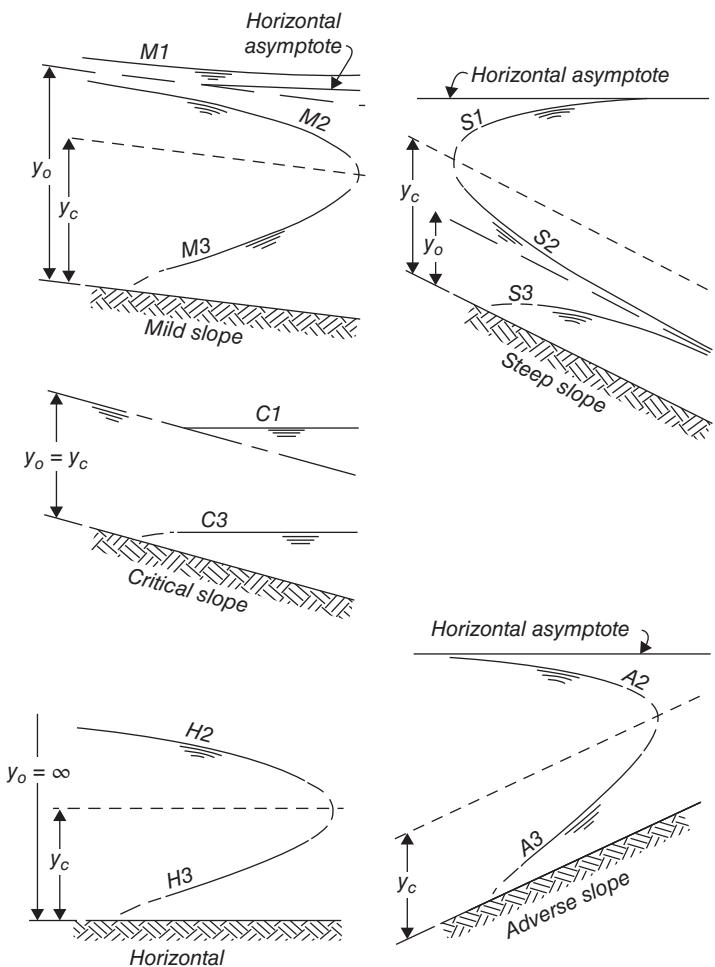
Whenever the flow is below the critical depth, it will, when it encounters an obstacle, jump to a conjugate depth greater than the critical flow. This is shown in Figure 5.4.

When you have a surface where the flow is rapid or changing with depth, you cannot accurately measure it with an open channel device that relies only on depth of flow as a measure of discharge.

A hydraulic jump occurs when a stream is moving faster than critical velocity and starts to slow down due to frictional or other forces. Critical flow shown above occurs when the stream passes through a control section, and starts to slow down (Figure 5.4). The flow then jumps from a subcritical depth to normal



**Figure 5.3** Water surface profiles and slopes for open channel flows.



Surface profiles (backwater curves) for gradually varied flow  
Flow is from left to right; vertical scales are greatly enlarged.

**Figure 5.4** Elements of a hydraulic jump.

depth if the channel slope permits that flow. If the channel is at a super-critical slope, then there will be little or no hydraulic jump.

The most common place this occurs is after a flowmeter. Look at the tailwater after the flowmeter to see if there is a hydraulic jump. If there is, the flowmeter may require additional hydraulic analysis because the relationship between discharge and flow is extremely flat, and large changes in flow result in extremely small and disproportionate changes in depth measured by the flowmeter.

## 5.4 Types of Flowmeters

There are several types of open channel flowmeters, and a few good electronic flowmeters. The basic ones you will encounter are the following:

Parshall shapes and their variations, including Palmer Bowlus flumes, cutthroat flumes, and other shapes

V-notch weirs ( $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $90^\circ$ , and compound shapes)

Broad crested weirs

Special shapes (parabolic and Sutro)

Electronic flowmeters

The properties of a Parshall flume are shown in Table 5.3. It is a critical flow device. It must have free outflow downstream if it is to measure accurately.<sup>3</sup> It must also have a reasonably quiescent upstream flow without sharp bends or corners for at least six weir lengths. It handles solids well and is accurate over a reasonably broad range of flows. When installed properly and calibrated and maintained, it can be of primary standard quality.

The Parshall flume is one of the most studied and the most widely used shapes for flow measurement. The geometry of the Parshall shape is critical and cannot be modified if the flume is to be used for accurate measurements. Accumulation of solids or films that might change the dimensions should also be avoided.

The problem of solids buildup in the Parshall flume has been solved by modification of the basic shape. These shapes are not impaired by solids buildup. The cutthroat flume, particularly has a level floor and does not accumulate mud and debris. The Parshall flume, and several other popular types, are also shown in Table 5.3.

The Palmer-Bowlus and the cutthroat flumes are also critical flow devices, varying only slightly in design and dimensions. The Palmer-Bowlus is often built as a slip-in form for circular pipes, and it is generally accurate within 1–10% depending upon installation conditions, flow, surges, channel slope, and other factors.

Many Parshall flumes and Parshall-type devices have specific locations for measurement. Unfortunately, the installation conditions are often ignored, and the only measurement of flow is taken at an incorrect depth. Measurement of flow in a Parshall flume requires two measurement points as shown at the wet well location in Table 5.3, labeled  $H_A$  and  $H_B$ . Note that there are two sensors, one upstream and one downstream of the Parshall device, and the differential in the water flow levels determines the flow through the flume.

For high accuracy, the flow should be measured by traversing the section using a portable flowmeter such as an ultrasonic flowmeter (typical unit made by Hach) or a Price current meter. Both can be used as “primary standard” devices in measurement of water flows. The Price current meter is the accepted standard device, and it has the ability to average flow over a few seconds or

**Table 5.3** Properties of a Parshall flume.

															Free-flow capacity		
W	A	Z	B	C	D	E	F	G	K	N	R	M	P	X	Y	Min- imum	Max- imum
Ft in.	Ft in.	Ft in.	Ft in.	Ft in.	Ft in.	Ft	Ft	Ft	In. in.		Ft in.	Ft in.	Ft in.	In. in.	cfs	cfs	
0-3	1-6-3/8	1-1/4	1-6	0-7	0-10.3/16	2	1/2	1	1	2.1/4	1-4	1-0	2-6-1/4	1	1.1/2	0.03	1.9
0-6	2-7/16	1-4.5/16	2-0	1-3.1/2	1-3.5/8	2	1	2	3	4.1/2	1-4	1-0	2-11.1/2	2	3	0.05	3.9
0-9	2-10-5/8	1-11.1/8	2-10	1-3	1-10.5/8	2.1/2	1	1.1/2	3	4.1/2	1-4	1-0	3-6.1/2	2	3	0.09	8.9
1-0	4-6	3-0	4-4.7/8	2-0	2-9.1/4	3	2	3	3	9	1-8	1-3	4-10.3/4	2	3	0.11	16.1
1-6	4-9	3-2	4-7.7/8	2-6	3-4.3/8	3	2	3	3	9	1-8	1-3	5-6	2	3	0.15	24.6
2-0	5-0	3-4	4-10.7/8	3-0	3-11.1/2	3	2	3	3	9	1-8	1-3	6-1	2	3	0.42	33.1
3-0	5-6	3-8	5-4.3/4	4-0	5-1.7/8	3	2	3	3	9	1-8	1-3	7-3.1/2	2	3	0.61	50.4
4-0	6-0	4-0	5-10.5/8	5-0	6-4.1/4	3	2	3	3	9	2-0	1-6	8-10.3/4	2	3	1.3	67.9
5-0	6-6	4-4	6-4.1/2	6-0	7-6.5/8	3	2	3	3	9	2-0	1-6	10-1.1/4	2	3	1.6	85.6

(continued)

Table 5.3 (Continued)

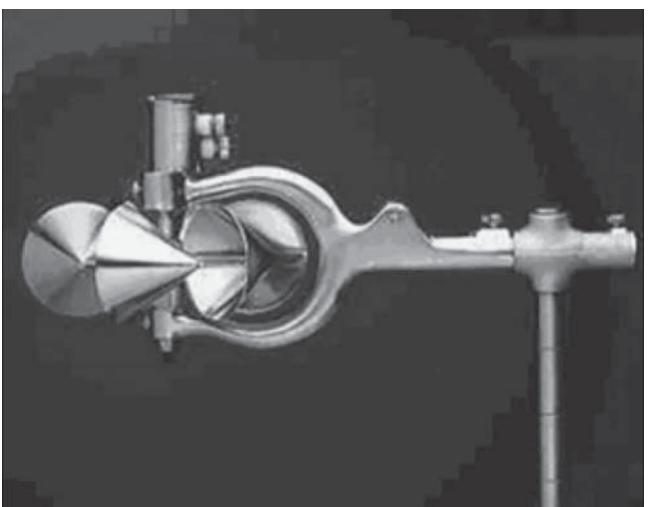
**a. Plan and sectional elevation of concrete Parshall measuring flume**

**b. Palmer Bowls flume**

**c. Cutthroat flume**

W	A	Z	B	C	D	E	F	G	K	N	R	M	P	Free-flow capacity			
														Min- imum	Max- imum		
Ft In.	Ft In.	Ft In.	Ft In.	Ft In.	Ft In.	Ft	Ft	In.	In.	Ft In.	Ft In.	Ft In.	In.	In.	In.	cfs	
6-0	7-0	4-8	6-10.3/8	7-0	8-9	3	2	3	3	9	2-0	1-6	11-3.1/2	2	3	2.6	103.5
7-0	7-6	5-0	7-4.1/4	8-0	9-11.3/8	3	2	3	3	9	2-0	1-6	12-6	2	3	3.0	121.4
8-0	8-0	5-4	7-10.1/8	9-0	11-13/4	3	2	3	3	9	2-0	1-6	13-8.1/4	2	3	3.5	139.5
10	14-3.1/4	6-0	14	12-0	15-7.1/4	4	3	6	6	13.1/2	8-0	6-0	32-0	12	9	6	200
12	16-3.3/4	6-8	16	14-8	18-4.3/4	5	3	8	6	13.1/2	9-0	8-0	35-0	12	9	8	350
15	25-6	7-8	25	18-4	25-0	6	4	10	9	18	11-0	9-0	40-0	12	9	8	600
20	25-6	9-4	25	24-0	30-0	7	6	12	12	27	12-0	10-0	48-0	12	9	10	1000
25	25-6	11-0	25	29-4	35-0	7	6	13	12	27	12-0	10-0	55-0	12	9	15	1200
30	26-6.3/4	12-8	26	34-8	40-4.3/4	7	6	14	12	27	12-0	10-0	64-0	12	9	15	1500
40	27-7.1/2	16-0	27	45-4	50-9.1/2	7	6	16	12	27	13-0	11-0	80-0	12	9	20	2000
50	27-7.1/2	19-4	27	56-8	60-9.1/2	7	6	20	12	27	13-0	11-0	95-0	12	9	25	3000

Parshall flume, with dimensions for various throat widths, and other common flume types.



**Figure 5.5** Pygmy current meter by Gurley instruments.

provide an “instantaneous” flow reading. The purported accuracy of the Gurley current meter (Figure 5.5) is approximately 2%. Other electronic flowmeters are accurate to within approximately 0.5%.

The advertised accuracy of the Price meter is 2%. The principal obstacles to the Price current meter are the jeweled pivot, upon which the rotating cups rest, and the need for maintenance of these pivots. The Price meter, which is larger than the Gurley meter but larger is size.

There have been several advances in the field of electronics, and that affects the flow metering industry. A few years ago the MagMeter<sup>©</sup>, which was manufactured by Fisher and Porter<sup>©</sup> (now owned by ABB), was a standard for measurement in closed conduits. Originally, it was used only in full pipe applications. The principle of operation relied upon Faraday’s Law where a circular orifice, slightly smaller in diameter than the pipe, had been placed. Inside the orifice was a coil that supplied a magnetic field. The flow of fluids through the orifice generates a current which is proportional to the velocity of water through the orifice. The unit is accurate to within 1–2%. But the device as then configured could not be used in a partially full pipe.<sup>4</sup> In order for a Faraday type device to work, the fluid must have some conductive properties. For example, green liquor in a pulp mill is non-conductive, and will not register in a Faraday type device.

Shortly after the introduction of the MagMeter<sup>©</sup>, someone had the bright idea of adding a bubbler on the bottom of the pipe. The air pressure to create the bubbles was an indication of the depth of flow. The magnetic orifice measures the velocity, and the bubbler measures the depth of flow. The signals are integrated and the flow is computed by velocity-area methods even when

the pipe is not full. The disadvantage of this type of meter is that there is an intrusion into the pipe which can catch debris and dirt, and those elements can create inaccuracies in flow measurement. The MagMeters<sup>©</sup> by themselves are generally a fairly expensive stand-alone flanged pipe fitting, and they are in pipe sizes up to 48 in. diameter.

An improvement on the MagMeter<sup>©</sup> employed a single magnetic sensor which is placed in the bottom of the pipe for measuring flow in full and partially full pipes. The sensor generates its own electric field, and the flow lines cut by moving water above the sensor generate a current which is measured electronically. The challenge of using these types of flowmeters is that they are intrusive and can catch debris and solids, and the sensor and its electrical cable has to be fastened securely to the inside of the pipe.

Other systems employ ultrasonic transmitters and sensors to both measure the depth of flow, and to measure the velocity of the water by doppler techniques. They are also highly accurate, but they measure the velocity in the pipes by placement of either two or four sensors around the pipe, and transmitters and receivers that create ultrasonic velocity profiles through the water by one or two paths. Slurries in the pipeline can interfere with velocity measurements because they often move at a velocity different than the fluid. If the pipe is partially full, the reflection path for an ultrasonic flowmeter is incomplete, and measurement results are unreliable. The advantage of the ultrasonic flowmeters is that they are externally installed, and do not require special fittings or flanges in the pipe; in many cases the maintenance is quite simple because the transmitter and receiver are mounted on the outside of the pipe.

Newer models of flowmeters now incorporate low power radar and sonic level measurements. One of these devices is shown in Figure 5.6. The unit is placed in the top of the sewer pipe, or other structure, and the flow is measured

**Figure 5.6** Hach  
Marsh-McBirney Flowdar  
radar flowmeter.



by doppler radar, and the water level is measured by ultrasonic reflection. The unit is programmable to allow compensation for irregular pipeline and channel shapes. The reported accuracy is 1% of full flow.

A word of caution should be inserted about irrational exuberance and significant figures in flow metering. Because of the sophisticated electronics in the flowmeters, they have the ability to report the flow to five or six significant figures. While it is wonderful to be able to report that the flow in a particular pipeline or sewer is 43 506.3 gal per hour based upon the flowmeter output, only the first two figures are really significant. Remember that even in electronic flowmeters the significance of additional figures is often misleading because of other inaccuracies and error sources.

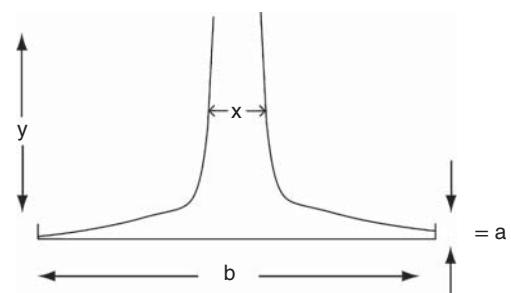
## 5.5 Weir Plates

For routine measurement applications where there are little or no solids or other debris in the flows, and where the flow does not vary widely, it is difficult to beat a weir plate measurement device for both installation cost and accuracy. Several of the weir plates and their equations are given in Figure 5.8 and Table 5.4. The most popular of these are the rectangular weirs and the v-notch weirs. In all cases except the proportional or Sutro weir shown in Figure 5.7, the water level is measured a bit upstream from the weir plate, with the level of the lowest point on the plate as a reference.

Installation conditions, such as setting the weir plates at an angle to the flow, or failure to account for the approach velocity, can cause both erratic and unreliable measurements. The failure to account for the velocity of the flow in the approach channel will cause the weir to measure between 10% and 15% low.

**Table 5.4** Standard discharge formulae for weirs.

Name	Discharge equation	Comments
60° v-notch	$Q = 1.43 H^{2.5}$	Approximate formula
90° v-notch	$Q = 2.49 H^{2.48}$	
Combination	$Q = 3.9 H^{1.72} - 1.5 + 3.3 Lh^{1.5}$	
Parabolic	$Q = 1.512 p^{0.478} h^2$	$Q \propto h^2$
Proportional	$Q = Ca^{1/2} b\sqrt{2g} \left( h - \frac{2}{3} \right)$	$0.625 < C < 0.600$ $Q \propto t$
Rectangular	$Q = 3.33 H^{3/2} (L - 0.2H)$	Fully contracted ends
Cipolletti	$Q = 3.367 LH^{1.5}$	
Submerged	$Q = 3.33 L (n H)^{3/2}$	$n$ = tabular correction for submergence ratio



**Figure 5.7** Sutro or proportional weir.

The discharge equation for a Sutro or proportional weir shape is linear due to the shape of the weir.

$$Q = \{Ca^{1/2}b\sqrt{2g}(h - a/3)\}$$

The author has written an article for *Chemical Engineering Magazine*, October 20, 1980, pp. 109–121, which highlights some of the material discussed in this chapter. The drawings for the weir figures are taken from that article.

The Sutro weir is mentioned because it is a proportional weir; the depth of the flow through the weir is directly proportional to the flow through the weir. It is widely used in sewage treatment grit removal facilities where a specific residence time is required to allow grit to settle out of the incoming wastewater so that it will not enter and damage the pumps.

More detailed information on flow measurement can be obtained from the *USBR Water Measurement Manual*.<sup>5</sup> The book, first published in the 1950s, is a classic, and provides a thorough treatment of open channel flow measurement. The book was revised and updated in 2001.

## 5.6 Alignment Errors

Open channel flow measurement devices require a straight, quiescent flow upstream and downstream of the device. Some of the most egregious and most common installation mistakes made include installation in locations where the flow is not uniform across the channel; installation where the flow is rapid (steep slope); installation where the flow approaching the device is highly turbulent; and installation where there is a downstream condition that causes the water to back up and flood the measuring device, as discussed in Chapter 3. For the most part, these conditions can be eliminated by good engineering controls and some planning and calibration.

In general, the location of a sampling and/or flow measurement station should have at least 10 pipe diameters (or channel widths) of a straight run above the flowmeter and at least five diameters downstream. Ideally the liquid should be sediment-free, or one should select a measurement device that is

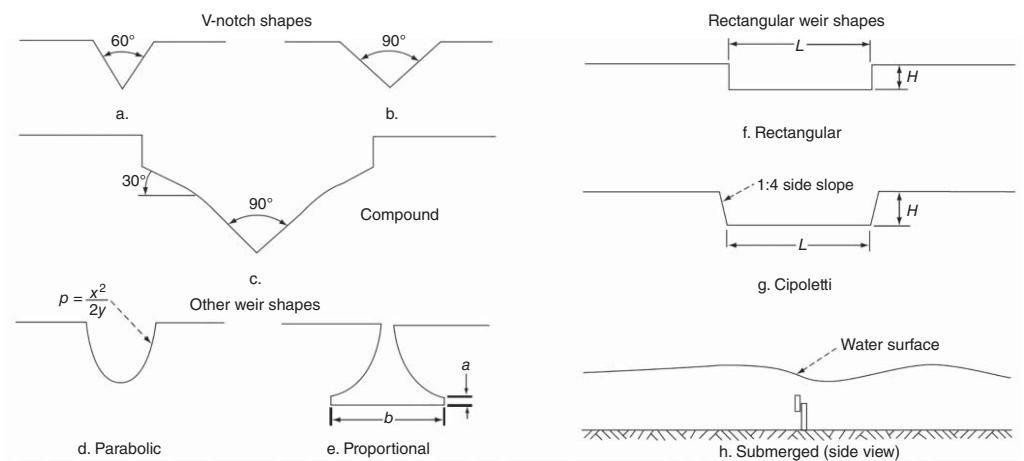


Figure 5.8 Other types of weirs commonly in use.

capable of handling solids. The flow should be subcritical, in that the depth should be greater than the critical depth – the consequences of rapid flow is that a great change in flow will only cause a small change in depth, and causes inaccuracies in measurement. Surging or waves should be eliminated in the vicinity of the flowmeter, even if a stilling basin is required.

The skewed flow distribution pattern may also affect the measurement accuracy of ultrasonic flowmeters, depending upon the placement of the sensors. Consider the momentum of a fluid as it turns a corner or changes direction, and locate your flowmeter accordingly. If the fluid has flow measurably higher (or deeper) on one side of a bend than the other, there is a good chance that the solids in the flow will be skewed as well, and any sampling will need to address the unequal distribution.

All open channel flowmeters should be calibrated upon installation, especially if an integrated flowmeter and sampler is to be used for measuring and sampling the effluent.

## 5.7 Samples and Sampling

The first requirement of a sample is to be representative of the conditions in the medium being sampled. In open channels or sewers, this is much more difficult than it seems. For example, there is no accepted way of sampling a two-phase fluid (oil and water) where one layer is floating on top of the other. If, however, the fluid is well mixed and/or emulsified, then the fluid can be readily and accurately sampled – but that is not the most common case.

There are a number of different schemes for the collection of representative samples. There are also a number of different types of samplers. In 1973, the USEPA commissioned a study of the various types of samplers and sampling theories. While the study was primarily concerned with stormwater, it is definitely applicable to all types of industrial flows and samplers.<sup>6</sup> The publication discusses samplers and sampling and makes some very interesting points about flow distributions and sampling equipment. Among the conclusions and findings in that report are the following items:

1. The sample concentration will be less than the flow concentration if the sampler is along the bottom of the conduit by about 12%, and may be up to 50% lower than the main flow if the sampling port is located at 90% to the main flow, unless the intake velocity of the sampler approaches seven times the flow velocity in the conduit.
2. The representation of suspended solids in the sample is highly dependent upon the particle size of suspended solids. Suspended solids below 60 µm are less affected by the sample intake velocity. Samples of 450 µm diameter (and presumably larger) are greatly affected by sample intake velocity. If the sample intake velocity is 0.25 of the conduit flow velocity, the concentration

of the larger particles may be two times more than the average of the conduit; at the average conduit flow velocity the sampled concentration equals the average in the conduit; and, at intake velocity five times the average fluid velocity, the 450 µm particles are undersampled by approximately 25%.

3. There is strong evidence that the diameter of the particle will be strongly skewed by particle size. The larger the particle, the greater the skew of the distribution, up to 60% increase near the bottom of the conduit.
4. Geometry of the sampler intake has little effect on the representativeness of the sample.
5. For composite samples, the variation of flow and concentration can undersample the stream concentrations up to 10% or oversample the concentrations by up to 12%, according to the figure on page 225 of the referenced publication *An Assessment of Automatic Sewer Flow Samplers* (see Endnote 6) see Figure 5.9.

q FLOW	CONC k	$1 - t$	$1 - \frac{t}{2}$	$\cos \frac{\pi t}{2}$	$e^{-t}$	$\sin \pi t$
	C	0.90 0.90 0.90 0.90	0.97 0.97 0.97 0.97	0.92 0.92 0.92 0.92	0.95 0.95 0.95 0.95	0.99 0.99 0.99 0.99
	t	1.35 0.90 0.86 0.87	1.09 0.97 0.96 0.96	1.26 0.90 0.87 0.89	1.14 0.97 0.95 0.95	0.99 0.90 0.89 0.97
	$1 - t$	0.68 0.95 0.92 0.92	0.87 0.98 0.97 0.97	0.72 0.98 0.95 0.93	0.82 0.96 0.95 0.95	0.99 1.12 1.09 0.97
	$\sin \pi t$	0.90 1.01 0.90 0.90	0.97 1.00 0.97 0.97	0.88 1.00 0.92 0.92	0.97 1.00 0.95 0.95	0.80 1.01 0.98 0.97

Line 1.  $T_C V_C$  - Simple composite

Line 2.  $T_C V_V$  - Volume proportional to flow rate ( $q$ )

Line 3.  $T_C V_V$  - Volume proportional to flow ( $Q$ ) since last sample

Line 4.  $T_V V_C$  - Time varied to give constant  $\Delta Q$

**Figure 5.9** Comparison of the accuracy of flow composite samplers under various combinations of flow and concentrations.



**Figure 5.10** One of several varieties of wastewater samplers. Shown without watertight cover.

Since the study was published, a number of sample manufacturers have discontinued manufacturing, and the most common type of sampling is flow-proportional sampling using a philosophy of fixed volume at a variable time interval, which is dictated by the flow in the conduit. Some of the most common samplers in current use employ a peristaltic pump through a  $\frac{3}{8}$  or  $\frac{1}{2}$  inch hose coupled to a flowmeter. The sampler is battery powered and is designed to fit through a manhole (Figure 5.10). The black box on the top of the unit is for flow monitoring, and contains the peristaltic pump. The container to collect the sample is inside the body of the sampler. The unit is designed to be hung from a platform or hook inside a manhole.

Other varieties of flowmeters collect one flow-proportional sample. The operating principle is that the sampler will work with the flowmeter to collect a sample every X cubic meters or gallons of flow in the conduit. The sample is deposited in a single large container. The sample size varies with the flow in the conduit, and there are two common challenges to using this type of flowmeter. In the first instance, if the flow is very low and much less than anticipated, the sample may be too small for the laboratory to analyze the

full set of parameters required. The second challenge is that if the flow is significantly larger than anticipated, the amount of sample collected may overflow the sampling container, skewing the sample in an unknown direction.

Another type of sampler collects samples at fixed intervals into separate bottles. In that instance, if a flow proportioned composite sample is desired, the flow must be determined for the period, and an aliquot of the sample must be composited according to the flow during the period sampled.

## 5.8 Conclusion

When we consider the possible errors in sampling and in flow measurement, and in the ability of the laboratory to analyze the sample accurately, it is a wonder that we can begin to know what is actually being discharged. Given the regulatory agency's willingness to impose substantial fines and penalties on the discharger, it is surprising that so little attention is paid to this issue. Based upon what has been stated so far, the ability of the sample to represent what is in the conduit is consistent, but may be off by between 15% or more. This is a strong argument for statistical basis for the permitting rather than a single set of permit numerical limits on a discharge.

## Notes

- 1 A laser measuring tool from Bosch has a stated accuracy of  $\pm 1.587$  mm or 1/16 inches.
- 2 Calculations on area of pipe made from <http://www.engineeringexcelexcelspreadsheets.com/2011/03/partially-full-pipe-flow-calculations>.
- 3 The Parshall flume relies on the difference in elevation of the water surfaces as it crosses the flume. A flooded discharge with backwater reaching up into the throat area is called a "submerged" flume. The submerged flume can still be used to measure discharges, but the accuracy decreases markedly. In one instance we encountered a flume connected immediately upstream of a pumping station wet well. Because the high water level in the pumping station allowed the water to back up into and flood the flume, the paper mill thought that it was using substantially more water than it actually was.
- 4 Any metering application that relies on Faraday's law will not work if the fluid is non-conductive.
- 5 [https://www.idwr.idaho.gov/files/water\\_measurement/2001\\_Bureau\\_of\\_Reclamation\\_Water\\_Measurement\\_Manual.pdf](https://www.idwr.idaho.gov/files/water_measurement/2001_Bureau_of_Reclamation_Water_Measurement_Manual.pdf).

- 6 *An Assessment of Automatic Sewer Flow Samplers, 1975*, by EG&G Washington Analytical Services Center, NTIS Publication No PB 250-087, now available on the Internet: <http://nepis.epa.gov/Exe/ZyPDF.cgi/9100RUUF.PDF?Dockey=9100RUUF.PDF>. An additional reference on automatic sampling and measurement is: [http://www.astm.org/DIGITAL\\_LIBRARY/STP/SOURCE\\_PAGES/STP582\\_foreword.pdf](http://www.astm.org/DIGITAL_LIBRARY/STP/SOURCE_PAGES/STP582_foreword.pdf) which is available from ASTM at a cost of approximately \$55.

## 6

# Troubleshooting and Emergency Planning

This chapter is based upon practice in troubleshooting problem areas and helping to prevent spills and discharge upsets. The principal practices in this chapter are an attempt to provide the reader with tools to analyze problems, and help prevent their recurrence.

When there is a discharge or condition in the effluent that causes an exceedance in the permit conditions, the first item of business is to find out just how bad it was. That requires inspection and cooperation from the laboratory to verify the analytical quantities as quickly as possible. The incident may require immediate reporting to a regulatory agency or public health agency, if harm is to be prevented<sup>1</sup> and one should not report occurrences without some degree of confirmation or proof. Prior to the enactment of the Clean Water Act in the US (1972), the discharge of hazardous chemicals was, although infrequent, a much more common occurrence than it is today.

## 6.1 Fault Tree Analysis

A fault tree is one of the tools that can be used to help protect and analyze a treatment system. It can be set up as a binary tree or as a probability tree for the purposes of analysis of decisions, faults and events. A simple example of a decision tree is shown in Figure 6.1. When analyzed from the initiating or bottom event to the top event, the fault tree is a decision tree; and when analyzed from the top event downward, it becomes a fault tree for reconstruction of an incident.

A typical fault tree consists of an analysis of an undesirable event with one or more possible causes. The causes are actions from an initiating event. The initiating events and contributing (intermediate) events are controlled by various types of logic gates, which indicate the likelihood of the event passing through to contribute to or cause the undesirable event. The logic gates can be assigned probabilities, or they can be gates that require a combination of one or more events (and gates), or they can pass one or more event through (either/or gates) to create the next level of undesirable event.

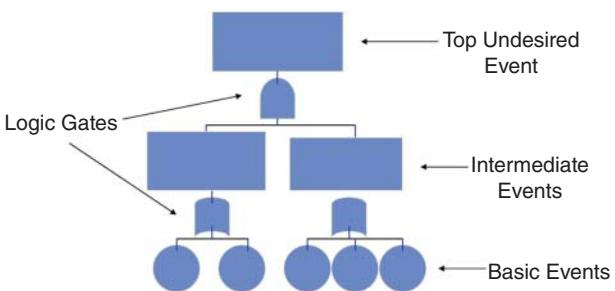
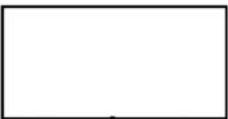


Figure 6.1 Example of a fault tree analysis program.

## THE LOGIC SYMBOLS . . .

Most Fault Tree Analyses can be carried out using only these four symbols.



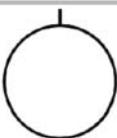
TOP Event...foreseeable, undesirable event, toward which all fault tree logic paths flow...or...  
Intermediate Event...describing a system state produced by antecedent events.



"OR" Gate...produces output if any input exists. Any input, individually, must be (1) necessary and (2) sufficient to cause the output event.



"AND" Gate...produces output if all inputs co-exist. All inputs, collectively, must be (1) necessary and (2) sufficient to cause the output event.



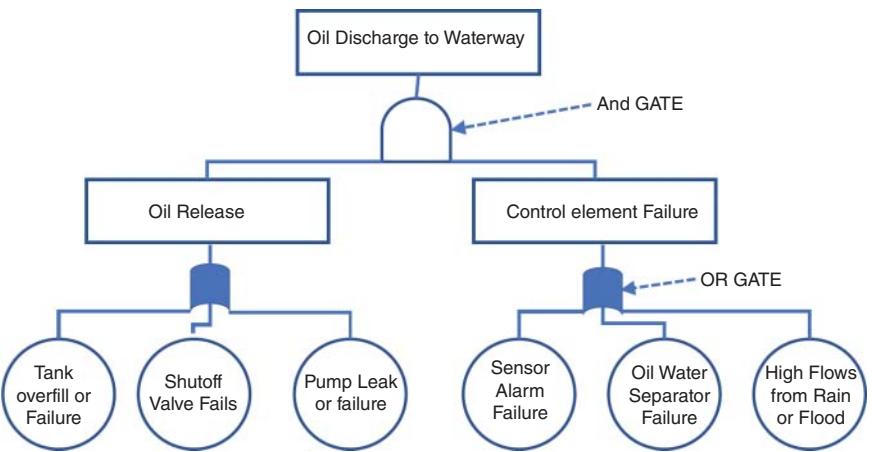
Basic Event...Initiating fault/failure, not developed further. (Called "Leaf," "Initiator," or "Basic.") The Basic Event marks the limit of resolution of the analysis.

EVENTS and GATES are NOT component parts of the system being analyzed. They are symbols representing the logic of the analysis. They are bi-modal. They function flawlessly.

Figure 6.2 Basic fault tree symbols.

Figure 6.2 lists the type of gates and symbology used in developing a fault tree. The OR gates will pass a fault through if even one of the contributing events occurs. An AND gate requires multiple contributing events for it to pass. AND gates are often limited to two events. An example of a discharge that causes an oil spill in a plant effluent is shown in Figure 6.3 in a fault tree format.

Figure 6.3 is a potential sequence of events that leads to an oil release to the environment. There are two types of intermediate events that can cause a release: (1) the oil release itself, and (2) a control element failure. These are independent events, and it would take both of them to occur for an oil discharge



**Figure 6.3** Fault tree analysis for an oil spill.

to the waterway. The basic events leading up to an oil release include: (1) tank overfill or tank failure; (2) OR fill shutoff valve failure; (3) OR pump leak. The plant has control elements *that must also fail*: they include an oil–water separator, and sensor alarms. Events leading to the control element failure are: (1) sensor alarm failure; (2) OR oil–water separator failure; (3) OR unanticipated high flows from rainfall or other sources which may cause short-circuiting of the control devices. The control element failure is independent from the oil release, and both intermediate elements must fail before an oil release can occur. If one or the other of the intermediate elements fails, nothing happens. But if both fail at the same time, an oil release occurs.

In order to use the fault tree successfully, one must assign probabilities to the various events and gates. Looking at Figure 6.4, and considering the oil release portion, the three initiating events each have a probability or frequency assigned to them. For example, if the tank overfill has a probability of once every 12 months, the shutoff valve failure occurs once every 24 months, and the pump fails once every 48 months, the respective initiating events could be coded in terms of months as: tank overfill, 1/12 or 0.0835; shutoff valve failure, 1/24 or 0.0418; and pump or leak failure, 1/48 or 0.0208. The control elements numbers are, respectively: sensor alarm failure 1/24 or 0.0418; separator failure 1/120 or 0.0083; and high flows 1/36 or 0.0278 (see Figure 6.4).

Because the elements are independent, any of the initiating events will cause an oil release or a control element failure. But, in order for there to be a discharge to the waterway, the control element must fail, *and* the oil release *must* occur at the same time.

An oil release probability would be  $1/24 + 1/24 + 1/48 = 0.217$ . A control element failure would have a probability of  $1/24 + 1/120 + 1/36 = 0.0280$ . To

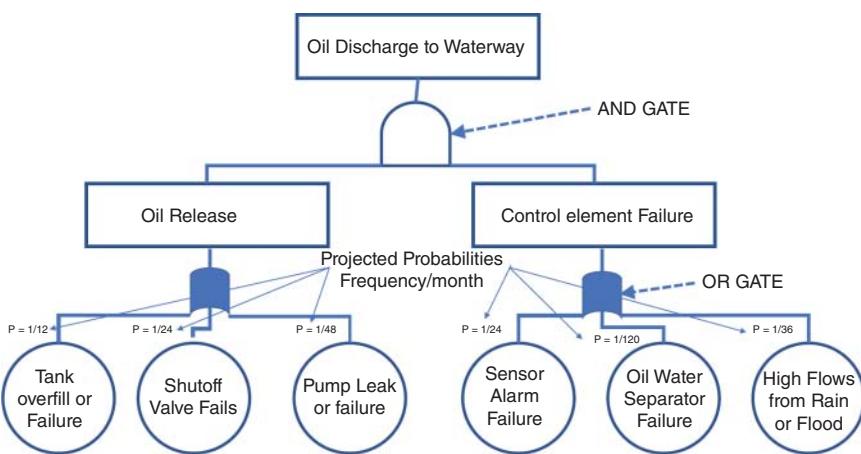


Figure 6.4 Calculation of fault tree probabilities.

get the probability of an oil discharge through an AND gate, multiply the joint probabilities for oil release and control element failure. The probability of an oil release is then:  $0.0280 \times 0.217 = 0.00608$  months, or once in almost 14 years.<sup>2</sup> One of the greatest uncertainties in the initiating or basic events might be the weather, or a higher frequency than that in the example.

## 6.2 Reverse Fault Tree Analysis

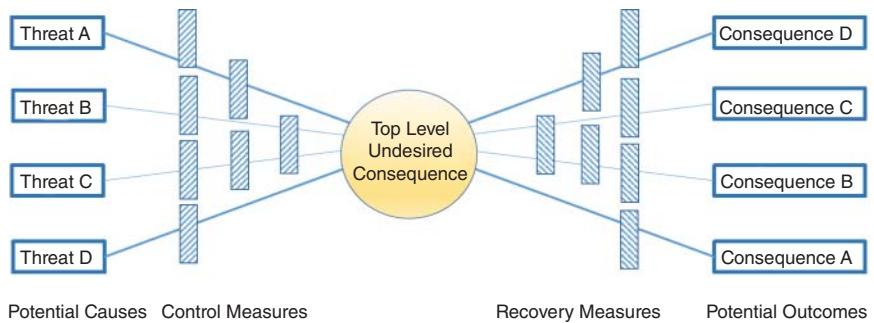
Assuming that we have an oil discharge event, we can employ the fault tree in Figure 6.4 in reverse to find probable causes for a spill event. We could also assign the event probabilities with some other basis, or use the information we have to calculate the probable reason for the event. The rules for OR and AND gates is that the probabilities must equal 100% for entry into each gate. The probabilities can be expressed as decimals. The distribution of the probabilities for the initiating events is shown in Table 6.1. The probabilities are summed for the initiating and intermediate events, and then presented as percentages or likelihoods. If an oil discharge is reported, the table can be used to help assess that the likelihood of the initiating event (i.e., the oil release) is a 72% probable cause, whereas control element failure would have a lesser probability. Going one step further, the likely culprits for the oil release would be tank overfilling, and shutoff valve failure.

### 6.2.1 Bow Tie Analysis

Another type of analysis useful in preventing unplanned discharges is “bow tie analysis.” This includes both the potential events and the possible prevention and recovery techniques, and prevention materials are shown graphically. The

**Table 6.1** Calculation of initiating and intermediate event probabilities for oil discharge release.

Event	Frequency (months)	Percentage	Probability
Tank overfill	1/12	0.0835	44.46%
Shutoff valve failure	1/12	0.0835	44.46%
Pump leak or failure	1/48	0.0208	11.08%
Sensor failure	1/24	0.0418	53.62%
Oil–water separator failure	1/120	0.00835	10.71%
High flows	1/36	0.0278	35.67%
Oil release		0.2086	72.80%
Control element failure		0.07795	27.20%



**Figure 6.5** Bow tie analysis example.

technique considers both threats and potential consequences from the events, as well as mitigation measures. Bow tie analysis is useful in forcing consideration of consequences and control measures. Figure 6.5 shows an example of a type of bow tie analysis.

Using our oil spill example from above, the following could be applicable:

*Top level undesired consequence:* Economic penalties, fines, and large costs for cleanup

- Threat A: Oil tank overflowing
- Threat B: Valve failure
- Threat C: Failure of oil–water separator
- Threat D: Control and alarm failures

**Control measures: First level** (1) Diking of tanks, (2) system design for prevention, (3) greater maintenance frequency on sensors, and (4) standby power for sensors.

**Control measures: Second level** (1) Spill control kits placed near potential sewer entrances, (2) Raising piping above ground to permit greater visual inspection, (3) Encasing delivery pipes within larger pipes for leak prevention, (4) Install automatic shutoff alarms around pumps to control leaks, (5) backup alarm systems,

**Control measures: Third level** (1) Increased video surveillance, (2) increased operator/guard surveillance, (3) increased frequency of preventive maintenance.

#### *Potential outcomes*

- Outcome A: Fish kill
- Outcome B: Expensive cleanup for floating oils, marine operations for recovery
- Outcome C: Increased regulatory scrutiny and fines
- Outcome D: Fire, other types of contamination

#### *Recovery/mitigation measures*

Booming, absorbent pads/spill kits, marine operations if spill reaches waterways<sup>3</sup>

- Operator retraining/accountability implementation
- Increased monitoring
- Drain covers/sealing drains/pigs or plugs to block off sewers
- Covering process areas to keep out rainfall
- Analysis with software such as ALOHA, or other programs
- Minimizing oil storage

These mitigation measures and outcomes are predicated on the idea that the spill will be large enough to warrant extra attention and specific recovery actions. Smaller spills might use only a few recovery/mitigation measures, and the potential outcomes could be much smaller and essentially insignificant.

### 6.3 Analysis: The Five Whys

One analytical technique that is sometimes overlooked is “The Five Whys.” Whenever there is an incident, a panel is formed to probe the incident, understand what caused it, and how to prevent a recurrence. One of the techniques for that investigation is the Five Whys of investigation. The technique is flexible, but starts with a top-level series of questions right after the description of the incident. For example:

**What:** We had an oil spill from the compressor building that reached the river and forced us to clean up the spill at a cost of \$20,000. (Continue with complete description of event and consequences and activities.)

**First Why:** Why did the spill occur?

**First Answer:** The pump was removed and the valve was opened.

**Second Why:** Where and why was the pump removed without locking out the shutoff valve?

...

**Fourth Why:** Are there other factors that we may have missed which could contribute to the cause of the incident or which could have hindered or increased the cost of remediation of the spill?

**Final Why:** Why and how can we improve the process by implementing better maintenance training and closer coordination between the Control Room and Operations?

**Final Answer:** We can, and here is a list of changes that we must make to prevent a recurrence.

## 6.4 Regulatory Requirements

Current regulations in the US mandate that any facility with over 2500 liters (660 gallons) of "oil"<sup>4</sup> storage above ground must have a spill prevention, control, and countermeasure plan, and calculations available showing the capacity of tank diking which exceeds the capacity of the largest single storage tank in a tank farm, plus an allowance for rainfall, or an aggregate of at least 25% of the total volume of all liquids in the tank farm storage area.<sup>5</sup> Software programs like ALOHA, CARVER+SHOCK, the CAMEO Suite,<sup>6</sup> and others can, if properly used, provide an estimate of worst-case scenarios and help in planning to prevent incidents. Some of the programs available will also address the volatilization of chemicals and allow one to estimate the potential impact on a nearby community and the impacts of hazardous chemical releases.

## 6.5 Software Solutions

Software and mapping programs such as Surfer<sup>®</sup> and gnuplot<sup>®7</sup> can assist the environmental professional to determine the likelihood of successful implementation of safety practices and contingency planning by defining graphical contours and visual displays. Detailed drainage maps of the area, plant sewer system mapping, with pipe sizes and slopes, and mapping of effective drainage areas of each individual sewer inlet can all provide good

solutions to help analyze spill pathways and suggest optimum locations for spill prevention measures.

## 6.6 Emergency Response Planning

One of the very important publications in any plant or commercial building is the Emergency Directory and Disaster Plan. The Emergency Directory should be updated several times per year, and should contain the names and contact information for all appropriate plant officials, instructions on who to call, in what order, what outside calls should be made, and the names of the senior plant officials who are authorized to make those contacts for outside assistance. The Emergency Directory should also list the availability of internal and external resources, and should include a map of such items as spill control supplies, first aid kits, fire-fighting supplies, and a detailed map and list of the plant sewer system inlets and hydrants. Other important items to be included are: reportable quantities for spills, contacts for hospitals and fire departments, and mapping of routes for ambulance and emergency medical services in case employee hospitalization is required. For situations where volatile chemicals are handled in the plant, it is also strongly suggested that the Emergency Plan be integrated with community mapping programs, so that in the event of a major spill or catastrophe the risk to the nearby community can be evaluated and appropriate actions taken in accord with the Local Emergency Planning Committee, police or fire departments, as the case may warrant. (*In a number of facilities, the Emergency or Disaster Plan is contained in a very few pages in the front of the plan, and those pages are highlighted with a red border or are on colored paper for easy identification. In that manner, the plant manager or person in charge can refer to those pages and not have to wade through a much thicker document to find needed information.*)

## Notes

- 1 A couple of examples may help illustrate the point.
  - (i) A chemical plant manufacturing biphenyls had a spill to the public sewer system. Biphenyls are very slowly biodegradable by most wastewater treatment facilities, with a very long residence time in the activated sludge basin. Biphenyls will pass through the treatment plant largely untreated, and be chlorinated in the chlorine contact tank, forming polychlorinated biphenyls or PCBs. The chlorination chemistry was not well understood at the time of the event, and if PCBs were formed, they could be biologically accumulative and enter humans using the river as a water supply.
  - (ii) Similar emergency response for spill situations occurred in Romania,

in 2000, and in the Colorado River in 2015. Gold mining often uses cyanides to enhance the extraction of gold from low quality ores. On January 30, 2000, a dike failed, releasing approximately 100 000 cubic meters of a cyanide-containing leaching water into the Tisza River. The Tisza flows into the Danube, and many communities receive drinking water from both rivers. The fish kill was very large, and many municipalities had to suspend their withdrawal of drinking water from the rivers until the toxic cyanide plug flow passed.

(iii) A remediation contractor working for the USEPA removed a plug from the Gold King Mine and released approximately 11 400 cubic meters (three million US gallons) of mine water and tailings, which included heavy metals such as cadmium, lead, arsenic, beryllium, and copper. The release was into the Animas River, near Silverton, Colorado, in 2015. The resulting controversy included charges that the USEPA did not provide timely notification to downstream communities who took water from the river, nor did the Gold King Mine warn the remediation contractor of the impending danger of a spill, despite the fact that they knew of the potential for such a spill.

- 2 Obviously these numbers are made-up frequencies for the proposed events, and should not be used for more than an illustration of how the fault tree analytical program works. This is particularly true with regard to the rainfall element.
- 3 See John Wiley's *Water Encyclopedia* for a discussion on the practices and limitations of oil spill booming and recovery operations.
- 4 An "oil" is generally undefined, in a regulatory sense, except by visual observation of the sheen that it makes on a waterway if present in quantities greater than  $15 \text{ mg l}^{-1}$ . However, it has been successfully argued that the difference between an "oil" and a chemical that floats on water is the fact that no one can write a chemical formula for an oil, but one can write a chemical formula for a compound.
- 5 The authority for the planning and control of spills can be found in Section 311 of the Federal Water Pollution Control Act (Chapter 40 of the Code of Federal Regulations, Part 112). The requirement for a Spill Prevention Control and Countermeasure Plan also applies to petroleum refueling stations, but since most of them have fuels storage in underground storage tanks, the SPCC requirements do not apply unless the facility has more than 159 000 liters (42 000 gallons) in storage. Most US petroleum stations are exempt from this requirement because they limit their quantities.
- 6 CARVER+SHOCK is a vulnerability assessment tool that is primarily used in the food industry to determine the likelihood of contamination. It is freely available on the Internet, and, with some ingenuity, can be useful in just about any non-food industry company to look at vulnerability of manufacturing operations. CAMEO Suite is a program suite prepared by the USEPA (Computer Aided Management of Emergency Operations), and freely available to all. The ALOHA program is part of the CAMEO software suite, and can be

- used to determine potential hazards from chemical releases and emergencies. ALOHA can model toxic gas clouds, flammable gas clouds, BLEVEs (boiling liquid expanding vapor explosions), jet fires, pool fires, and vapor cloud explosions. ALOHA also grids the threat zone estimates which can be plotted on maps using an accompanying program, MARPLOT, which is also part of the CAMEO Suite.
- 7 SURFER is a product of Golden Software, Inc., Colorado, USA, and is a commercial software with a temporary free license. Gnuplot is available from SourceForge.net and is free. Both can be used to produce contour elevations from point data.

## 7

# Chemistry and Analyses

Chemistry is an exacting and careful science. The field has produced many advances in pushing back detection limits, with the consequence that compounds that were undetected just a few years ago can now be measured with high accuracy and precision. As a consequence, the environmental data that were produced prior to 1975 are of less value because the information does not include trace compounds, which may also contribute to water quality degradation.

An environmental engineer or scientist cannot operate without access to a good quality laboratory. This is not a treatise on analytical chemistry, but an attempt to provide some of the basics of a very complicated subject, highlight the purpose of the tests, and provide some background on the significance of the compounds.

In recent years, much of the emphasis on what is important in effluents from treatment plants has shifted to a focus on trace compounds including cosmetics and medicines, often identified as “emerging contaminants of concern.” While these compounds are principally found in municipal discharges, they do occasionally wind up in industrial effluents, and trace quantities of industrial chemicals and metals are now being found therein. In municipal discharges, the alleged source is the personal care products and medicines that are flushed down the toilet. Many of these compounds have the ability to affect aquatic organisms, but they are present at levels too low to regulate, and occasionally at levels too low to detect without a very sensitive mass-chromatograph/mass spectrograph, which is expensive and requires a trained chemist to operate and maintain.

## 7.1 Aquatic Testing

The regulatory answer for detection of some of these very low-level aquatic compounds is to require the discharger to perform additional testing using an in-situ test with aquatic species.<sup>1</sup> These tests are designed to measure the

survivability of the aquatic organisms when exposed to toxic chemicals that may be harmful, but at levels too low for detection, or which are not specifically regulated in the discharge permit. The USEPA has developed several versions of aquatic testing protocols in their acute testing manual; each of the protocols have minor differences which may significantly influence the outcome of the test. The most recent 5th edition (EPA-821-R-02-012) calls for using fish of 1–14 days in age, and it requires a minimum renewal level of the effluent being tested at 48 hours. These requirements are new, and tend to make this test more sensitive than previous editions.

The basic acute test uses a series of five test chambers, each containing a specific concentration of the effluent diluted with standard laboratory water plus a control. A common dilution series such as 100%, 50%, 25%, 12.5%, and 6.25% is often used. The dilution ratios are sometimes specified in the NPDES (National Pollution Discharge Elimination System) permit. Since each discharge is different, the dilution ratios may reflect the differences.

To conduct the test, 10 test fish are placed into each chamber, and their survival and water quality of the test chambers are monitored for 96 hours. All tests are conducted in replicate (two, four, or five replicates, depending upon species). The number of fish surviving at each test concentration at the end of the test is compared with the number surviving in the control chamber, and the differences are used to calculate the sample concentration toxic to 50% of the test fish. The concentration of the effluent at which half of the fish survive is the “lethal concentration 50%” or LC50. If 50% of the fish survive in a 25% concentration of effluent, the toxicity concentration of the effluent is 100%/25% or four toxic units. The test results are then reported as percent survival in 100% effluent.

The most common organisms used in these biological tests are either *Daphnia magna* or fathead minnows, but other species can be used as well, even rainbow trout, according to the test protocols cited at in the references at the end of this chapter. There are over 45 different species listed in the EPA manual, ranging from water fleas to rainbow trout, but fathead minnows are by far the most commonly used organism. The tests are generally run by specialty laboratories and services, and can add several thousand dollars to the cost of obtaining the permit, and a month or two in the submission of permit data.

## 7.2 Bacterial Testing

Bacterial testing on an effluent stream is generally performed only with respect to the efficiency of the disinfection function at the treatment plant. Because there is a water quality standard for various classifications of streams and water-bodies, the goal is to limit the overall numbers of coliform organisms (the principal indicator of fecal contamination), as a limit to water quality.

A moment's reflection will allow one to recall that beaches and various waterbodies have been closed when the bacterial count is too high.<sup>2</sup> The coliform test is non-discriminating, and does not compare coliform derived from animal sources versus human sources. The human source coliform is of greater concern because it is often associated with human diseases.

A few years ago, the Millipore Company was promulgating a system that tested for both fecal coliform and fecal streptococcus bacteria. Their argument was that the number of fecal coliform should not be the only indicator, as coliform was generated in the feces of all warm-blooded animals, and the likelihood of disease transmission between animals and humans was believed to be minimal. The fecal strep incubation in wastewater was, and still is, viewed as a direct indicator of the presence of human contamination in wastewater.<sup>3</sup> The Millipore Company indicated that the ratio between fecal coliform and fecal strep could serve as an indicator of animal versus human contamination.

Other water quality indicators also provide indications of human wastes in the environment, including some of the phosphorus and nitrogen compounds.

### 7.3 Dissolved Organic Materials – BOD, COD, and TOC

By far the most common test used, and perhaps one of the most useless tests used in analyses of wastewater, is the 5-day biochemical oxygen demand ( $BOD_5$ ) test.<sup>4</sup> It is useless as a control parameter, and provides information “after the horse has left the barn.” From an operational standpoint, the  $BOD_5$  test is very easy to spoof, and is unreliable below a value of  $20\text{ mg l}^{-1}$ . That does not stop some regulatory agencies from specifying the  $BOD_5$  value in their permits. The  $BOD_5$  test has a number of problems. A few of these are mentioned below.

Sloppy technique is one of the worst and greatest adverse influences on the BOD, especially on high  $BOD_5$  wastes. A careful reading of the  $BOD_5$  test protocol indicates that a known quantity of waste is to be added to a  $BOD_5$  bottle before the bottle is incubated. The resulting oxygen depletion in the BOD bottle is divided by the dilution ratio, and even a small difference in the measured value of dissolved oxygen (DO) difference between the initial and final value is magnified by the dilution ratio – especially with strong wastes, which require large dilution factors.

The  $BOD_5$  test is to be run in an environment where the carbonaceous demand is consumed by “acclimated” bacteria. The acclimated bacteria are supposed to have the enzymes required to digest the waste material. If the necessary nutrients and bacterial enzymes are not present, the  $BOD_5$  test will measure erroneously low. Similarly, there are a large number of compounds which can invalidate the  $BOD_5$  test, including mercury compounds, chromic acid ( $\text{Cr}^{6+}$ ) compounds, copper compounds, a number of miscellaneous

heavy metals and a number of pharmaceutical wastes including acetonitrile, acrylonitrile, and adiponitrile.<sup>5</sup>

The  $\text{BOD}_5$  test is based upon the Winkler dissolved oxygen test. In it the concentration of oxygen is measured by titration of a manganous sulfate and alkaline sodium azide solution with dilute sulfuric acid in the presence of starch, which is added near the end-point of the titration. A small error in formulation of the reagents, or the reading of the color change at the end of the titration, can contribute to the error in measurements.

Advances in membrane and electrode technology have simplified the test procedures, and a membrane measurement of dissolved oxygen, with proper calibration, is considered accurate. The wet chemistry method is still accepted for calibration.

In some instances, there has been a tendency to insert the DO probe in the BOD bottle "just to see how things are doing." The DO probe consumes oxygen, and even a brief measurement will change the ultimate results.

The accuracy and precision of the  $\text{BOD}_5$  test decrease at low BOD levels. *Standard Methods* indicates that the test is also highly variable. In developing the test protocol, the test committee ran standardization tests for 14 months, and 421 triplicate analyses on a known standard solution of glucose–glutamic acid; the  $\text{BOD}_5$  of this solution is  $198 \text{ mg l}^{-1}$ . Inter-laboratory measurements reported that the mean of the standard solutions analyses was  $204 \text{ mg l}^{-1}$  with a standard deviation of  $10.4 \text{ mg l}^{-1}$ .<sup>6</sup> The control limits for the standard sample are  $\pm 30.5 \text{ mg l}^{-1}$  (plus or minus approximately 3 standard deviations).

Despite some regulatory practice that issues permits with very low  $\text{BOD}_5$  numbers, the statistical reliability of values below  $20 \text{ mg l}^{-1}$  does not exist.<sup>7</sup> However, this has not stopped the regulatory community from regularly issuing permits with  $\text{BOD}_5$  values less than  $3 \text{ mg l}^{-1}$ .<sup>8</sup>

The BOD test is occasionally run for 20 days to measure ultimate carbon demand. The results of the longer time are even more subject to potential interferences due to nitrogenous demand than the 5-day test. Both are very easy to spoof.

The test version most often used for regulatory purposes requires that an aliquot of waste be placed in a BOD bottle and sealed to prevent air intrusion. The measured oxygen depletion of the oxygen in the bottle after 5 days of incubation in a dark place at  $20^\circ\text{C}$  determines the  $\text{BOD}_5$  of a waste. The immediate oxygen uptake of the waste can also be measured by a Warburg respirometer. In it, a sample of the liquid is placed in a submerged and sealed glass flask that contains a center well for potassium hydroxide. The flask is connected to a manometer. The flask is stirred so that the oxygen above the liquid level will be transferred into the waste. As the oxygen in the flask is consumed, the partial pressure of the air in the flask is lowered, and the difference between that and the atmospheric pressure is measured on a manometer. A drawing of the adaptation of the Warburg respirometer is shown in Figure 7.1.

Aug. 5, 1969 MASATOSHI YAMAGUCHI ET AL 3,459,032  
MANOMETER CALIBRATING DEVICE AND METHODS

Filed July 6, 1967

2 Sheets-Sheet 1

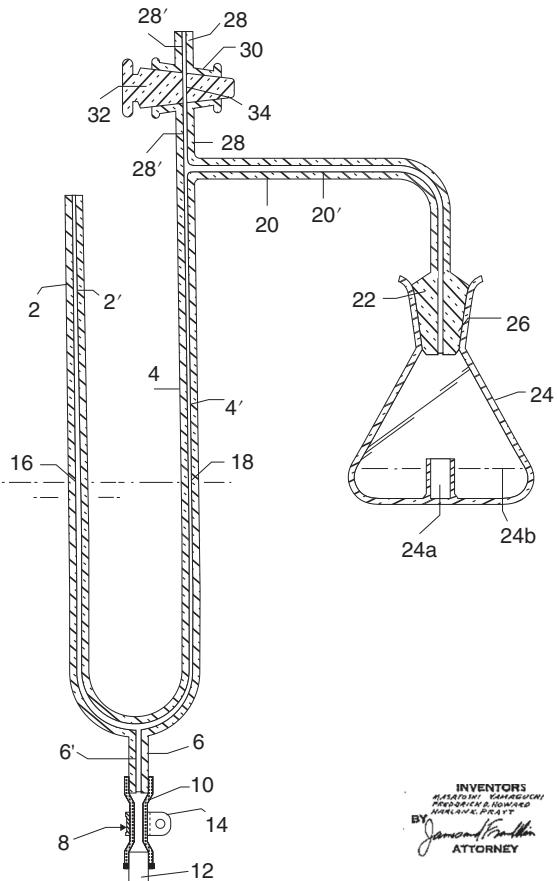


Figure 7.1 Warburg respirometer – drawing from US Patent Office.

The Hach Company has developed a manometric test for the BOD that is, in many instances, similar to the Warburg respirometer. The Hach test uses amber glass bottles with plastic screw cap lids and magnetic stirrers in the bottles. The BOD bottles and magnetic stirrers are placed in a refrigerator. The baseplate containing the stirrer also contains a fan and small heater to help maintain the temperature in the refrigerator.

The plastic bottle cap is connected to a piece of tubing, and a manometer that measures the change in atmospheric pressure. Inside the bottle is a stainless steel rod that has a cup containing potassium hydroxide. The manometer

**Figure 7.2** BOD bottle.

is calibrated in units equivalent to BOD<sub>5</sub>. The practical advantage of the Hach system is that the manometer can provide a fairly rapid indication of any potential toxicity or shock-load problems, sometimes in time to allow the operator of the wastewater treatment plant to make adjustments to the system. The manometric BOD can also be used to estimate uptake coefficients and rate constants for wastewater.

The BOD test is sensitive to time, temperature, nutrient, and acclimatization. It comprises several portions. The BOD bottle itself is a narrow-mouthed, 300 ml glass bottle with a ground glass stopper or plug and a lip at the top for a water seal (see Figure 7.2). Before the bottle is put into the incubator, water is added to the funnel neck around the seal to insure that there is an air-free seal. The top of the bottle is often further covered with foil or plastic wrap to prevent evaporation from the water seal.

Common practice is to put the BOD bottles in an incubator which will hold them at  $20 \pm 0.5^{\circ}\text{C}$ .<sup>9</sup> The trend is to have a specialized incubator for the BOD test.

Earlier we mentioned some of the problems with the BOD test. Here are some common ways of spoofing the test to give “low” results. The first of these is to select unacclimated seed materials. In order for the BOD test to be representative, the bacteria must be able to digest and hydrolyze the waste materials in the bottle. For that purpose the bacteria in the bottle must have the necessary enzymes to help them digest the material. If the enzymes are missing, it

may take several days or weeks for their development – resulting in a low BOD reading.

The bacteria in the BOD bottle also need nutrients and a buffer solution, and something to suppress the development of nitrification of the wastes. If the sample is missing any of those components, in their right proportions, the reading will be in error. Similarly, failure of the water seal will allow air to enter the bottle and the readings will be low.

If the Winkler test is to be run to determine the DO level in the bottle, a volume-specific aliquot must be taken from the bottle – approximately 200 ml – and carefully measured. This process can introduce an additional error into the measurement of the BOD.

The reagents and the calculations need to be similarly carefully measured and formulated. Errors in any of those values will cause an entire series of BOD measurements to be biased.

The three other ways of spoofing a BOD sample are: (i) by incorrectly measuring the dilution ratio – this is particularly true of strong wastes at dilutions of 20 : 1 or more; (ii) by incorrectly measuring the DO reduction in the bottle or measuring it without sufficient depletion or too much depletion – both can affect the BOD calculation (the BOD residual in the bottle has to be above a certain value, and the oxygen depletion also needs to be above a specific value for the BOD test to be valid); (iii) by allowing a bacterial toxin into the waste. Formaldehyde, phenols and other compounds mentioned above can be toxic, and reduce bacterial activity in the BOD bottle, thus generating a low number for BOD.

Similarly, if the incubation temperature is not within specified ranges, the test is useless and needs to be re-run, unless it is run specifically to determine oxygen demand at a specific temperature – but if that is the case, the results are not equivalent to the standard BOD<sub>5</sub> test.

### 7.3.1 BOD vs ThOD

The theoretical oxygen demand (ThOD) is the calculated oxygen demand of all organic compounds in a waste. For most purposes, look at the compound and resolve it into its most elemental oxidized state (see Table 7.1).

If there is no nitrification of the waste, the carbonaceous BOD is approximately calculated by the following formula:

$$\text{ThCOD} = \frac{16[2c + 0.5(h - cl - 3n) + 3s + 2.5p + 0.5na - o]}{\text{mol.wt}} \text{ mg O}_2/\text{mg}$$

for a compound with the general composition C<sub>c</sub>H<sub>h</sub>Cl<sub>cl</sub>N<sub>n</sub>Na<sub>na</sub>O<sub>o</sub>P<sub>p</sub>S<sub>s</sub> (where some of the compounds can be omitted if they are not present).<sup>10</sup>

There are three parts to the BOD demand. The first is the initial demand, which occurs when the waste is added to the dilution water. This demand is

**Table 7.1** Theoretical oxidation products of common organic compounds.

Element	End oxidation product
Hydrogen	H <sub>2</sub> O
Nitrogen	NO <sub>3</sub> , N <sub>2</sub> O <sub>3</sub>
Carbon	CO <sub>2</sub>
Sodium	Na <sub>2</sub> O
Sulfur	SO <sub>3</sub>
Phosphorus	P <sub>2</sub> O <sub>5</sub>

almost immediate. The second demand is from the carbonaceous demand, when the acclimated bacteria have time to digest the carbon in the sample, and estimated by the following formula.

$$\text{BOD}_{(t)} = \text{BOD}_{(i)}(1 - e^{-kt})$$

where  $t$  is the time in days,  $i$  is the initial BOD, and  $k$  is a rate constant that can vary from 0.2 to about 0.6 but which is usually 0.2.

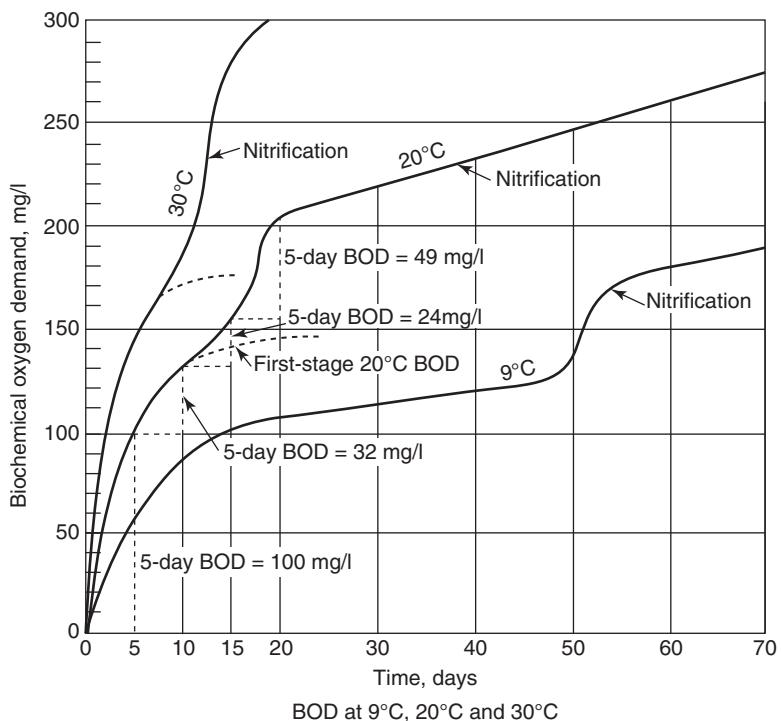
An additional factor that needs to be mentioned is the criticality of the BOD test to be influenced by variations in temperature. In general, the temperature affects the kinetic rate of degradation. Since the standard rate is measured at 20°C, the formula for conversion of the rate constant is:  $k/k_o = e^{Ct(T - T_o)}$ .  $Ct$  is the adjustment coefficient,  $T$  and  $T_o$  are temperatures, and  $k$  and  $k_o$  are the rate constants at the temperatures.

The rate of biochemical reaction doubles for each 10°C rise in temperature up to about 30–40°C, at which point the bacteria are thermally inactivated, and most bacterial activity stops (see Table 2.18). This is also demonstrated in Figure 7.3. Note the apparent steepness of the rate of oxygen demand with respect to time as the temperature increases.

The third part to the BOD is the nitrogenous demand. This demand often represents the oxidation of ammonia and some proteins. It occurs late in the incubation of the BOD test, when the oxygen content starts dropping. The correction for nitrogen demand is the addition of ammonium chloride to the dilution water.

If nitrification demand is considered in the computation of theoretical BOD, the formula given above is slightly modified:

$$\text{ThBOD} = \frac{16[2c + 0.5(h - cl) + 2.5n + 3s + 2.5p + 0.5na - o]}{\text{mol wt.}}$$



**Figure 7.3** Variation of BOD and rate constant with temperature.

We will revisit the ThBOD later when we consider computer modeling of wastewater treatment plants.

Additionally, the variables and influences on the BOD test are not consistent, nor are they properly logged – the test uses most of the sample and one cannot re-run the test on the same waste unless there is a sufficiently large quantity available. The fundamental problem with the BOD test is its inherent inaccuracy and lack of precision, and ability to be influenced by unknown variables, especially at low values.

### 7.3.2 Chemical Oxygen Demand

The chemical oxygen demand (COD) test oxidizes the organic material in wastewater in an acidic solution with either a permanganate oxidizer or a hexavalent chromium oxidizer. The dichromate oxidation is the currently accepted standard, and one must be careful in interpreting COD measurements if the oxidizing agent is not known. Dichromate COD measures about 90% of the ThOD, and permanganate COD oxidizes around 77% of the ThOD, but either represents a more complete oxidation than BOD, and typically the

**Table 7.2** Relationship between  $\text{BOD}_5$ , COD, and TOD for certain compounds.

Compound	TOD	COD	$\text{BOD}_5$	TOC (mg O <sub>2</sub> ·mg <sup>-1</sup> )
<i>Acids</i>				
Formic acid	0.35	0.35	0.25	0.26
Acetic acid	1.06	1.00	0.80	0.40
Benzene-sulfonic acid	1.62	1.50	0–0.5	0.45
<i>Aldehydes</i>				
Formaldehyde	1.07	1.06	0.6–0.8	0.40
Acetaldehyde	1.82	1.80	1.30	0.54
Benzaldehyde	2.42	1.90	1.50	0.79
Furfural	1.66	1.60	0.3–0.8	0.62
<i>Alcohols</i>				
TBA	2.59	2.20	—	0.64
Isopropanol	2.40	2.20	1.20	0.60
Methanol	1.50	1.40	0.90	0.37
Ethyleneglycol	1.30	1.29	0.80	0.39
<i>Amines</i>				
MEA (monoethanolamine)	2.49	1.3–2.0	0.8–1.0	0.39
DEA (diethanolamine)	2.13	1.60	0.2–0.4	0.46
<i>Phenols</i>				
Phenol	2.40	2.30	1.80	0.76
Cresols	2.52	2.40	1.6–1.8	0.78
<i>Miscellaneous</i>				
MEK	2.44	2.30	1.5–1.8	0.66
Acrylonitrile	3.17	1.40	0.70	0.68
Caprolactame	2.10	0.60	0.40	0.64
Ethylene oxide	1.82	1.74	0.10	0.54
Propylene oxide	2.21	1.80	0.20	0.62
Isopropylether	2.80	1.5–1.7	0.20	0.70
MTBE	2.72	2.50	—	0.68

TOD, COD, and  $\text{BOD}_5$  equivalences of oxygenated compounds (mg O<sub>2</sub> per mg of compound).

Source: Francois Berne and Jean Cordonnier, *Industrial Water Treatment. Refining, Petrochemicals, and Gas Processing Techniques*. Houston: Gulf Publishing Company, 1995.

current value for BOD is that it represents about 66% of the value obtained by dichromate COD. COD is best used in analysis of waters with a chloride content less than  $1000 \text{ mg l}^{-1}$ , and COD values usually between 30 and  $700 \text{ mg l}^{-1}$ , but Hach Chemical company has a series of COD tests that will take one from 0.7 to  $15\,000 \text{ mg l}^{-1}$  COD.<sup>11</sup> The chromium-based COD test will oxidize 90% or more of most organic compounds – but where there are industrial wastes, there are compounds that are “refractory” (compounds not readily oxidized by the COD test with either reagent). These difficult-to-oxidize compounds include some alcohols and carboxyl acids, as well as other substances.<sup>12</sup>

Generally, it is possible to write an equation listing the chemical formula of a compound and predict the COD based upon the stoichiometric formula of the compound. While this approach is interesting in a research laboratory, in wastewaters one has no idea of the amount or type of compounds, let alone their chemical formulae.

In the dichromate COD, the reaction byproducts include  $\text{Cr}^{3+}$ , and the chromate is determined by colorimetry or by titration. The titration with starch is also colorimetric and turns dark blue–black when complete.

### 7.3.3 TOC

Total organic carbon (TOC) is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide ( $\text{CO}_2$ ) by either catalytic combustion or wet chemical oxidation. The  $\text{CO}_2$  formed is then either measured directly by an infrared detector or converted to methane ( $\text{CH}_4$ ) and measured by a flame ionization detector. The amount of  $\text{CO}_2$  or  $\text{CH}_4$  in a sample is directly proportional to the concentration of carbonaceous material in the sample. The test measures total carbon, including bicarbonates and carbonates. In order to get an accurate value, the carbonate and bicarbonate must be measured independently and subtracted from the final result.

BOD, COD, and TOC are not always infallible nor stoichiometric. Tables 7.2 and 7.3<sup>13</sup> show the BOD, COD, and TOC ratios for several selected compounds. Note the variability in the results.

## 7.4 Common Ion Species

The ion species discussed here are some of the most important inorganic compounds found in the aquatic environment. They are found abundantly in the Earth's crust. The relative importance of the ion species and the reaction constant or stability constant is important because of the large number of reactions in which these chemicals participate. Carbonate chemistry and the reactions with calcium enter into most aquatic reactions, including saltwater reactions.

**Table 7.3** BOD, COD, and TOC for selected compounds and aromatic chemicals.

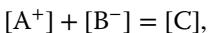
	Jet A tank	Gasoline tank	Diesel tank	Crude tank	Lub refinery	Sanitary WW	Refinery blend	MBR feed
BOD	1510	3450	1199	116	692	72	554	489
COD	6190	5230	3380	794	962	176	1100	878
TOC	1340	1010	792	34.8	190	30.2	227	199
COD/BOD <sub>5</sub>	4.1	1.5	2.8	6.8	1.4	2.4	2.0	1.8
COD/TOC	4.6	5.2	4.3	22.8	5.1	5.8	4.8	4.4
TOC/BOD <sub>5</sub>	0.89	0.29	0.66	0.30	0.27	0.42	0.41	0.41
TKN	97.1	45.6	105	38.6	14.8	46.8	20.6	20
NH <sub>3</sub> -N	60.8	26.7	40.8	36.9	0.39	45.6	4.13	6.38
NH <sub>3</sub> -N/TKN	0.63	0.59	0.39	0.96	0.03	0.97	0.20	0.32

Source: *Comparative Evaluation of MBR/RO and PAC Enhanced MBR/RO Treatment of Refinery Oily Wastewater*, William Conner, John Liu, John Yee. Saudi Armaco, Box 10260, Dhahra, 31311 Saudi Arabia. MBR, membrane bio-reactor; TKN, total Kielldahl nitrogen.

**Table 7.4** Disassociation constants for common chemicals in water.

Reaction	Equilibrium constant	Log K
H <sub>2</sub> O = H <sup>+</sup> + OH <sup>-</sup>	$K_w$	-14.0
H <sub>2</sub> CO <sub>3</sub> = H <sup>+</sup> + HCO <sub>3</sub> <sup>2-</sup>	$K_1$	-6.2
[HCO <sub>3</sub> <sup>-</sup> ] = H <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	$K_2$	-10.2
H <sub>3</sub> PO <sub>4</sub> = H <sup>+</sup> + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$K_1$	-2.2
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> = H <sup>+</sup> + HPO <sub>4</sub> <sup>2-</sup>	$K_2$	-7.2
HPO <sub>4</sub> <sup>2-</sup> = H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup>	$K_3$	-12.2
NH <sub>4</sub> OH <sup>-</sup> + H <sup>+</sup> = NH <sub>4</sub> <sup>+</sup> + H <sub>2</sub> O	$K$	9.2
Al <sup>3+</sup> + OH <sup>-</sup> = Al(OH) <sup>2+</sup>	$K_{(AlOH^{2+})}$	9.0
Al <sup>3+</sup> + 4(OH <sup>-</sup> ) = Al(OH) <sub>4</sub> <sup>-</sup>	$K_{(Al(OH)_4^-)}$	32.5
Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup> = CaCO <sub>3</sub>	$K_{(CaCO_3)}$	3.2
Ca <sup>2+</sup> + HPO <sub>4</sub> <sup>2-</sup> = CaHPO <sub>4</sub>	$K_{(CaHPO_4)}$	2.7
Ca <sup>2+</sup> + PO <sub>4</sub> <sup>3-</sup> = CaPO <sub>4</sub> <sup>-</sup>	$K_{(CaPO_4^-)}$	6.5
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH = 5Ca <sup>2+</sup> + 3PO <sub>4</sub> <sup>3-</sup> + OH <sup>-</sup>		-49
CaCO <sub>3</sub> = Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>		-8
Al(OH) <sub>3</sub> = Al <sup>3+</sup> + 3OH <sup>-</sup>		-30.4
Al <sub>1.4</sub> PO(OH) <sub>1.2</sub> = 1.4Al <sup>3+</sup> + PO <sub>4</sub> <sup>3-</sup> + 1.2OH <sup>-</sup>		-32.2

The reaction constants are also referred to as disassociation constants (see Table 7.4). They have the form of



where the disassociation constant is expressed as  $K_c = \frac{[A^+][B^-]}{[C]}$  and the concentrations of the compounds are expressed in moles.

### 7.4.1 Most Important Chemicals in the Water Environment

Most of the important aquatic inorganic chemistry involves a relatively limited set of cations – aluminum, calcium, iron, magnesium, manganese, phosphorus, and sodium – and a similar set of anions – chlorine, nitrogen, oxygen, and sulfur – for the simple reason that these are the abundant elements.

This does not preclude any of the many other reactions listed in the following sections, nor the importance of being able to control and manipulate the ions and ion species in the aquatic environment. Carbon chemistry was not included in this list because it is the foundation of organic chemistry, and there are libraries filled with organic chemistry reactions and interactions; this book could not begin to discuss adequately.

Recent analytical advances have discovered the presence of personal care products and medicines in the environment. This is often caused by careless or negligent disposal of various household products into municipal sewers. The conventional wastewater treatment plant was never designed to remove these compounds, and they pass through it untreated. The environmental impact of trace quantities is affecting the development of frogs and other aquatic species, reportedly to the detriment of those species. The concern is that the modification of those species is a warning to humans and all other higher species – that we are poisoning ourselves at the genetic level, and that these compounds are creating subtle changes in the development of human embryos.

### 7.4.2 pH

Normally written as pH, this is the negative logarithm of the hydrogen ion concentration in water. The pOH is the negative logarithm of the concentration of hydroxyl ions in aqueous solution. Water dissociates into  $\text{OH}^-$  and  $\text{H}^+$  ions, which exist in equilibrium. The disassociation constant of water is generally written without the denominator, or  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ . In most instances, the pH will be on a log scale between 1 and 14, where a solution with pH 1 contains 0.1 M of hydrochloric acid and a solution with pH 14 contains 0.1 M sodium hydroxide. With stronger solutions of acids and bases it is possible to have numbers of acidity or alkalinity above 14 or below 1, but at those levels, the solutions are generally referred to as a molar solution of the acid or base, and the pH is not calculated.

### 7.4.3 Carbonate Chemistry

The chemistry of the carbonates and bicarbonates is important in water treatment, both because it plays a role in the biological treatment and because a knowledge of it is also useful in dealing with various types of precipitation for industrial wastes and scale prevention for boiler waters. Some of the following concepts pre-date molar chemical theory, and to the modern student of chemistry, the calculation of equivalents of calcium carbonate and balancing equations using carbonate equivalents is archaic in view of the modern molar theories of chemical interactions. However, the system is still widely used, especially in boiler water treatment and water softening, and shows no signs of going away.

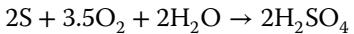
The most common measures of carbonate chemistry are the acidity and alkalinity tests. Acidity is measured by the titration of water to the phenolphthalein endpoint. It is complete at about pH 8.5. All waters with a pH of less than 8.5 are assumed to have some acidity. Acidity due to CO<sub>2</sub> takes place between pH 4.5 and pH 8.5, and the phenolphthalein endpoint is between pH 8.2 and pH 8.4. Below pH 4.5 the acidity is considered as mineral acidity. The titration is performed with 0.02 N NaOH (N/50 NaOH).

Sources of acidity include the dissolution of carbon dioxide to create carbonic acid and the presence of other minerals. For carbonate acidity:

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 \approx 4.45 \times 10^{-7}$$

Mineral acidity in water is generally associated with any water that has a pH of less than 4.5. Titration of mineral acidity is assumed complete by the time the pH of 4.5 is reached.

Sources of mineral acidity include the oxidation of sulfur pyrites to sulfurous and sulfuric acids, and other mineral compounds to their equivalent acid forms. These acids are often found in drainage associated with coal mines and in the anthracite coal-producing areas of Pennsylvania and West Virginia; it is not uncommon, even today, to find streams with a pH of less than 4.5 due to the presence of acid mine drainage caused by the oxidation of sulfur in coal formations. The same is true in many mine waters, including the Gold King Mine drainage water in Colorado (2015) which was accidentally released during an USEPA directed effort at remediation.



The oxidation from sulfur to sulfuric acid takes place through a number of natural routes, including biochemical routes.<sup>14</sup>

### 7.4.4 Alkalinity

Alkalinity is due to the presence of salts, principally in the form of bicarbonates and salts of weak acids. It is measured by titration with 0.02 N H<sub>2</sub>SO<sub>4</sub>.

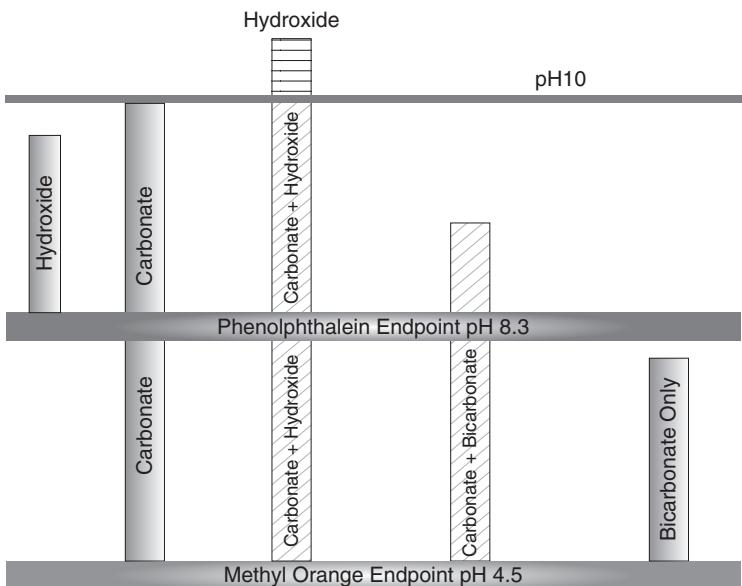


Figure 7.4 Graphical representation of alkalinity determination by titration.

(N/50 H<sub>2</sub>SO<sub>4</sub>). If the initial pH is above 8.3 the titration is done in two steps using phenolphthalein endpoint as a first indicator. Methyl orange is used as the second endpoint. The titration is performed with 0.02 N H<sub>2</sub>SO<sub>4</sub>. Alkalinity is necessary and vital in the wastewater treatment process, especially nitrogen and phosphorus removal by biological means, and without sufficient alkalinity, biological denitrification does not occur.

Water can have both acidity and alkalinity at the same time (see Figure 7.4). Hydroxide alkalinity gets consumed by the time the pH is 8.3, but carbonate alkalinity only gets half neutralized by that point. Samples having bicarbonate alkalinity have a pH between 8.3 and 11. Samples having high hydroxide alkalinity have a pH usually above 10.

In a mixed sample having hydroxide and carbonate alkalinity, the correction for hydroxide alkalinity is: total alkalinity (minus) carbonate alkalinity or

$$\text{Alk}_{\text{OH}} = \text{Alk}_{\text{total}} - 2\text{Alk}_{\text{carbonate}} \text{ (from pH 8.3 to pH 4.5)}$$

The relationship between the various species is both shown and described by the following chemical relationships, when temperature  $T$  is given in kelvin ( $^{\circ}\text{C} + 273.18$ ):

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = K_1 = 10^{(14.8435 - 3404.71/T) - 0.032786T}$$

$[H^+][CO_3^{2-}]/[HCO_3^-] = K_2 = 10$  ( $6.498 - 2909.39/T - 0.02379T$ )  
and  $[Ca^{2+}][CO_3^{2-}] = K_s = 4.82 \times 10^{-9}$  approximately.

Looking at the overall equilibria, we can find the following relationships:

Total carbonate species,  $C_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$$a_0 = [HCO_3^-]/C_t$$

$$a_1 = [HCO_3^-]/C_t$$

$$a_2 = [CO_3^{2-}]/C_t$$

and, by a series of algebraic manipulations, the following relationships are developed:

$$a_0 = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}; a_1 = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{[K_2]}{[H^+]}}; a_2 = \frac{1}{\frac{[H^+]^2}{(K_1 K_2)} + \frac{[H^+]}{K_2 + 1}}$$

and for a  $CO_2$  saturated system  $a_0 + a_1 + a_2 = 1$ .

However, as in most situations, where the water is at less than saturation point but is in equilibrium with the atmosphere, the following general relationships hold:

Electroneutrality must be satisfied, so that

$$[\text{cations}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [\text{anions}]$$

Alkalinity of the system is  $[Z] = [C] - [A]$  and after some more appropriate manipulations,

$$[Z] = a_1[C_t] + 2a_2[C_t] + K_w/[H^+] - [H^+]$$

For groundwater from limestone-bearing rock, it is usually saturated with  $CaCO_3$  but not with  $CO_2$ , and

$$2[Ca^{2+}] + [Z'] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

where  $[Z'] = \text{Alkalinity} - [Ca^{2+}]$ .

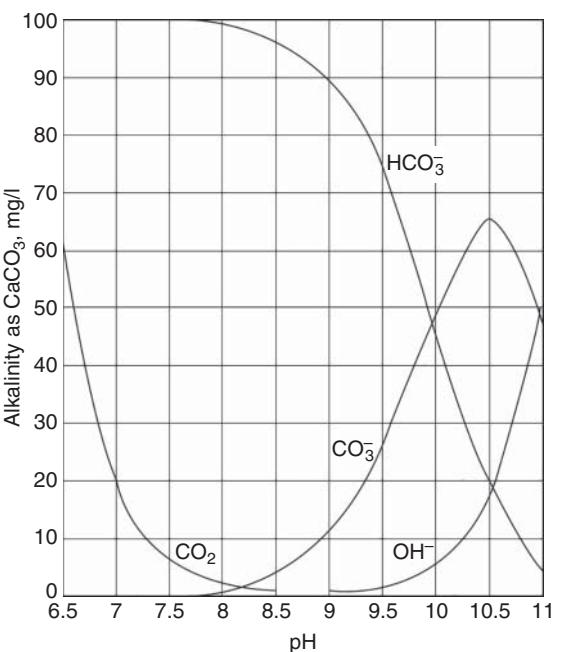
And finally, with a bit more manipulation and substitution, we get a formula for  $C_t$ :

$$\frac{(a_1 + 2a_2)}{a}(C_t)^2 - \frac{([Z'] + [H^+] - K_w/[H^+])}{b}(C_t) - \frac{2K_s/a_2}{c} = 0,$$

$$\text{which is the form } C_t = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$$

so that the quadratic equation can be used to calculate the carbonate species – see Figure 7.5. The values on the vertical axis show the three forms of alkalinity sum to a total alkalinity of  $100 \text{ mg l}^{-1}$ .

**Figure 7.5** Relationships in carbonate alkalinity.



## 7.5 Hardness

Hardness is often responsible for scale forming in water in cooling towers and in pipes. It is almost always caused by divalent metallic ions present in the water. To obtain a complete profile on the hardness, it is necessary to run a cation balance on the waters in question.

Hardness is classified in two ways, as carbonate and non-carbonate hardness, and also classified with respect to the ions calcium and magnesium. The hardness in water not chemically related to bicarbonates is non-carbonated hardness.

$$\begin{aligned}\text{Total hardness} &= \text{Calcium hardness} + \text{Magnesium hardness} \\ &\quad + \text{Non-carbonate hardness}\end{aligned}$$

and

$$\text{Alkalinity(mg l}^{-1}\text{)} = \text{Carbonate hardness(mg l}^{-1}\text{)}$$

For each ion fraction:

$$\text{Hardness(mg l}^{-1}\text{) as CaCO}_3 = M^{2+}(\text{mg l}^{-1}) \times 50 / (\text{eq. wt of } M^{2+})$$

So that for iron the equivalent weight would be  $55.845/2$  (MW/valence) or 27.9225, but we can approximate, and the multiplier would be  $50/55.9$

or 0.895. Sometimes there is more alkalinity in the water than is necessary to satisfy the divalent cations. This is particularly true in alkaline waters. This is known as negative non-carbonate hardness and is associated with the presence of  $K^+$  and  $Na^+$  ions in the water. It is necessary to know the hardness of the water in domestic water treatment and in chemical precipitation, as the latter often represents a specific chemical demand both in ion exchange and in chemical precipitation. It is also useful to know because, in chemical precipitation, it is often easier to use chemical "water softening" techniques to assist in the removal of specific ions and other materials. The trend for water conditioning seems to be moving towards membrane treatment, as it does not require as much chemical treatment.

$$\text{Non-carbonate hardness(NCH)} = \text{Total hardness} - \text{Alkalinity}$$

The relationships between the forms are shown in Figure 7.6.

The overall approach for analyzing water includes, first, to chart the ion balance in the water and then to make decisions about the way in which to treat the water to remove the excess ions.

Given the following analyses shown in the problem below, look first at the ion balance and then transform the ions to  $CaCO_3$  equivalents. The pH is 7.5 as shown in the right-hand columns of ions. Note that it does not count in the sum of ions.

You may find it useful to use some of the data for common chemicals in water treatment, shown in Tables 7.5 and 7.6.

First, all alkalinity is bicarbonate because of  $pH = 7.5$ .

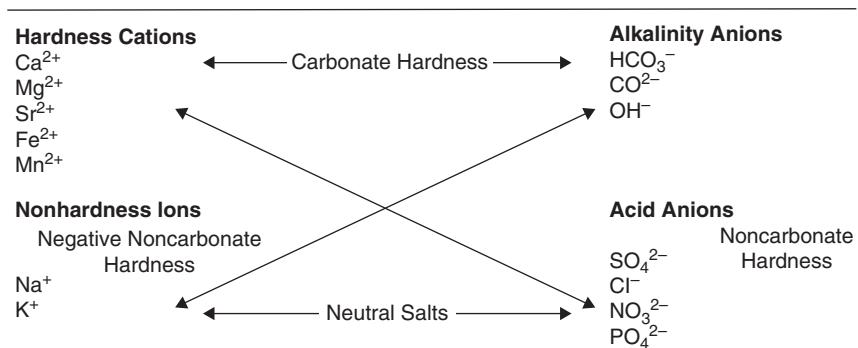


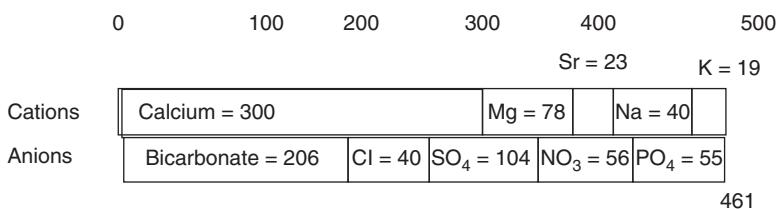
Figure 7.6 Hardness relationships in water.

**Table 7.5** Calcium carbonate equivalents for common ions in water.

Substance	Molecular weight	Equivalent weight	Substance to $\text{CaCO}_3$ equivalent	$\text{CaCO}_3$ equivalent to substance
Calcium Ca	40.1	20.05	2.50	0.40
Iron 2+ $\text{Fe}^{2+}$	55.8	27.9	1.79	0.56
Iron 3+ $\text{Fe}^{3+}$	55.8	18.6	2.69	0.37
Hydrogen $\text{H}^+$	1.01	1.01	50	0.02
Lead 2+ $\text{Pb}^{2+}$	207	103.5	0.48	2.07
Magnesium $\text{Mg}^{2+}$	24.3	12.2	4.12	0.24
Manganese $\text{Mn}^{2+}$	54.9	27.5	1.82	0.55
Nitrate $\text{NO}_3^-$	62.0	62.0	0.81	1.24
Sodium $\text{Na}^+$	23.0	23.0	2.18	0.46
Bicarbonate $[\text{HCO}_3^-]$	61.0	61.0	0.82	1.22
Chloride $\text{Cl}^-$	35.5	35.5	1.41	0.71
Sulfate $\text{SO}_4^{2-}$	96.1	48.05	1.04	0.96
Carbonic acid $\text{H}_2\text{CO}_3$	62	31.0	1.61	0.62
Calcium hydroxide $\text{Ca(OH)}_2$	74.1	37.1	1.35	0.74
Hydroxyl	17.0	17.0	2.94	0.34

**Table 7.6** Water softening example.

Cation	Concentration ( $\text{mg l}^{-1}$ )	$\text{CaCO}_3$ equivalent	Anion	Concentration ( $\text{mg l}^{-1}$ )	$\text{CaCO}_3$ equivalent
Calcium	120.2	301			
Magnesium	19	78	Chloride	25	35
Manganese	0	0	Phosphate	52	55
Strontium	20	23	Bicarbonate	133	109
Iron		0	pH	7.5	0
Sodium	18	40	Nitrate	69	56
Potassium	15	19	Sulfate	198	206
	Sum	461		Sum	461



**Figure 7.7** Ion balance example.

Next, calculate the  $\text{CaCO}_3$  equivalents as shown below and construct a bar chart.

$$\text{Ca} = 2 \times 120.2 \times (50/40.078) \approx 300 \quad \text{Mg} = 2 \times 19 \times (50/24.305) \approx 78$$

$$\text{Sr} = 2 \times 20 \times (50/87.6) \approx 24 \quad \text{K} = 1 \times 15 \times (50/39.098) \approx 19$$

$$\text{Na} = 1 \times 18 \times (50/22.9897) \approx 40 \text{ and so on.}$$

Then run an ion balance :

Cations = anions, or 461 = 461 as shown in Table 7.6.

Next create a figure like Figure 7.7.

Note that the cation order is calcium, magnesium, manganese, strontium, iron, sodium, and potassium, and the anion order is bicarbonate, chloride, sulfate, nitrate, silicate, and phosphate.

$$\text{Total hardness} = 401 \text{ mg l}^{-1} \text{ as } \text{CaCO}_3$$

$$\text{Total bicarbonate alkalinity} = 206 \text{ mg l}^{-1} \text{ as } \text{CaCO}_3$$

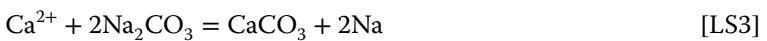
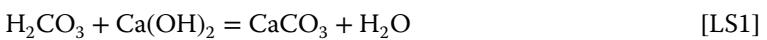
$$\text{Carbonate hardness} = \text{alkalinity} = 206 \text{ mg l}^{-1} \text{ as } \text{CaCO}_3$$

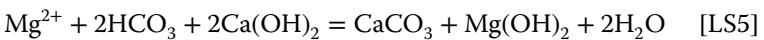
$$\text{Non-carbonate hardness} = 195 \text{ mg l}^{-1} \text{ as } \text{CaCO}_3$$

## 7.6 Chemical Water Softening

The process of removing hardness from water is important to many municipalities, especially where the groundwater is drawn from limestone formations. The carbonate hardness will form deposits on heat exchangers and individual house hot-water heaters.<sup>15</sup>

The information in square brackets [ ] indicates the type of softening equations, for example, [LS1] is the lime softening equation (note underlined values indicate precipitates)





Note that the total hardness exceeds the total alkalinity. This is where lime-soda softening is applied.

Now develop the dosage equations for the reactions. Because we converted the dosages to equivalents of  $\text{CaCO}_3$ , the reactions are in milligram per liter per dose of  $\text{CaCO}_3$ . For the  $\text{HCO}_3^-$  we need  $103 \text{ mg l}^{-1}$  of lime. For the balance of the calcium we need sodium bicarbonate in an amount of  $(300 - 206) \times 2 = 188 \text{ mg l}^{-1}$ . For the manganese and strontium, we need  $2 \text{ mg l}^{-1}$  of lime and  $1 \text{ mg l}^{-1}$  of sodium carbonate per  $\text{mg l}^{-1}$  of each, so the lime dosage is  $101 \times 2 = 202 \text{ mg l}^{-1}$  and the sodium carbonate is  $101 \text{ mg l}^{-1}$ .

The total lime dose is then  $103 + 202 \text{ mg l}^{-1} = 305 \text{ mg l}^{-1}$ . The total sodium carbonate is  $188 + 101 \text{ mg l}^{-1} = 289 \text{ mg l}^{-1}$ . Note that both of these compounds are measured as  $\text{CaCO}_3$  equivalents.

Conversions factors for lime and  $\text{Na}_2\text{CO}_3$  are as follows:

$$1 \text{ mg l}^{-1} \text{ lime} = 1 : 35 \text{ mg l}^{-1} \text{ of } \text{CaCO}_3$$

$$1 \text{ mg l}^{-1} \text{ sodium carbonate (solution)} = 0.94 \text{ mg l}^{-1} \text{ of } \text{CaCO}_3 \text{ or}$$

$$1 \text{ mg l}^{-1} \text{ of sodium carbonate } (\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}) \text{ (powder)} = 0.35 \text{ mg l}^{-1} \text{ of } \text{CaCO}_3.$$

The residual materials in the water will be  $\text{Mg}(\text{OH})_2$  and  $\text{CaCO}_3$  at their solubility products, plus sodium forms of the anions. The final pH of the water will be between 10 and 11. At a pH of about 10.3 the concentration of calcium and magnesium will be about  $2.7$  and  $9.2 \text{ mg l}^{-1}$ , respectively.

For removal of non-carbonate hardness,  $\text{NaOH}$  can be substituted for  $\text{Na}_2\text{CO}_3$ . The problem with this process is the residual pH. At the high pH, even with filtration, there is still a tendency for the residual carbonate to precipitate. So the pH is reduced by adding either  $\text{H}_2\text{SO}_4$  or  $\text{CO}_2$  to a more normal range of pH between 8.5 and 9.5.

### 7.6.1 Excess Lime Process

The excess lime process is not a preferred process for removing Mg in water. It is primarily focused on the removal of carbonate alkalinity. One may use it where there is no significant non-carbonate hardness.

Given the following analysis:

$$\text{pH} = 7 : 1; \text{Ca} = 180 \text{ mg l}^{-1}; \text{Mg} = 60 \text{ mg l}^{-1}; \text{Alk} = 260 \text{ mg l}^{-1};$$

$$T = 25^\circ \text{C}.$$

First calculate the carbonic acid concentration.

$\text{HCO}_3^-$  is all bicarbonate form because of the pH.  $\text{Alk} = 260 \text{ mg l}^{-1}$ ; and from *Standard Methods* (Method 4500  $\text{CO}_2$ ):

$$K_1 = [\text{H}][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 10^{-6.36}$$

or calculate the value of  $K_1$  from above work

$$K_2 = [\text{H}][\text{CO}_3^-]/[\text{HCO}_3^-] = 10^{-10.33}$$

or calculate it from the work above.

All the units are in  $\text{CaCO}_3$ .

$$\text{HCO}_3^- = [\text{TALK} - 5 \times 10^{(\text{pH}-10)}]/[1 + 0.94 \times 10^{(\text{pH}-10)}]$$

where TALK is total alkalinity and  $\text{CO}_3^- = 0.94 \times [\text{HCO}_3^-] \times 10^{(\text{pH}-10)}$ ,  $\text{OH} = 5 \times 10^{(10-\text{pH})}$ , and free  $\text{CO}_2 = 2 \times [\text{HCO}_3^-] \times 10^{(6-\text{pH})}$ .

When one plugs in the values, the following is found:

$$\text{TALK} = 260 \text{ mg l}^{-1};$$

$$\begin{aligned} \text{HCO}_3^- &= [260 - 0.5 \times 10^{(-7-10)}]/[1 + 0.94 \times 10^{(-7-10)}] \\ &= 255.5/1.00094 = \mathbf{259.79 \text{ mg l}^{-1}} \end{aligned}$$

$\text{CO}_3^- = 0.94 \times 259.79 \times 10^{-3} = 0.244 \text{ mg l}^{-1}$ , which is so small that it can be ignored, and using the definition of  $K_1$  above:

$$\begin{aligned} [\text{H}_2\text{CO}_3] &= [\text{H}][\text{HCO}_3^-]/K_1 = 10^{-7} \times 0.425821/10^{-6.36} \\ &= 153.85 \text{ mg l}^{-1} \text{ as } \text{CaCO}_3 \end{aligned}$$

Now find the carbonic acid fraction. Because alkalinity is defined in terms of  $\text{CaCO}_3$ , we need to back-calculate to  $[\text{HCO}_3^-] = 260 \text{ mg l}^{-1}$ , and if  $\text{CaCO}_3 = X \text{ mg l}^{-1}$   $[\text{HCO}_3^-] \times 50/\text{eq. wt or } 260 = 50 \times X/61 = 317.2 \text{ mg l}^{-1}$  of  $[\text{HCO}_3^-]$  or  $317.2/61 = 5.2 \times 10^{-3} \text{ mol l}^{-1}$

Then calculate the species constants  $K_1$  and  $K_2$ :

$$K_1 = 3.47 \times 10^{-7} \text{ and } K_2 = 3.1 \times 10^{-11}, \text{ and } \alpha_1 = [\text{HCO}_3^-]/C_t = 1/[10^{-7}/3.47 \times 10^{-7} + 1 + 3.1 \times 10^{-11}/10^{-7}] = 0.7761; \text{ and } C_t = 5.2 \times 10^{-3}/0.7761 = 6.7 \times 10^{-3} \text{ mol l}^{-1}.$$

Then, since  $C_t = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^-$  which gives  $C_t = 155 \times 10^{-3} \text{ mol l}^{-1}$ , then it is  $155 \text{ mg l}^{-1}$  as  $\text{CaCO}_3$  because the molecular weight is approximately 100.

## 7.7 Nitrogen

There are five forms of nitrogen that are important to the environmental engineer: ammonia ( $\text{NH}_3$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), dinitrous oxide ( $\text{N}_2\text{O}$ ), and organic nitrogen. Of these, nitrite is one of the least important, except as an intermediate reaction product, because it does not last long in the

environment. Organic nitrogen is found in all proteins and cellular matter, and as that matter decays, it can be an important source of ammonia. Nitrate is also important because as a natural oxidation product of organic oxidation, it represents the end point. Nitrate is also important because in drinking water, in concentrations greater than  $10 \text{ mg l}^{-1}$ ,<sup>16</sup> it can pose a health risk to infants and cause them to develop methemoglobinemia, or the “blue baby” syndrome. When very young children, mostly infants below six months old, ingest large quantities of nitrate, their bodies convert it to nitrite in their digestive system and the nitrite reacts with the hemoglobin in the blood, forming high amounts of methemoglobin. Since methemoglobin does not carry oxygen, too much of this enzyme in the blood causes the infant’s tissue and organs to be deprived of oxygen, resulting in the light blue tinge to their skin.

Ammonia and nitrate are arguably the two most important forms; ammonia is ubiquitous and is excreted by all animals, used as fertilizers, and released by decaying organic matter; nitrate is the oxidized form of ammonia, and is a vital part of most fertilizers.

The principal reactions associated with the ammonia to nitrate pathway are (see Figure 7.8):



The first reaction takes place with *nitrosomonas*. The second reaction takes place with *nitrobacter*. However, the rate of reaction of *nitrobacter* is about three times the reaction rate for *nitrosomonas*, so nitrite does not accumulate. On a molecular basis it requires about  $4.6 \text{ mg l}^{-1}$  of oxygen to oxidize  $1 \text{ mg l}^{-1}$  of ammonia to nitrate.

Ammonia in water has two forms: as a dissolved gas, and as an ionized product. The relationship is pH-dependent. Un-ionized ammonia is highly toxic to some forms of aquatic life, while the ammonium ion is significantly less toxic. The distribution of ammonia between those two forms in water is controlled by pH, temperature, and ionic strength (see Figure 7.9).

In freshwater sediments at pH 8.0 and  $27^\circ\text{C}$ , about 3% of the total ammonia is present in the un-ionized form, while in saline water of the same temperature and pH, about 4% of the total ammonia is in un-ionized form.

The USEPA’s chronic water quality criterion for un-ionized ammonia in marine waters is  $0.035 \text{ mg l}^{-1}$   $\text{NH}_3$ , based on the sensitivity of various types of shrimp and fish. The comparable saltwater final acute value for ammonia is  $0.465 \text{ mg l}^{-1}$   $\text{NH}_3$ . For freshwater, the USEPA has established an un-ionized ammonia four-day average chronic standard of about  $0.02 \text{ mg l}^{-1}$   $\text{NH}_3$ . When the pH decreases and the temperature decreases, the standard value falls to approximately  $0.01 \text{ mg l}^{-1}$   $\text{NH}_3$ .

Acute:chronic ratios for ammonia:ammonium ion range from 3 to  $43 \text{ mg l}^{-1}$   $\text{NH}_3$ ; 96-hour LC50s were reported as low as  $0.08 \text{ mg l}^{-1}$   $\text{NH}_3$ . The results

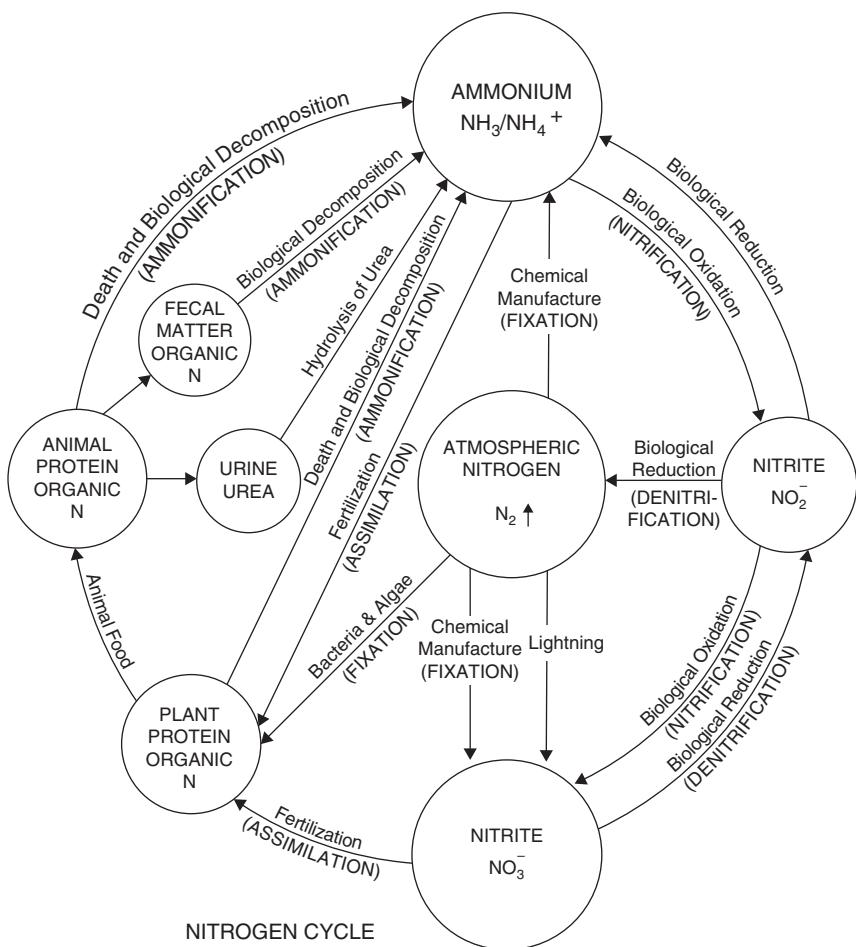
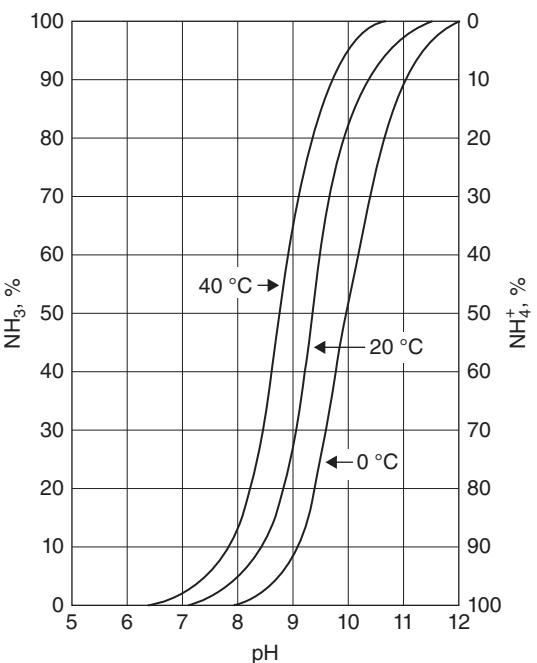


Figure 7.8 Nitrogen in the environment.

vary widely depending upon the species used to run the test, and salmonids are among the most sensitive to ammonia. In short, ammonia, especially un-ionized ammonia (anything over pH about 8.3) is toxic to many forms of aquatic life. Ammonia complexes with other metals can also increase toxicity, especially with some of the heavier metals such as nickel and cadmium. Many biological treatment plants, except those that operate with an extremely long sludge retention time, such as extended aeration, cannot successfully meet the ammonia standard in the effluent, and ammonia toxicity has become a problem in a number of wastewater treatment plants. Many publicly owned treatment works (POTWs) now operate with an ammonia limitation on their effluent.

**Figure 7.9** Effects of pH and temperature on distribution of ammonia and ammonium ion in water.



Ammonia is detected by Nesslerization, and by ion-specific electrodes. The Nessler reagent is a combination of potassium, mercury, and iodine, and is often used in combination with a digestion or distillation of the sample. The method for determination of organic nitrogen requires an acid digestion of the organic matter in an acid medium and collection of the ammonia gas, followed by Nesslerization of the sample.

Nitrate and nitrite are determined by colorimetry, often involving use of a cadmium salt, and relies on preparation of a calibration curve for each individual determination. Newer analytical methods are available from Hach Chemical. For information on their accuracy or repeatability, contact the Hach Technical Service Group.

## 7.8 Phosphorus

Phosphorus is an important environmental nutrient and fertilizer. One of the principal problems with phosphorus is that, in an aquatic environment, at concentrations around  $0.2 \text{ mg l}^{-1}$ , it can cause algal blooms. The principal form of phosphorus found in the environment is  $[\text{PO}_4^{2-}]$ . Because phosphorus is used in agriculture as a nutrient (fertilizer is measured in ratios of nitrogen:phosphorus:potassium, or NPK), unless it is applied at agronomic rates,

the excess will find its way into the environment. Another major source of phosphorus is urine. Most adults discharge between 0.4 and 1.4 g per day of PO<sub>4</sub> in their urine. According to one estimate, if one could collect the urine and feces from the world's population, it would account for 22% of the total global phosphorus demand.<sup>17</sup> One of the chief secondary sources of phosphate in the environment is detergent manufacture, but it is also widely used as an undercoating to prepare metallic surfaces for painting.

Phosphorus is also a part of the Krebs cycle, which is the aerobic breakdown path for all organic chemicals, and phosphorus is a vital part of adenosine triphosphate (ATP), which is an essential building block to the structure of all life.

One final but unusual use of phosphorus. Phosphorus comes as red and white (sometimes called yellow) phosphorous. The latter is extremely reactive and will burn spontaneously when dry and exposed to air – it is often used in warfare. Red phosphorus is much less flammable and non-toxic. Principal uses are in fertilizers, pesticides, cleaning aids, and detergents, and it has some uses in the manufacture of methamphetamine.

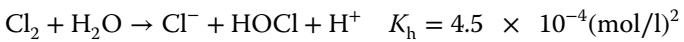
## 7.9 Sulfur

The principal forms of sulfur in the aquatic environment are as sulfate (SO<sub>4</sub>), sulfite (SO<sub>3</sub>), and hydrogen sulfide (H<sub>2</sub>S). Hydrogen sulfide is generally the byproduct of anaerobic decomposition, and it is a toxic and noxious gas, slightly soluble in water. Sulfate and sulfite are the oxidized forms of sulfur, and are formed from the hydrolysis of sulfur dioxide (SO<sub>2</sub>). Certain metals, including cadmium, are precipitated with hydrogen sulfide in a reaction that yields CdS. This compound is extremely insoluble and the reaction is used to remove cadmium from wastewater ( $\log_{10} K_{sp} = 14.36 \pm 0.26$ ).<sup>18</sup> Other di- and trivalent metals are also removed very well by sulfide precipitation. One of the principal compounds in the aquatic environment is calcium sulfate (CaSO<sub>4</sub>), formed when the sulfate ion is neutralized with calcium. The resulting compound is only slightly soluble (around 1600 mg l<sup>-1</sup> in water), and when pure is used to form gypsum, Plaster of Paris, and in the formation of stucco.

## 7.10 Chlorine

Chlorine is an oxidizing gas. It is very important in the water environment because it is one of the principal substances used for disinfection. It also makes a very strong acid, and many types of salts, including basic sodium chloride, one of the principal ingredients in salt water.

Because chlorine is highly reactive, it seldom exists as a free ion, but rapidly and strongly combines with other elements. In combination with hydrogen it forms hydrochloric acid. In water, however, it forms a two-tiered disinfection compound as it converts to an equilibrium mixture of chlorine, hypochlorous acid ( $\text{HOCl}$ ), and hydrochloric acid ( $\text{HCl}$ ):



The subject is treated more fully in the chapter on disinfection, but chlorination is more effective in acidic solutions than in alkaline solutions. There are other reactions with ammonia in water (chloramines) which have disinfection power. One of the most important things about chlorine is its abundance and low cost. One of the biggest disadvantages is that, if released into the environment as a gas, it can be highly toxic.

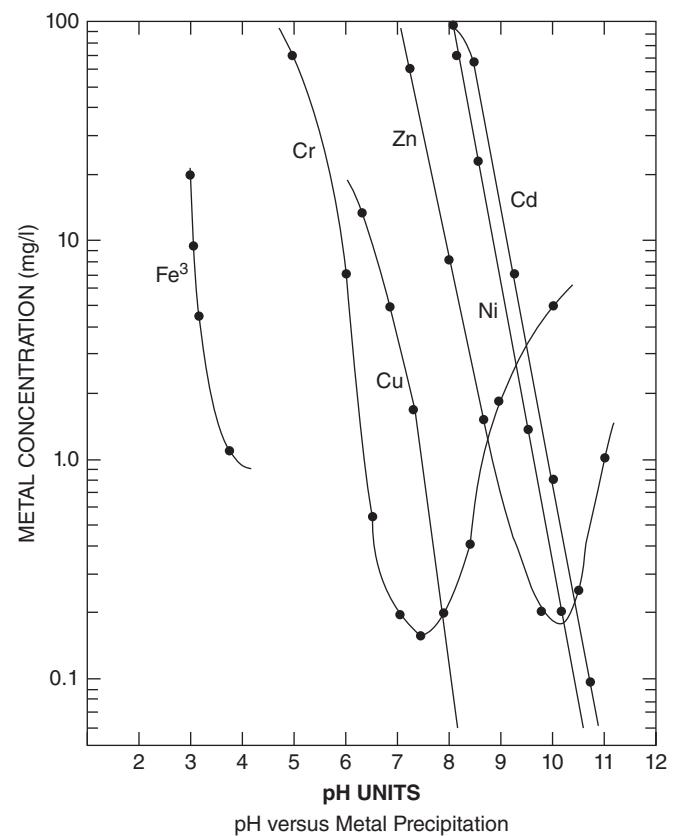
Chlorine also reacts strongly with organic compounds to form highly stable organic compounds. Among some of the more important are the chlorophenols. This group includes several disinfectants such as chlorophenol, and the chlorination of naphthalenes and other linked products can lead to DDT (dichlorodiphenyltrichloroethane), a large variety of pesticides, chemical warfare agents, a variety of toxic organic compounds that are biologically resistant to degradation, and even 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).

## 7.11 Other Halogens

Other halogens, principally fluorine ( $\text{F}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ), all have similar reactions in water and with organics, but with the increasing molecular weight and ionic activity, the disinfection power can vary greatly. Fluorine is not necessarily a good disinfectant, while bromine and iodine are much better, and bromine has been used as a disinfectant in swimming pools. Bromine is also easier to handle because it exists as a liquid at room temperature (melts at  $7^\circ\text{C}$ , and boils at  $58^\circ\text{C}$ ) and is relatively easy to handle as a corrosive liquid. Iodine, by comparison, is solid at room temperature (melts at  $113.5^\circ\text{C}$ ), and is a much less powerful disinfectant.

## 7.12 Metals

Most metals are detected by inductively coupled plasma arc, or by flame absorption or emission spectra. The solubility of various metal hydroxides and reaction products is quite well known, and many metals are preferentially removed from water by pH adjustment and selective precipitation. Figure 7.10 shows the solubilities of various metal ions in water as a function of pH.



**Figure 7.10** Metal solubilities at various pH levels. Source: USEPA Electroplating and Metal Finishing Source Control Manual, citing R. Weiner, Die Abwasser der Galvanotechnik und Metallindustrie, 4th Ed., Eugen G. Leuze Verlag, 1973.

Moreover, the USEPA has performed a study of heavy metal removal from electroplating wastes (Cd, Ni, Cu, Cr, Zn) and found that raising the pH of the wastewater to between eight and nine with lime, and treating it with hydrogen sulfide, precipitation, and filtration will remove most of these metals down to the low parts per billion range, where they are suitable for discharge into a POTW.<sup>19</sup> However, where a number of mixed metals are present in a waste stream, segregation of the streams and pretreatment or separate enhanced treatment with membrane filtration may be warranted.

Sulfite precipitation of metals is excellent but often creates a toxic waste disposal problem. More often than not, the metals are hazardous wastes by classification and can be disposed of only after solidification and/or reclamation.

Cadmium is especially difficult to reclaim and even worse to dispose of. It is moderately easy to precipitate either as a hydroxide or as a sulfide. One of the principal sources of cadmium is from plating solutions where it is used to enhance the flexibility and corrosion resistance of the plating being applied. Because of its toxicity and relatively low melting point, cadmium is moderately dangerous to smelt for recovery. The popularity of Ni–Cd batteries has made this problem even more difficult. No one wants Cd but everyone takes the Ni. Currently, in the United States there are no Cd recovery facilities. The closest cadmium reclamation facilities are in the UK and Japan, and Cd requires an export license from the EPA.

Table 7.7 is a list of some of the solubility compounds of common metals.

Radium<sub>226</sub> is a special element. It is part of the decay series of uranium, and it has a long half-life (1600 years). It is one of the 33 known isotopes of radium, but it is the most common. It is mentioned because it is common, unusual, and deadly. Radium has no medicinal value, and essentially zero commercial value. It is the most highly radioactive substance on Earth. It is found with uranium, and any geological formation that includes granite will have some radium in the groundwater. The radium is also a precursor to radon gas, which is also reactive. Radium itself is chemically similar to calcium, and if ingested will deposit in the bones where it can do great damage. Radium and its daughter, radon, are also found in petroleum wastes and sludges, and are classified as a NORM (naturally occurring radioactive material). Radium can be effectively removed by ion exchange, and co-precipitation with barium sulfate. NORM may be responsible for health problems commonly attributed to petroleum exposure.

## 7.13 Solids

Solids are measured in five ways: total solids by evaporation; filterable solids by filtration through a 0.45 µm filter; filterable solids by filtration through a 0.2 µm filter; volatile solids [specify which fraction] by ignition; and settleable solids (a volumetric test rather than a gravimetric test). Total solids includes everything that will dry at about  $105 \pm 3^\circ\text{C}$ . Suspended solids has two definitions, depending upon the type of filter used. The *Standard Methods* definition uses a 0.45 µm filter, and the ASTM/NREL procedure uses a 0.2 µm filter.<sup>20</sup> Each will give different weights, and in some cases, when modeling the biological process using activated sludge models, it may be important to run both sets of filtration samples.

The volatile solids test is an ignition test at 550°C, where the final sample weight is corrected for the oven dry weight, and the difference between the suspended solids and the final weight after ignition of the sample is determined and calculated as the volatile suspended solids. VSS is also a measure of the active biomass in a wastewater treatment plant liquor.

**Table 7.7** Metal solubility products and solubility constants for inorganic compounds at 25°C.

Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$
Aluminum hydroxide	$\text{Al}(\text{OH})_3$	$4.6 \times 10^{-33}$	Copper(I) iodide	$\text{CuI}$	$1.1 \times 10^{-12}$	Magnesium arsenate	$\text{Mg}_3(\text{AsO}_4)_2$	$2.1 \times 10^{-20}$	Silver iodide	$\text{AgI}$	$8.3 \times 10^{-17}$
Aluminum phosphate	$\text{AlPO}_4$	$6.3 \times 10^{-19}$	Copper(I) sulfide	$\text{Cu}_2\text{S}$	$2.5 \times 10^{-48}$	Magnesium carbonate	$\text{MgCO}_3$	$3.5 \times 10^{-8}$	Silver nitrite	$\text{AgNO}_2$	$6.0 \times 10^{-4}$
Barium carbonate	$\text{BaCO}_3$	$5.1 \times 10^{-9}$	Copper(II) arsenate	$\text{Cu}_4(\text{AsO}_4)_2$	$7.6 \times 10^{-36}$	Magnesium fluoride	$\text{MgF}_2$	$3.7 \times 10^{-8}$	Silver oxalate	$\text{Ag}_2\text{C}_2\text{O}_4$	$3.6 \times 10^{-11}$
Barium chromate	$\text{BaCrO}_4$	$2.2 \times 10^{-10}$	Copper(II) carbonate	$\text{CuCO}_3$	$1.4 \times 10^{-10}$	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	$1.8 \times 10^{-11}$	Silver sulfate	$\text{Ag}_2\text{SO}_4$	$1.4 \times 10^{-5}$
Barium fluoride	$\text{BaF}_2$	$1.0 \times 10^{-6}$	Copper(II) chromate	$\text{CuCrO}_4$	$3.6 \times 10^{-6}$	Magnesium oxalate	$\text{MgC}_2\text{O}_4$	$7 \times 10^{-7}$	Silver sulfide	$\text{Ag}_2\text{S}$	$6 \times 10^{-51}$
Barium hydroxide	$\text{Ba}(\text{OH})_2$	$5 \times 10^{-3}$	Copper(II) ferrocyanide	$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	$1.3 \times 10^{-16}$	Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2$	$1 \times 10^{-25}$	Silver sulfite	$\text{AgSO}_3$	$1.5 \times 10^{-14}$
Barium iodate	$\text{Ba}(\text{IO}_3)_2$	$1.5 \times 10^{-9}$	Copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	$2.2 \times 10^{-20}$	Manganese(II) carbonate	$\text{MnCO}_3$	$1.8 \times 10^{-11}$	Silver thiocyanate	$\text{AgSCN}$	$1.0 \times 10^{-12}$
Barium oxalate	$\text{BaC}_2\text{O}_4$	$2.3 \times 10^{-8}$	Copper(II) sulfide	$\text{CuS}$	$6 \times 10^{-37}$	Manganese(II) hydroxide	$\text{Mn}(\text{OH})_2$	$1.9 \times 10^{-9}$	Strontium carbonate	$\text{SrCO}_3$	$1.1 \times 10^{-10}$
Barium sulfate	$\text{BaSO}_4$	$1.1 \times 10^{-10}$	Copper(II) thiocyanate	$\text{Cu}(\text{SCN})_2$	$4.0 \times 10^{-14}$	Manganese(II) sulfide	$\text{MnS}$	$2.5 \times 10^{-13}$	Strontium chromate	$\text{SrCrO}_4$	$2.2 \times 10^{-5}$
Barium sulfite	$\text{BaSO}_3$	$8 \times 10^{-7}$	Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	$1.0 \times 10^{-60}$	Mercury(I) bromide	$\text{Hg}_2\text{Br}_2$	$5.6 \times 10^{-23}$	Strontium fluoride	$\text{SrF}_2$	$2.5 \times 10^{-9}$
Barium thiosulfate	$\text{BaS}_2\text{O}_3$	$1.6 \times 10^{-5}$	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$1.0 \times 10^{-36}$	Mercury(I) chloride	$\text{Hg}_2\text{Cl}_2$	$5.0 \times 10^{-13}$	Strontium oxalate	$\text{SrC}_2\text{O}_4$	$4 \times 10^{-7}$
Bismuthyl chloride	$\text{BiOCl}$	$1.8 \times 10^{-31}$	Iron(II) carbonate	$\text{FeCO}_3$	$3.2 \times 10^{-11}$	Mercury(I) chromate	$\text{Hg}_2\text{CrO}_4$	$2.0 \times 10^{-9}$	Strontium sulfate	$\text{SrSO}_4$	$3.2 \times 10^{-7}$
Bismuthyl hydroxide	$\text{BiOOH}$	$4 \times 10^{-10}$	Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	$8.0 \times 10^{-16}$	Mercury(I) cyanide	$\text{Hg}_2(\text{CN})_2$	$5 \times 10^{-40}$	Strontium sulfite	$\text{SrSO}_3$	$4 \times 10^{-8}$

Bismuth(III) sulfide	$\text{Bi}_2\text{S}_3$	$1 \times 10^{-97}$	Iron(II) sulfide	$\text{FeS}$	$6 \times 10^{-19}$	Mercury(I) iodide	$\text{HgI}_2$	$4.5 \times 10^{-29}$	Thallium(I) bromate	$\text{TIBrO}_3$	$1.7 \times 10^{-4}$
Cadmium carbonate	$\text{CdCO}_3$	$5.2 \times 10^{-12}$	Iron(III) arsenate	$\text{FeAsO}_4$	$5.7 \times 10^{-21}$	Mercury(I) sulfate	$\text{Hg}_2\text{SO}_4$	$7.4 \times 10^{-7}$	Thallium(I) bromide	$\text{TIBr}$	$3.4 \times 10^{-6}$
Cadmium hydroxide	$\text{Cd(OH)}_2$	$2.5 \times 10^{-14}$	Iron(III) ferrocyanide	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	$3.3 \times 10^{-41}$	Mercury(I) sulfide	$\text{Hg}_2\text{S}$	$1.0 \times 10^{-47}$	Thallium(I) chloride	$\text{TiCl}$	$1.7 \times 10^{-4}$
Cadmium iodate	$\text{Cd(IO}_3)_2$	$2.3 \times 10^{-8}$	Iron(III) hydroxide	$\text{Fe(OH)}_3$	$4 \times 10^{-38}$	Mercury(I) thiocyanate	$\text{Hg}_2(\text{SCN})_2$	$3.0 \times 10^{-20}$	Thallium(I) chromate	$\text{Ti}_2\text{CrO}_4$	$9.8 \times 10^{-15}$
Cadmium sulfide	$\text{CdS}$	$8.0 \times 10^{-27}$	Iron(III) phosphate	$\text{FePO}_4$	$1.3 \times 10^{-22}$	Mercury(II) sulfide	$\text{HgS}$	$1.6 \times 10^{-52}$	Thallium(I) iodate	$\text{TiIO}_3$	$3.1 \times 10^{-6}$
Calcium carbonate	$\text{CaCO}_3$	$3.8 \times 10^{-9}$	Lead(II) arsenate	$\text{Pb}_3(\text{AsO}_4)_2$	$4.0 \times 10^{-36}$	Mercury(II) thiocyanate	$\text{Hg}(\text{SCN})_2$	$2.8 \times 10^{-20}$	Thallium(I) iodide	$\text{TlI}$	$6.5 \times 10^{-8}$
Calcium chromate	$\text{CaCrO}_4$	$7.1 \times 10^{-4}$	Lead(II) azide	$\text{Pb}(\text{N}_3)_2$	$2.5 \times 10^{-9}$	Nickel(II) carbonate	$\text{NiCO}_3$	$6.6 \times 10^{-9}$	Thallium(I) sulfide	$\text{Ti}_2\text{S}$	$6 \times 10^{-22}$
Calcium fluoride	$\text{CaF}_2$	$5.3 \times 10^{-9}$	Lead(II) bromate	$\text{Pb}(\text{BrO}_3)_2$	$7.9 \times 10^{-6}$	Nickel(II) hydroxide	$\text{Ni(OH)}_2$	$2.0 \times 10^{-15}$	Thallium(I) thiocyanate	$\text{TiSCN}$	$1.6 \times 10^{-4}$
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	$5.5 \times 10^{-6}$	Lead(II) bromide	$\text{PbBr}_2$	$4.0 \times 10^{-5}$	Nickel(II) sulfide	$\text{NiS}$	$3 \times 10^{-19}$	Thallium(III) hydroxide	$\text{Ti}(\text{OH})_3$	$6.3 \times 10^{-46}$
Calcium iodate	$\text{Ca}(\text{IO}_3)_2$	$7.1 \times 10^{-7}$	Lead(II) carbonate	$\text{PbCO}_3$	$7.4 \times 10^{-14}$	Scandium fluoride	$\text{ScF}_3$	$4.2 \times 10^{-18}$	Tin(II) hydroxide	$\text{Sn}(\text{OH})_2$	$1.4 \times 10^{-28}$
Calcium oxalate hydrate	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$1.96 \times 10^{-8}$	Lead(II) chloride	$\text{PbCl}_2$	$1.6 \times 10^{-5}$	Scandium hydroxide	$\text{Sc(OH)}_3$	$4.2 \times 10^{-18}$	Tin(II) sulfide	$\text{SnS}$	$1 \times 10^{-26}$
Calcium hydrogen phosphate	$\text{CaHPO}_4$	$1 \times 10^{-7}$	Lead(II) chromate	$\text{PbCrO}_4$	$2.8 \times 10^{-13}$	Silver arsenate	$\text{Ag}_3\text{AsO}_4$	$1.0 \times 10^{-22}$	Zinc carbonate	$\text{ZnCO}_3$	$1.4 \times 10^{-11}$

(continued)

**Table 7.7** (Continued)

Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	$1 \times 10^{-26}$	Lead(II) fluoride	$\text{PbF}_2$	$2.7 \times 10^{-8}$	Silver acetate	$\text{AgC}_2\text{H}_3\text{O}_2$	$2.0 \times 10^{-3}$	Zinc cyanide	$\text{Zn}(\text{CN})_2$	$3 \times 10^{-16}$
Calcium sulfate	$\text{CaSO}_4$	$9.1 \times 10^{-6}$	Lead(II) hydroxide	$\text{Pb}(\text{OH})_2$	$1.2 \times 10^{-5}$	Silver azide	$\text{AgN}_3$	$2.0 \times 10^{-8}$	Zinc hydroxide	$\text{Zn}(\text{OH})_2$	$1.2 \times 10^{-17}$
Calcium sulfite	$\text{CaSO}_3$	$6.8 \times 10^{-8}$	Lead(II) iodate	$\text{Pb}(\text{IO}_3)_2$	$2.6 \times 10^{-13}$	Silver benzoate	$\text{AgC}_7\text{H}_5\text{O}_2$	$2.5 \times 10^{-5}$	Zinc iodate	$\text{Zn}(\text{IO}_3)_2$	$3.9 \times 10^{-6}$
Chromium(II) hydroxide	$\text{Cr}(\text{OH})_2$	$2 \times 10^{-16}$	Lead(II) iodide	$\text{PbI}_2$	$7.1 \times 10^{-9}$	Silver bromate	$\text{AgBrO}_3$	$5.5 \times 10^{-5}$	Zinc oxalate	$\text{ZnC}_2\text{O}_4$	$2.7 \times 10^{-8}$
Chromium(III) hydroxide	$\text{Cr}(\text{OH})_3$	$6.3 \times 10^{-31}$	Lead(II) sulfate	$\text{PbSO}_4$	$1.6 \times 10^{-8}$	Silver bromide	$\text{AgBr}$	$5.3 \times 10^{-13}$	Zinc phosphate	$\text{Zn}_3(\text{PO}_4)_2$	$9.0 \times 10^{-33}$
Cobalt(II) carbonate	$\text{CoCO}_3$	$1.4 \times 10^{-13}$	Lead(II) sulfide	$\text{PbS}$	$3 \times 10^{-29}$	Silver carbonate	$\text{Ag}_2\text{CO}_3$	$8.1 \times 10^{-12}$	Zinc sulfide	$\text{ZnS}$	$2 \times 10^{-25}$
Cobalt(III) hydroxide	$\text{Co}(\text{OH})_3$	$1.6 \times 10^{-44}$	Lithium carbonate	$\text{Li}_2\text{CO}_3$	$2.5 \times 10^{-2}$	Silver chloride	$\text{AgCl}$	$1.8 \times 10^{-10}$			

Settleable solids is run in a calibrated cone-shaped glass container. It is a measure of the compaction ability of the active biomass to settle in a given period of time – usually 45 minutes. The results for settleable solids are give in  $\text{mll}^{-1}$ , and are a measure of how well the biosolids in the mixed liquor are going to settle in the clarifier.

## 7.14 Organic Chemicals

The field of organic chemistry is extremely broad, and would require several volumes to discuss with any useful information. Almost all organic compounds are measured by a combination of extraction and some type of thermal analyses, gas chromatography, mass spectrophotometry, and flame ionization, and some are analyzed by non-thermal techniques including liquid chromatography. However, in the environmental field, the most common set of compounds will be from petroleum derivatives. Again, that field is also very complex and would require several volumes to discuss adequately, but a brief discussion of the principal components of fuels would be in order.

BTEX (benzene, toluene, ethyl benzene, and xylene) are highly volatile, and some of the most frequently encountered petroleum derivatives encountered in the environmental business. They are part of the complex mixture that comprises gasoline and diesel oil; the issue of leaking underground storage tanks has dominated the environmental field for a number of years, and there is a well-documented history of the successful and unsuccessful attempts to remove these compounds from underground waters. BTEX compounds are flammable, volatile, soluble, and carcinogenic. Higher homologs of petroleum compounds are much more carcinogenic, but much less soluble. In the US and Europe, there has been an interest in the BTEX family because of the carcinogenicity. There are drinking water standards for the BTEX compounds: benzene ( $0.005 \text{ mg l}^{-1}$ ); ethylbenzene ( $0.7 \text{ mg l}^{-1}$ ); toluene ( $1 \text{ mg l}^{-1}$ ), and xylene (total for all forms =  $10 \text{ mg l}^{-1}$ ). The drinking water standard levels reflect to a large degree the concern for the compounds' ability to cause cancer by long-term exposure.

These and many other petroleum compounds will naturally degrade under both aerobic and anaerobic conditions, but the aerobic degradation rate is three or more times greater than the anaerobic degradation rate. Thus, the most common solutions for BTEX contamination in the groundwater is to (i) remove the material which is free product by evaporation – by forcing air through the ground to cause the compounds to evaporate; and (ii) remove the compounds from drinking water by a combination of aeration of the groundwater, and/or by providing oxygen to the groundwater to maintain aerobic conditions.

If one is dealing with a petroleum spill, recognize that petroleum is a mixture of many compounds of different molecular weights, densities, and solubilities.

When a spill occurs on water, there are different fractions that can be recovered easily. Some have estimated that only 10% of a crude oil spill is material that will float.<sup>21</sup> The balance will either sink or remain suspended in the water. The lighter compounds will disappear quickly in the environment, leaving the higher molecular weight compounds, such as naphthalenes, anthracenes, and asphaltenes, as residual. Some of these compounds can be recovered and/or biodegraded with great difficulty. Many of the compounds have some very slight solubility, and that can exert a BOD, and at the same time, be somewhat resistant to unacclimated bacteria. In Ecuador, investigating older oil spills and drill pits, for example, our team could not find BTEX in the open environment due to biodegradation and warm temperatures which caused evaporation of the BTEX compounds.

## Notes

- 1 See <http://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods> for the 5th and most current edition. There is a 4th edition of the manual available from: <http://www3.epa.gov/npdes/pubs/atx.pdf>.
- 2 Quoting from the State of Georgia Water Quality Standards: [http://epd.georgia.gov/sites/epd.georgia.gov/files/related\\_files/site\\_page/EPA\\_Approved\\_WQS\\_May\\_1\\_2015.pdf](http://epd.georgia.gov/sites/epd.georgia.gov/files/related_files/site_page/EPA_Approved_WQS_May_1_2015.pdf). Bacteria: For the months of May through October, when water contact recreation activities are expected to occur, fecal coliform not to exceed a geometric mean of 200 per 100 ml based on at least four samples collected from a given sampling site over a 30-day period at intervals not less than 24 hours. Should water quality and sanitary studies show fecal coliform levels from non-human sources exceed 200/100 ml (geometric mean) occasionally, then the allowable geometric mean fecal coliform shall not exceed 300 per 100 ml in lakes and reservoirs and 500 per 100 ml in free flowing freshwater streams. For the months of November through April, fecal coliform not to exceed a geometric mean of 1000 per 100 ml based on at least four samples collected from a given sampling site over a 30-day period at intervals not less than 24 hours and not to exceed a maximum of 4000 per 100 ml for any sample. The State does not encourage swimming in surface waters since a number of factors which are beyond the control of any State regulatory agency contribute to elevated levels of fecal coliform.
- 3 Personal communication from Millipore Corporation with publication No. 2016-02-01-142519-1 in PDF.
- 4 There is a difference of opinion on the usefulness of  $BOD_5$ . As a design parameter, it can be quite useful as it helps define the oxygen demand, but as a control parameter for operation of a treatment plant, and indicator of water quality, it is less useful because of the lag time between the sampling and the results. By protocol, the minimum time is 5 days for incubation, and the lag

between the sampling and the analysis is generally around 7 days for reporting and receipt of the results. Most industrial and municipal wastewater treatment plants do not hold their wastewater more than 12–24 hours, and  $\text{BOD}_5$  results will tell the operator what he was treating 5–7 days ago. Similarly,  $\text{BOD}_5$  results for a river will indicate the water quality of the river 5 days travel-time downstream.

- 5 See Third Century of Biochemical Oxygen Demand, by Rodger B. Baird and Roy-Keith Smith, published by the Water Environment Federation, 2002.
- 6 APHA, AWWA & WEF, *Standard Methods*, 19th ed., p. 5–3.
- 7 In some states, treatment plants are issued permits with a  $\text{BOD}_5$  level in their permit of less than  $3 \text{ mg l}^{-1}$ . While not a regular practice, it does occur for treatment plants discharging to lakes where communities are using the lake for a water supply.
- 8 The Georgia Environmental Protection Division of Department of Natural Resources, has limited the Gwinnett County Water Reclamation Facility to a  $\text{BOD}_5$  value under  $4 \text{ mg l}^{-1}$  in their effluent. In fairness, the GCWRF has advanced treatment, including phosphorus removal and membrane filtration. The effluent  $\text{BOD}_5$  is less than the comparable value for the water in Lake Lanier, the water supply source for Atlanta, Gainesville, and other North Georgia Communities.
- 9 A discussion with Sheldon Manufacturing ([www.shellab.com](http://www.shellab.com)) indicated that the trend in BOD incubators has changed to all solid-state cooling/heating units because they are more efficient. The older-style small heater unit that was manufactured to convert refrigerators into BOD incubators is no longer in use because it cannot hold the temperature specification within  $0.5^\circ\text{C}$ .
- 10 Roger B. Baird and Roy-Keith Smith, Third Century of Biochemical Oxygen Demand, published by the Water Environment Federation, pages 71–75.
- 11 See: [http://www.hach.com/cms-portals/hach\\_com/cms/documents/pdf/Methods-Guidelines>SelectingtheCorrectCODProcedure.pdf](http://www.hach.com/cms-portals/hach_com/cms/documents/pdf/Methods-Guidelines>SelectingtheCorrectCODProcedure.pdf).
- 12 “Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals,” by Yoon-Chang Kim, Satoshi Sasaki, Kazuyoshi Yano, Kazunori Ikebukuro, Kazuhito Hashimoto and Isao Karube, published in *Water Research*, Feb. 1999.
- 13 [http://waterfacts.net/Treatment/Activated\\_Sludge/BOD-COD-TOC/COD\\_Ratio\\_Examples/cod\\_ratio\\_examples.html](http://waterfacts.net/Treatment/Activated_Sludge/BOD-COD-TOC/COD_Ratio_Examples/cod_ratio_examples.html).
- 14 Biochemical and other oxidation pathways for the formation of sulfuric acid are given in the following presentation: [http://www4.ncsu.edu/~franzen/public\\_html/Poland/Poznan08a/Sulfur\\_Cycle.pdf](http://www4.ncsu.edu/~franzen/public_html/Poland/Poznan08a/Sulfur_Cycle.pdf).
- 15 In Terre Haute, Indiana, for example, home hot-water heaters needed to be replaced on average about every 5–7 years because of calcium carbonate scale buildup. If the house had a water softener, the average hot-water heater life was over 23 years. See Widder, S.H. and Baechler, M.C. (2013) Impacts of Water Quality on Residential Water Heating Equipment, Department of

- Energy publication PNL22921: [https://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22921.pdf](https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22921.pdf)
- 16 The USEPA limits  $\text{NO}_3$  in drinking water to  $10 \text{ mg l}^{-1}$ ; WHO limits are  $50 \text{ mg l}^{-1}$ . For nitrite,  $\text{NO}_2$ , the EPA limit is  $1 \text{ mg l}^{-1}$ , and the WHO limit is  $0.5 \text{ mg l}^{-1}$ ; also see [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/nitratenitrite2ndadd.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/nitratenitrite2ndadd.pdf)
  - 17 "Global potential of phosphorus recovery from human urine and feces", by James R. Mihelcic, Lauren M. Fry, and Ryan Shaw, *Chemosphere*, Vol. 84 Aug 2011, pp. 832–839.
  - 18 "Solubility of cadmium sulfide (greenockite) in sulfidic waters at 25 degrees C", by Kostas D. Daskalakis and George R. Helz, *Environmental Science & Technology*, 1992, 26 (12), pp. 2462–2468. DOI: <https://doi.org/10.1021/es00036a019>
  - 19 *Sulfide Precipitation of Heavy Metals*, USEPA Publication Number EPA-600/2-80-139 1980. The publication is available on the Internet at the EPA website.
  - 20 <http://www.nrel.gov/biomass/pdfs/42621.pdf>, *Determination of total solids in biomass and total solids in liquid process samples* NREL TP 510-42 621 (1980).
  - 21 *Characterization and Properties of Petroleum Fractions* by Edier Briceno Aranguri, published by ASTM, Stock Number MNL50–2005.

## 8

# Basic Water and Wastewater Treatment Techniques

This chapter is a collection of various techniques for removing various compounds and substances that are not covered in later chapters. For example, there are several ways of removing ammonia and nitrate from industrial wastewater. Those techniques are substantially different from the ones used for treating and removing nitrate and ammonia in wastewater where there is active biomass, such as in a wastewater (sewage or biological) treatment plant. Some ideas may be useful, and others less so.

## 8.1 Removal of Metals

One of the easiest ways to remove most metals from wastewater is by precipitation – either batch precipitation or continuous precipitation, followed by filtration. In order to accomplish that, one has to control the solubility of the metals, generally by adjusting the pH of the solution or by co-precipitating them with other compounds. Then filter the solution to remove the suspended non-settling materials, and dewater and treat the sludge accordingly.

Here's how it's done. Start by looking at the tables of solubility products and see what goes with what, matching the anions with the cation metals you have in your waste stream. (The solubility values are found in Table 7.7 in the previous chapter. Further data are given in Tables 8.1–8.5.) Some of the most common low solubility products are found with hydroxide and sulfide ions. But there are specific considerations for each compound you have to treat. Taking another look at Figure 7.10 from the previous chapter, one can see that there are preferential levels of pH for optimum metal removal by precipitation. The optimum removal of  $\text{Cr}^{3+}$  occurs at a pH of about 7.4, while the optimum level of zinc precipitation occurs at a pH of about 10.3, and if the wastewater has, in addition, nickel or cadmium, even a higher pH will be necessary to precipitate Cd or Ni to their lowest levels. Optimizing the removal of one metal necessarily de-optimizes the removal of another metal.

**Table 8.1** Selective comparison of solubility products or solubilities\* for certain metal compounds.<sup>1</sup>

Metal cation	Hydroxide	Sulfide, sulfate, sulfite	Phosphate	Carbonates and other
Aluminum	$4.6 \times 10^{-33}$		$9.84 \times 10^{-21}$	$*5420 \text{ g l}^{-1}$
Barium	$5 \times 10^{-3}$	$*73.3 \text{ g l}^{-1}$ ; $1.1 \times 10^{-10}$ ; $8 \times 10^{-7}$	$*9 \text{ mg l}^{-1}$ as $\text{Ba}_2\text{P}_2\text{O}_7$	$2.58 \times 10^{-9}$
Chromium(III)	$6.3 \times 10^{-31}$			
Chromium(II)	$2 \times 10^{-16}$			
Copper	$2.2 \times 10^{-20}$	$2.5 \times 10^{-48}$	$1.4 \times 10^{-37}$	$1.4 \times 10^{-10}$
Cadmium	$2.5 \times 10^{-14}$	$8.0 \times 10^{-27}$	$2.5 \times 10^{-33}$	$1.1 \times 10^{-12}$
Lead	$1.43 \times 10^{-20}$	$3 \times 10^{-28}$ $2.53 \times 10^{-8}$		$7.4 \times 10^{-14}$
Mercury	$3.6 \times 10^{-26}$	$2 \times 10^{-53}$ $6.5 \times 10^{-27}$		$3.6 \times 10^{-14}$

**Table 8.2** Solubility products of cadmium ions in water.

Compound name	Formula	Solubility product
Cadmium arsenate	$\text{Cd}_3(\text{AsO}_4)_2$	$2.2 \times 10^{-33}$
Cadmium carbonate	$\text{CdCO}_3$	$10^{-12}$
Cadmium hydroxide	$\text{Cd(OH)}_2$	$7.2 \times 10^{-15}$
Cadmium phosphate	$\text{Cd}_3(\text{PO}_4)_2$	$2.53 \times 10^{-33}$
Cadmium sulfide	$\text{CdS}$	$10^{-27}$

**Table 8.3** Solubility products of various iron compounds.

Compound	Formula	Solubility product
Iron(II) carbonate	$\text{FeCO}_3$	$3.13 \times 10^{-11}$
Iron(II) fluoride	$\text{FeF}_2$	$2.36 \times 10^{-6}$
Iron(II) hydroxide	$\text{Fe(OH)}_2$	$4.87 \times 10^{-17}$
Iron(II) sulfide	$\text{FeS}$	$8 \times 10^{-17}$
Iron(III) hydroxide	$\text{Fe(OH)}_3$	$2.79 \times 10^{-39}$
Iron phosphate	$\text{FePO}_4 + 2\text{H}_2\text{O}$	$9.91 \times 10^{-16}$

**Table 8.4** Solubility products for zinc compounds in water.

Compound	Formula	Solubility product
Zinc arsenate	$\text{Zn}_3(\text{AsO}_4)_2$	$2.8 \times 10^{-28}$
Zinc carbonate	$\text{ZnCO}_3$	$1.46 \times 10^{-10}$
Zinc hydroxide	$\text{Zn}(\text{OH})_2$	$3 \times 10^{-17}$
Zinc selenide	$\text{ZnSe}$	$3.6 \times 10^{-26}$
Zn sulfide: (Alpha form)	$\text{ZnS}$	$2 \times 10^{-25}$
(Beta form)		$3 \times 10^{-23}$

**Table 8.5** Solubility products for mercury in water.

Compounds	Formula	Solubility product
Mercury(I) bromide	$\text{Hg}_2\text{Br}_2$	$6.4 \times 10^{-23}$
Mercury(II) bromide	$\text{HgBr}_2$	$6.2 \times 10^{-20}$
Mercury carbonate	$\text{Hg}_2\text{CO}_3$	$3.6 \times 10^{-17}$
Mercury sulfide (black)	$\text{HgS}$	$2 \times 10^{-53}$
Mercury sulfide (red)	$\text{HgS}$	$2 \times 10^{-54}$
Mercury hydroxide (yellow precipitate when $\text{OH}^-$ ions contact $\text{Hg}^+$ ions)	$\text{HgO}$	$3.6 \times 10^{-26}$

The solution may involve two-level and two-tank pH control. An expensive solution to a removal problem, and the consequence of the removal of Cr and Cu between pH 7 and 8, would be poor removal of many other metals.

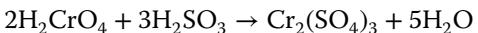
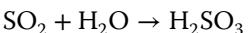
However, there is a problem with this solution because precise pH control is often difficult to achieve, and obviously, two tanks and control systems for pH control are twice as expensive as one. One possible solution is to remove the metals by sulfide or phosphate precipitation.

Note that for some cations, solubility products are not available due to their form or lack of commercial interest. In that regard, the chemical handbooks are of little use because they list solubility of metals in grams per 100 ml of water, and list a chemical as insoluble if it is less than 1 g/100 ml.

## 8.2 Chromium

Chromium is a special case. Hexavalent chromium ( $\text{Cr}^{6+}$ ) is highly toxic, and while it was used, and is still used, in some non-comfort cooling towers and

as a passivator for corrosion control, it also served as a bactericide, and it can be found in some industrial processes, in electroplating, and some oil well drilling and gas fracking. In order to precipitate Cr<sup>6+</sup>, one first has to reduce it to Cr<sup>3+</sup> by using an acid solution of pH 2–2.5 with sodium or calcium bisulfite, or sulfur dioxide gas (SO<sub>2</sub>), or with ferrous sulfate or other sulfite-containing compounds. The reduction makes possible the removal of chromium as the trivalent hydroxide, which precipitates under alkaline conditions. Typical reactions for SO<sub>2</sub> reduction are as follows:

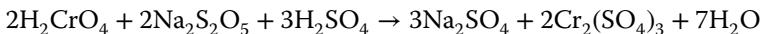


*Caution:* SO<sub>2</sub> is a toxic gas and it has an OSHA limit of 2 ppm (v) in air, so if used as a treatment system, it needs to be in a well ventilated and monitored area. Never try this reaction if there is cyanide of any form in the water – see below.

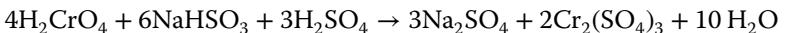
### 8.2.1 Other Chromium Reduction Reactions

Representative reactions for reduction of hexavalent chromium under acidic conditions using sulfite chemicals instead of SO<sub>2</sub> are shown below:

(a) Using sodium metabisulfite with sulfuric acid:

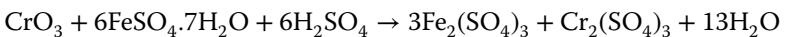


(b) Using sodium bisulfite with sulfuric acid:



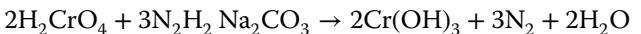
A similar reaction can be obtained by using sodium sulfite. Sodium sulfide is also acceptable as a reducing compound.

The reaction with ferrous sulfate merely reduces the chromium(VI) to chromium(III) when it needs to be precipitated with hydroxide or preferably with sulfite. Where ferrous sulfate is readily available, it can be used for reduction of hexavalent chromium – the reaction is as follows:



The difficulty of using ferrous sulfate as a reducing agent is that, while it is effective, if the solution needs to be filtered, either the sludge or the liquid, the presence of trivalent iron makes that much more difficult because it tends to coat (slime) the filter medium and is difficult to remove.

Hexavalent chromium can also be reduced to trivalent chromium in an alkaline environment using sodium hydrosulfite, or hydrazine as shown below. The reaction is somewhat advantageous because they cause the chromium to be precipitated as a hydroxide.



In a recent article, Wang, Bush, Sullivan and Liu proposed a method for simultaneous reduction of chromium(VI) and arsenic(III) under acidic conditions.<sup>2</sup> There are also proprietary compounds that can reduce chromium(VI) to chromium(III) in an alkaline medium.

### 8.3 Arsenic

Arsenic is an unusual and highly toxic metal. It can have oxidation states or valences anywhere from +5 to −3. Arsenic is relatively soluble at  $37\text{ g l}^{-1}$ . The most common form is  $\text{As}_2\text{O}_3$  but there are many other forms, including weak acids which are less soluble.<sup>3</sup> Most encounters with arsenic would be with the forms  $\text{H}_3\text{AsO}_4$ ,  $\text{AsO}_4^{3-}$ , and  $\text{H}_2\text{AsO}_3^-$  from the aquatic form of naturally occurring compounds in rock. The distribution of arsenic in water is quite wide. The USGS has an excellent website discussing the geochemistry of arsenic in the Willamette Basin in Oregon<sup>4</sup> and in the US overall.<sup>5</sup>

When arsenic is encountered in groundwater or drinking water, it should be removed because it is a health risk. The USEPA has established the permissible level of arsenic in drinking water as  $10\text{ }\mu\text{g l}^{-1}$ . One of the best techniques for removal would be the absorption on iron oxides. As an example, arsenic groundwater contamination in India and Bangladesh came to worldwide attention in 1995. The arsenic contamination of the groundwater was well above the WHO standard of 10 ppb, and many residents were exhibiting symptoms of arsenic poisoning. Because the communities were poor and relied upon “tube wells” for their water from the contaminated source, a simple solution was obtained using plastic buckets with iron filings and scrap, followed by filtration through carbon and sand.<sup>6</sup>

Where arsenic is present, one of the accepted techniques for removal is treatment with ferric chloride, or activated aluminum, or oxidation with hydrogen peroxide to insure that the arsenic is in the highest oxidation state, followed by exposure to ferric ions.<sup>7</sup> The arsenic will bind tightly to the iron oxide. The used iron and aluminum arsenic compounds should be treated as a hazardous waste and disposed of accordingly so that it cannot be reused, as the arsenic will volatilize under high heat.

### 8.4 Cadmium

Cadmium is largely used in electroplating. It is quite poisonous to aquatic and human life and it does bio-accumulate.<sup>8</sup> Cadmium was used in nickel-cadmium batteries, but such batteries are being gradually phased out because of the toxicity of cadmium, and the difficulty in obtaining safe disposal. If cadmium is in the wastewater, there are three preferential techniques for removal: hydroxide,

phosphate, and sulfide precipitation. Cadmium carbonate is quite insoluble, but other forms are much more insoluble as illustrated in Table 8.2.

## 8.5 Iron

Iron removal is relatively easy, as the solubility product of  $\text{Fe}^{3+}$  even as the hydroxide is quite low. The principal thing about iron is that it has two forms: the 2+ and the 3+ oxidation states. Iron can be removed satisfactorily in the 2+ oxidation state, by precipitation with other compounds. However, in the 3+ oxidation state, iron naturally forms a highly insoluble precipitate – but it is difficult to filter as it forms a slime, and that dramatically reduces the filtration efficiency and increases the head losses. Iron in the 2+ state is a blue-green color in water, or in low concentrations, and mainly invisible. Iron in the 3+ oxidation state is highly visible as a rust-colored precipitate. So, if you have iron (even as little as  $0.3 \text{ mg l}^{-1}$ ) that you need to remove from the water, oxidize it and filter it because that's the cheapest alternative. As an aside note, iron will cause staining on fixtures and porcelain in concentrations as low as  $0.3 \text{ mg l}^{-1}$ . In a recent water treatment assignment for boiler water feed, we had to oxidize the iron with hydrogen peroxide to convert it to the  $\text{Fe}^{3+}$  state and filter it out with a pre-filter before the feed stream was sent either to an ion exchange system or to a reverse osmosis system – because the iron would blind either the membrane, or the resin, whichever was used first. One other note: the iron slimes, once deposited on filter cloths, tanks, and so on, are best removed in a buffered acidic solution of pH 3–5 with a non-foaming detergent.

## 8.6 Zinc

Zinc is widely used in electroplating as a corrosion cover for ferrous metals. The zinc oxidizes in the air and forms a coating that prevents further corrosion to the underlying base metal. Zinc is slightly soluble in water, and it is an essential nutrient for human life, but there are water quality standards for zinc of the order of  $0.05 \text{ mg l}^{-1}$ , varying from State to State.<sup>9</sup>

## 8.7 Mercury

Mercury is a heavy (density  $13.6 \text{ g cm}^{-3}$ ) metal, and liquid at room temperature. It has a wide number of uses, many associated with pressure measurement, manometers (sphygmomanometers), and so on, as well as uses for contacts in

electrical switches. Mercury is also quite toxic, despite the fact that it was, at one time, used as a treatment for venereal disease, and has been used as a fungicide and bactericide. It is bio-accumulative, and is often found with zinc. Some industries, including chlorine manufacturing, still use carbon electrodes submerged in a pool of mercury to generate the disassociation of salt that generates chlorine.<sup>10</sup> Despite the fact that mercury has an extremely low vapor pressure of 0.002 mmHg at 25°C, the current practice is to keep mercury out of schools and classrooms, and engage in a thorough cleaning program if there is even the slightest amount of mercury spilled. The Center for Disease Control (CDC) has the following guidance on mercury in their TOXIFACTS:

Because mercury occurs naturally in the environment, everyone is exposed to very low levels of mercury in air, water, and food. Between 10 and 20 nanograms of mercury per cubic meter ( $\text{ng m}^{-3}$ ) of air have been measured in urban outdoor air. These levels are hundreds of times lower than levels still considered to be “safe” to breathe. Background levels in nonurban settings are even lower, generally about  $6 \text{ ng m}^{-3}$  or less. Mercury levels in surface water are generally less than 5 parts of mercury per trillion parts of water (5 ppt, or 5 ng per liter of water), about a thousand times lower than “safe” drinking water standards. Normal soil levels range from 20 to 625 parts of mercury per billion parts of soil (20–625 ppb; or 20 000–625 000 ng per kilogram of soil).<sup>11</sup>

Similarly, the National Institute for Occupational Health and Safety (NIOSH) recommendations on mercury exposure are:

Threshold limit value (TLV):  $0.025 \text{ mg m}^{-3}$  as time-weighted average (skin); OSHA permissible exposure limit (PEL): C  $0.1 \text{ mg m}^{-3}$

NIOSH recommended exposure limit (REL): Hg vapor: time-weighted average  $0.05 \text{ mg m}^{-3}$  skin

Other: C  $0.1 \text{ mg m}^{-3}$  skin

NIOSH IDLH (immediately dangerous to life and health):  $10 \text{ mg m}^{-3}$  (as Hg)

Contact with halides and ammonia need to be avoided, as violent reactions can occur.

If you have mercury in the water, the best bets for removal are with sulfide, iodide, hydroxide, and bromide.

## 8.8 Radium

It is unlikely that one will encounter radium in wastewater, unless you are dealing with mine waters. Then the water tends to be quite salty (greater salinity than seawater), and it may contain radium (Table 8.6).

**Table 8.6** Characteristics of radium-bearing waters from Piast Mine in western Poland. Note that figures are given in dm<sup>3</sup>, which is equivalent to liters.

Parameter	Unit	Type A	Type B
Conductivity	S cm <sup>-1</sup>	151 000	91 000
pH		7.25	7.53
TDS at 378 K	mg dm <sup>-3</sup>	124 300	85 300
<sup>226</sup> Ra	Bq dm <sup>-3</sup>	62.76	3.449
<sup>228</sup> Ra	Bq dm <sup>-3</sup>	34.67	5.1
<i>Cations</i>			
Ca <sup>2+</sup>	mg dm <sup>-3</sup>	6500	1840
Mg <sup>2+</sup>	mg dm <sup>-3</sup>	3750	1980
Na <sup>+</sup>	mg dm <sup>-3</sup>	34 720	28 050
K <sup>+</sup>	mg dm <sup>-3</sup>	299	268
Fe	mg dm <sup>-3</sup>	0.05	0.05
Mn <sup>2+</sup>	mg dm <sup>-3</sup>	0.05	0.05
Ba <sup>2+</sup>	mg dm <sup>-3</sup>	1480	—
Total	mg dm <sup>-3</sup>	46 740	32 140
<i>Anions</i>			
Cl <sup>-</sup>	mg dm <sup>-3</sup>	77 350	50 830
SO <sub>4</sub> <sup>2-</sup>	mg dm <sup>-3</sup>	0	2140
CO <sub>3</sub> <sup>2-</sup>	mg dm <sup>-3</sup>	0	0
HCO <sub>3</sub> <sup>-</sup>	mg dm <sup>-3</sup>	24.4	67.1
SiO <sub>4</sub> <sup>4-</sup>	mg dm <sup>-3</sup>	2	3.45
Br <sup>-</sup>	mg dm <sup>-3</sup>	241	155
J <sup>-</sup>	mg dm <sup>-3</sup>	10.9	11.2
Total	mg dm <sup>-3</sup>	77 630	53 210

Radium is the one element that has little or no practical use, but which is extremely dangerous and it is the international standard for radioactivity – the most radioactive substance on earth. Radium is in the calcium family, and because it is an alpha emitter, it is something that one should not handle.

Radium is soluble in a number of dilute acids, but can be removed by chemical precipitation with sulfates to  $2.1 \times 10^{-2}$  mg l<sup>-1</sup>, and that is well above the drinking water standard which is 5 becquerels (picocuries) per liter, and still unsafe to drink. One of the most effective methods for radium removal is by addition of barium sulfate to the radium-containing waters. The coprecipitation can render

**Table 8.7** Results of radium removal trials – results are in Be/l.

	Analysis		Average $^{228}\text{Ra}$	Analysis		Average $^{226}\text{Ra}$	Contents
	1	2		1	2		
	3.371	3.608	3.4895	6.47	7.07	6.77	Raw water
7478A	2.219	2.191	2.205	4.66	4.45	4.555	100% sand
7479A	0.01	0.024	0.017	0.01	0	0.005	10% $\text{MnO}_2$ , 90% sand
7460A	0.037	0.037	0.037	0	0	0	20% iron, 20% $\text{BaSO}_4$ , 60% sand
<i>DOWEX radium removal resin – control</i>							
7458A	0.006	0.001	0.0035	0.02	0.1	0.06	Dowex Resin
7463A	0.417	0.451	0.434	0.86	0.96	0.91	Dowex Resin

the radium concentration in water less than 1 Bq/l.<sup>12</sup> The precipitate will be a hazardous radioactive waste, and must be properly placarded and disposed of in a nuclear landfill. The author has had some success removing radium from saline mine water by using manganese-treated greensand (glauconite), regenerated with potassium permanganate. Dow Chemical also makes a specific resin for ion exchange of radium from salt waters.

The data in Table 8.7 from 2007 experiments at the Central Mining Institute, Katowice, Poland, illustrate the removal ability of barium sulfate on radium. In the table, the leftmost column is the laboratory control number of the tests on the raw and treated mine waters.

The conclusions from the study are shown below:

The majority of the tests were conducted on Piast Mine water. The mine water had the following characteristics, as measured by the Radiometric Laboratory. No attempt was made to determine other chemical characteristics of the mine waters other than radium.

In order to evaluate the radium removal ability of the various substances added to the zeolites mixtures, we ran experiments with sand, iron and barium sulfate separately. The results are shown in the table [Table 8.7]. The Piast Mine water has a natural radioactivity level of 3.49 Bq/l as  $\text{Ra}^{228}$  and 6.77 Bq/l as  $\text{Ra}^{226}$ . When the Piast mine water was filtered through fine-grained sand, having a grain size less than 0.1 mm (estimated) the analysis indicated that only a very small portion of radium had been removed. The counts after filtration were: 2.205 Bq/l as  $\text{Ra}^{228}$  and 4.555 Bq/l as  $\text{Ra}^{226}$  respectively. A second test using barium sulfate

and iron and sand alone produced superior results, with the respective counts of 0.037 Bq/l as Ra<sup>228</sup> and 0 Bq/l as Ra<sup>226</sup>. This test is possibly the best result obtained, and it is the barium sulfate rather than the iron which is responsible for the precipitation.

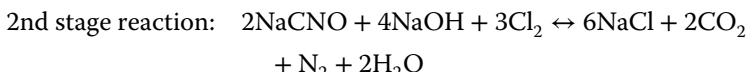
## 8.9 Anions

### 8.9.1 Cyanide

Cyanide (CN<sup>-</sup>) complexes well with many substances and is used in surface finishing of metals, and gold extraction. The ferric and ferrous cyanide is used in the laboratory as an oxidation promoter, and it is also used in making the pigment Prussian Blue. The potassium salt of cyanide (KCN) is used in gold mining where dilute solutions are sprayed on low-quality ore to dissolve the metal from the rock. Potassium cyanide is quite toxic, as is sodium cyanide.

The active agent here is the cyanide because it bonds to the iron in hemoglobin in the blood, preventing the iron from collecting oxygen. The compounds need to be handled with proper safety equipment in a well-ventilated environment.

Cyanides are best destroyed through alkaline chlorination. Never let a waste stream containing cyanide become acidic. Raise the pH to between 10 and 12, and add sufficient chlorine to destroy the cyanide. Normally the cyanide is in the form of sodium cyanide (see Table 8.8), which is destroyed through the following two-stage reactions:



The pH must be at least 10 by addition of caustic materials, generally NaOH. After that, the oxidation reduction potential (ORP) is then increased to approximately (+) 250 mV by addition of an oxidizing agent (for example, hypochlorite). ORP is monitored to track the sharp change that occurs (typically 50 mV) when all the cyanide is oxidized to cyanate. This reaction takes place in 15–30 min with continuous mixing.

If the treatment system is a batch system or even a continuous system, the second phase of the treatment is conducted at pH 8.5 to 9. Additional alkaline materials (NaOH) may be required to maintain the pH, and additional oxidant (chlorine) may be required to raise the ORP to +300 mV.<sup>13</sup>

Cyanides can also be destroyed by the use of hydrogen peroxide at a pH of 10, in the presence of a catalyst.<sup>14</sup> The precious metals mining industry has also generated a number of publications on the destruction of cyanates and their compounds by use of Fe(IV) in the wastewater.<sup>15</sup>

**Table 8.8** Toxicity of cyanide compounds.

Toxicity of potassium cyanide	Toxicity of sodium cyanide
Lethal dose or concentration (LD, LC):	Lethal dose or concentration (LD, LC):
LD50 (median dose)	LD50 (median dose)
5 mg kg <sup>-1</sup> (oral, rabbit)	6.44 mg kg <sup>-1</sup> (oral, rat, oral)
10 mg kg <sup>-1</sup> (oral, rat)	4 mg kg <sup>-1</sup> (oral, sheep)
5 mg kg <sup>-1</sup> (oral, rat)	15 mg kg <sup>-1</sup> (oral, mammal)
8.5 mg kg <sup>-1</sup> (oral, mouse)	8 mg kg <sup>-1</sup> (oral, rat)
US health exposure limits (NIOSH) – air:	US health exposure limits (NIOSH) – air:
PEL (Permissible)      TWA 5 mg m <sup>-3</sup>	PEL (Permissible)      TWA 5 mg m <sup>-3</sup>
REL (Recommended)      C 5 mg m <sup>-3</sup> (4.7 ppm)	REL (Recommended)      C 5 mg m <sup>-3</sup> (4.7 ppm)
IDLH (Immediate danger) 25 mg m <sup>-3</sup>	IDLH (Immediate danger) 25 mg m <sup>-3</sup> (as CN)

### 8.9.2 Nitrates and Nitrites

Nitrates and nitrites represent a unique challenge for the wastewater treatment engineer. In domestic wastewater, the formation of nitrates is often encouraged because of the toxicity of ammonia and the natural conversion of ammonia to nitrite and then nitrate. Nitrates, and to a lesser extent nitrites, can serve as an oxygen reservoir in a biological treatment system. In drinking water situations and some industrial waste situations, nitrate is undesirable. We will focus on nitrate because the conversion of nitrite to nitrate by biological means is very fast, and the nitrite does not generally accumulate.

There are several ways of removing nitrate from wastewater. Unfortunately the two best ways are through ion exchange and biological treatment. Anion exchange can be a very efficient removal agent for nitrate, but there is a caveat. Assuming you have an ion exchange system, what do you do with the regenerant? It will contain all the nitrate you have removed, only in a much smaller volume which may be harder to treat and destroy. One author, Van der Hoek, reported success in biologically treating and denitrifying spent regenerant solutions using a sequencing batch reactor.<sup>16</sup> The regenerant is treated separately, and the bacteria do not contact the raw water solution. It is believed that the batch system also requires the addition of methanol to facilitate the nitrate removal. Biological reduction of nitrate is not covered here but in the material on biological wastewater treatment. It takes a reducing environment of around -100 mV in order to get the nitrate to reduce to ammonia and then to N<sub>2</sub> gas.

There are other possible mechanisms for nitrate reduction using catalysts, but they are considerably more expensive and difficult to manage.<sup>17</sup>

## 8.10 Solvents and Oils

Solvents, petroleum, and oils are ubiquitous in industrial wastewaters. As such, they often present a specialized challenge, especially if either the solvents or oils contain phenols or chlorinated products. Oils generally are lighter than water, but there is a special category of oils (water-soluble oils) formulated to produce a stable emulsion which does not want to separate. Most of the time, these water-soluble oils are used in machining and have a milky appearance with an oily smell. (Caution: many of these oils are excellent media for growing bacteria and molds which can easily create contact dermatitis. Be careful in handling them and always wear protective gloves.)

If you have emulsified oils, generally they will be “worn” or “worked,” and the working process tends to loosen the chemical bonds that are holding the oil droplets or molecules in emulsification. If you have emulsified oils, try lowering the pH of the wastewater to 2 and wait a few minutes. If the oil breaks, it will result in an oil layer on the top of the water. If, after a few minutes, the oil does not break into distinct layers, add a trivalent metal, usually ferric sulfate or aluminum sulfate, in increasing measured doses until the emulsion does break. Then neutralize the waste back to near-neutral but less than pH 8 with milk of lime. The lime will precipitate the sulfate, giving  $\text{CaSO}_4$  and  $\text{Al(OH)}_3$  or  $\text{Fe(OH)}_3$ . The flocs will also help to bring down the other suspended solids in the solution and clarify it, leaving a light yellow liquid. At that point, the demulsified oil can be skimmed off or removed by flotation.

If one has free oil, it should first be removed by use of a chevron style or wire mesh style coalescer. The principle these machines operate on is that the free oil travels a tortuous pathway and will collide and coalesce and float to the surface where they are ready for collection.

If the stream is clean and has little or no suspended solids and is not chemically emulsified, consider using a cloth-type coalescer. These are usually made of polyethylene or polypropylene plastic felt spun into a coarse yarn and wrapped around a plastic filter element. The coalescer elements are often very similar in design and sizing to large cartridge filters. The flow is generally from outside to inside, under pressure, and the oil is collected at the top of a pressure chamber and released for recovery by a float switch. This type of coalescer is excellent at breaking physical emulsions with low to moderate head losses.

The coalescers generally will remove free oils to less than 20 ppm, and in some instances below 15 ppm, (after which there is no visible sheen on the liquid). By comparison, an API separator (Figure 8.1) is significantly larger and will remove oils to about 30–50 mg l<sup>-1</sup>, with some units removing oils to lower

levels. The API separator was developed by the American Petroleum Institute and it uses gravity separation. The API separator design is contained in API Specification 421. Some of the features are described below:

*Length to width ratio.* A minimum length to width ratio of 5 : 1 is recommended for all API separator designs to keep operating conditions close to plug flow.

*Depth to width ratio.* A minimum depth to width ratio of 0.3–0.5 is recommended.

*Maximum channel width and depth.* The maximum API separator channel width is 20 ft; maximum depth is 8 ft.

*Horizontal velocity.* Maintain a horizontal velocity of no more than 3.0 ft s<sup>-1</sup>

*Inlet distribution.* Tanks should have baffles to minimize the effect of high wastewater inlet velocities into the separator; it is recommended that the inlet be configured with baffles to diffuse the inlet flow across the width of the tank.

*Oil particle size.* An API separator is fairly good at removing oil particles larger than 150 µm under the current specification and design basis. Removal of smaller diameter oil particles will require specialized design, downstream treatment, or other facilities.

*Design features.* Additional features inside the separator include baffles to prevent short-circuiting, a scraper to remove settled solids from the tank floor, and a floating oil skimmer at the end of the unit to help keep oil from the discharge, and a method for removing accumulated oils from the surface of the separator on a continuous or intermittent basis, and if the escape of volatile organics is of concern, hatch covers on the elements of the separator to reduce the loss of VOCs. Depending upon the oil and its volatility and flammability, inert gas (nitrogen, carbon dioxide, or other) may be necessary to reduce the possibility of fire or explosion.

## 8.11 Chlorinated Organics

The discussion of chlorinated organics is extremely broad, and a simple discussion of the properties and toxicity of the subject has filled a number of libraries. This introduction is primarily focused on some of the principles of dealing with some of the more common chlorinated organic compounds, and not a treatise on organic chemistry.

Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub>, is a powerful solvent in a family of chlorinated compounds, and is still used as a paint stripper and degreaser in many industrial applications. It is also highly carcinogenic. Other common solvent compounds include PERC (tetrachloroethylene or cleaning fluid), carbon tetrachloride (now generally excluded from use because of its toxicity), and compounds such as chloroform, 1,1,2 trichloroethane, methylchloroform,

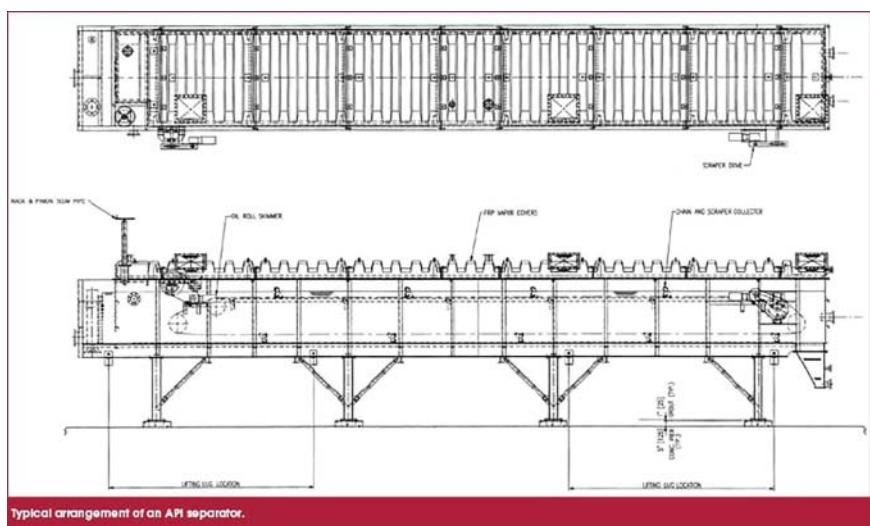


Figure 8.1 API separator from DKV Refinery, Salambatta, Hungary.

and many other compounds. These compounds are generally highly volatile, and often not used in large quantities.

Methylene chloride (and acetone, not a chlorinated solvent) are generally used as solvents in the chemical laboratory, and without extremely careful handling, these compounds may show up in GC/MS analyses in low quantities – they are as a result of laboratory contamination, and may not be in the water stream.

The caution here is that one should walk through the process under study and pay particular attention to areas where machining or painting are being performed, and how these waste materials are handled for disposal. In most instances the wastes from processes using these solvents should be kept out of the wastewater stream, as their presence will only cause regulatory headaches.<sup>18</sup> If one has to deal with chlorinated pesticides or chlorinated solvents, do your research on the compounds in the OSHA or other databases to understand what the effects can be. The consequences of discharging chlorinated organic compounds in wastewater can be severe. Just ask General Electric (see below).

### 8.11.1 PCBs

PCBs or polychlorinated biphenyls were widely used in electrical transformer oils worldwide back in the mid 1900s. Insurance companies demanded the

PCBs in transformer oils because they were much less flammable than other oils, and helped in transformer cooling. PCBs were banned in the US in the mid-1970s, and even today their handling and disposal is regulated under the Toxic Substances Control Act in concentrations above 50 ppm, more or less in anything, including wiping rags, soils, and so on. While it may be unlikely that one encounters PCBs in their environmental practice in the US, the oils are still in use in other parts of the world. The oils are extremely bio-accumulative, and are known to be toxic and carcinogenic.

PCBs can be found as contaminants in other oils, but by themselves are generally heavier than water, are composed of two benzene rings either fully or partially chlorinated, and linked together by an oxygen atom. They are similar in structure to dioxins, and need to be handled cautiously. They can be reductively dechlorinated by a number of bacteria, or totally dechlorinated in a reaction with sodium metal in an oil environment. However, that is a specialized treatment, not generally found in environmental practice. The removal of PCBs is a matter of regulatory interest, and can result in litigation, as the following example shows.

General Electric Corporation near Albany, NY, discharged PCBs into the Hudson River from the 1940s to the late 1970s. As a consequence of several lawsuits, and tens of years of litigation with the New York Department of Environmental Conservation and the USEPA, GE is slowly dredging the river to remove PCB-contaminated sediments in the river bottom. This is a massive undertaking, requiring millions of dollars and many years to complete. If the dredging was not expensive enough, the contaminated sediments will have to be handled in a special landfill or incinerated because they contain the PCBs.

### 8.11.2 DDT

This caution regarding chlorinated or fluorinated organic compounds also applies to chlorinating and fluorinating chemical processes and pesticide manufacturing operations.<sup>19</sup> The most notable of these was the manufacture of dichlorodiphenyltrichloroethane (DDT). DDT has been effectively banned by the USEPA for agricultural use as an insecticide, but it is occasionally possible to find DDT and dichlorodiphenyldichloroethylene (DDE) in the wastewaters from agricultural manufacturing plants or even the runoff from chemical or old landfills.<sup>20</sup> Note that DDT, under the right environmental conditions, will decay by shedding some chlorine to DDE and DDD (dichlorodiphenyldichloroethane), which are endpoints and relative dead-ends for further biological degradation. The finding of DDE in a water or solid sample is taken as proof that DDT was present.<sup>21</sup>

But DDT is not the only highly regulated or listed pesticide. Table 8.9 shows the current trade names for common pesticides that have been banned by the USEPA.

**Table 8.9** List of banned or highly regulated pesticides, both organic and inorganic.

Chemical name	CAS registry number (or EDF substance ID)
Aldrin	309-00-2
Azodrin	6923-22-4
1,4-benzoquinone, 2,3,5,6-tetrachloro-	118-75-2
2,3,4,5-bis (2-butylene) tetrahydrofurfural	126-15-8
Bromoxynil butyrate	EDF-186
Camphechlor	8001-35-2
Carbofuran	1563-66-2
Carbon tetrachloride	56-23-5
Chlordane	57-74-9
Chlordanimeform	6164-98-3
Chlorobenzilate	510-15-6
Daminozide	1596-84-5
DDD	72-54-8
DDT	50-29-3
1,2-dibromo-3-chloropropane (DBCP)	96-12-8
1,2-dibromoethane	106-93-4
1,2-dichloroethane	107-06-2
Dieldrin	60-57-1
Endrin	72-20-8
EPN	2104-64-5
Gamma-lindane	58-89-9
Heptachlor	76-44-8
Hexachlorobenzene	118-74-1
Methamidophos	10265-92-6
Methyl parathion	298-00-0
Mevinphos	7786-34-7
Mirex	2385-85-5
Nitrofen	1836-75-5
Parathion	56-38-2
Pentachlorophenol	87-86-5
Phenylmercuric oleate (PMO)	EDF-185
Phosphamidon	13171-21-6
2,4,5-t	93-76-5
Terpene polychlorinates (strobane6)	8001-50-1
2,4,5-TP acid (silvex)	93-72-1
2,4,5-trichlorophenol	95-95-4

## Notes

- 1 Source for some of the data is: Generalic, Eni. "Solubility product constants." *EniG. Periodic Table of the Elements*. KTF-Split, 14 Feb 2016, 25 Mar 2016. [http://www.periodni.com/solubility\\_product\\_constants.html](http://www.periodni.com/solubility_product_constants.html).
- 2 Zhaojun Wang, Richard T. Bush, Leight A. Sullivan, and Jianshe Liu (2013) "Simultaneous Redox Conversion of Chromium (VI) and Arsenic (III) under acidic conditions." *Environmental Science and Technology* 47, 6486–6492. doi:<https://doi.org/10.1021/es400547p>
- 3 <http://www.lenntech.com/periodic/water/arsenic/arsenic-and-water.htm> lists the following data for arsenic compounds: arsenic(III) hydride 700 mg/l [which may be H<sub>2</sub>As]; arsenic acid H<sub>3</sub>AsO<sub>4</sub>·½H<sub>2</sub>O, 170 g/l; and arsenic sulfide 0.5 mg/l.
- 4 [http://or.water.usgs.gov/pubs\\_dir/Html/WRIR98-4205/as\\_report6.html](http://or.water.usgs.gov/pubs_dir/Html/WRIR98-4205/as_report6.html)
- 5 <http://water.usgs.gov/nawqa/trace/arsenic>
- 6 [https://en.wikipedia.org/wiki/Arsenic\\_contamination\\_of\\_groundwater](https://en.wikipedia.org/wiki/Arsenic_contamination_of_groundwater)
- 7 A treatment of the subject of activated aluminum treatment for arsenic removal from drinking water can be found in the joint book by the AWWA, *Water Quality and Treatment*, 5e.
- 8 <http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxicid=15>
- 9 USEPA (1988). *Zinc Water Quality Standards Criteria Summaries: A Compilation of State/Federal Criteria*. EPA 440/5-88/019. Available from [www.epa.gov/nscep](http://www.epa.gov/nscep).
- 10 In Romania, at a chemical company on the Danube River, an Ag chemical plant was also manufacturing chlorine by the mercury cell process. It was memorable because the mercury cell room operators all had blue gums, which was a symptom of acute mercury poisoning.
- 11 <http://www.atsdr.cdc.gov/toxprofiles/tp46.pdf>
- 12 *Removal of Barium and Radium from Groundwater*, USEPA Water Research Lab publication EPA/600/M-86-021 Feb., 1987; and Baker, A.C. and Toque, C. (2005). A review of the potential for radium from luminising activities to migrate in the environment. *Journal of Radiological Protection* 25: 127–140. doi:<https://doi.org/10.1088/0952-4746/25/2/001>
- 13 See "Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol" by J.R. Pargaa, S.S. Shuklab, and F.R. Carrillo-Pedrozac, *Waste Management* 23 (2003) pp. 183–191; and <http://www.nmfrc.org/bluebook/sec623.htm>.
- 14 <http://www.h2o2.com/industrial/applications.aspx?pid=106&>
- 15 <http://www.nmfrc.org/bluebook/sec623.htm>
- 16 J.P. Van der Hoek, P.J.M. Van der Van, et al. "Combined ion exchange /biological denitrification of nitrate removal from ground water under different process conditions," *Water Research* 22 (6), 1988, pp. 679–684; and

- Jan Peter Van der Hoek and Abraham Klapwijk (1987). Nitrate removal from ground water. *Water Research* 21 (8): 989–997.
- 17 See the article from JASCE: [http://ascelibrary.org/doi/10.1061/\(ASCE\)0733-9372\(1997\)123:4\(371\)](http://ascelibrary.org/doi/10.1061/(ASCE)0733-9372(1997)123:4(371)) The full citation is: Kapoor, A. and Viraraghavan, T. (1997). Nitrate Removal From Drinking Water – Review. *Journal of Environmental Engineering*, 10.1061/(ASCE)0733-9372(1997)123:4(371), 371–380. The references are extremely helpful, but the publication itself is for sale through ASCE.
- 18 In more than one instance, where chlorinated organics are being discharged to the wastewater treatment plant, the recommended solution is separate treatment of the effluent stream away from any biological wastes, and the type of separation may include pouring quick setting cement in the area sewers to block off the possibility of wastes entering the treatment works.
- 19 A number of years ago, while working under a USTDA contract, we had the opportunity to visit a chemical plant near Brasov, Romania. This visit was several years after the ban on chloro-fluorocarbons was instituted, but while they were still being phased out. Among the chemical products being manufactured were trichloroethylene by the 1940s vintage Milk of Lime Process, where a lime solution is sprayed into a chlorination reaction to stop the chlorination. The wastewater had a layer of bright red chlorophenols, intermixed with wastes from a local, inefficient artificial tire plant which created black streaks in the chlorophenols on the mixing basin. Added to the waste was the manufacture of DDT pesticide. The wastewater plant was largely out of commission, and the biological decay rates were immeasurable because of the toxic compounds in the wastewater. At the time, the plant was discharging into a river that fed the Black Sea. Probably the worst chemical plant I have ever seen.
- 20 The discharge of wastewaters from the Kettleman Hills landfill outside Los Angeles, CA, and the discharge of wastewater from the chemical plant, which manufactured DDT, chlordane, and other pesticides, were the subject of a major lawsuit by EPA against several companies that operated the plant over the years. At one time, one of the proposed solutions to remediation of the contamination of the Los Angeles basin with DDT and DDE was to cover the entire Los Angeles Basin with a layer of 15 cm of ocean sand, effectively sealing the DDT/DDE in the sea floor.
- 21 A good reference on the toxicity issues surrounding DDT is: *Of Acceptable Risk: Science and the Determination of Safety*, by William Lowrance (1976).

**9**

## Biological Wastewater Treatment

### 9.1 The Microbial World

If you are going to treat wastewater by biological means, you will find greater success if you understand some of the basics of the microbial world. Any discussion of industrial waste treatment should include a brief introduction into the chemistry, microbiology, and content of industrial and domestic wastewater, and some of the problems and challenges affiliated with wastewater treatment. Some of the basics of the chemistry have been addressed in previous chapters – especially the subjects of chemical and biochemical oxygen demand (BOD). It is important to understand the difference between the two, and which one is useful for operational control of a wastewater treatment system.

There are a number of distinct types of microorganisms found in wastewater. The principal functions and types are shown in Table 9.1.

There is a distinct order to the microbiological families. It starts with a Kingdom, and there are different kingdoms for plants and animals.

Each Kingdom is then split into smaller groups, called Phyla.

Each Phylum is split into smaller groups called Classes.

Each Class is split into Orders.

Each Order is split into Families.

Each Family is split into Genera, and

Each Genus is split into Species. A Species is a single organism, not a group.

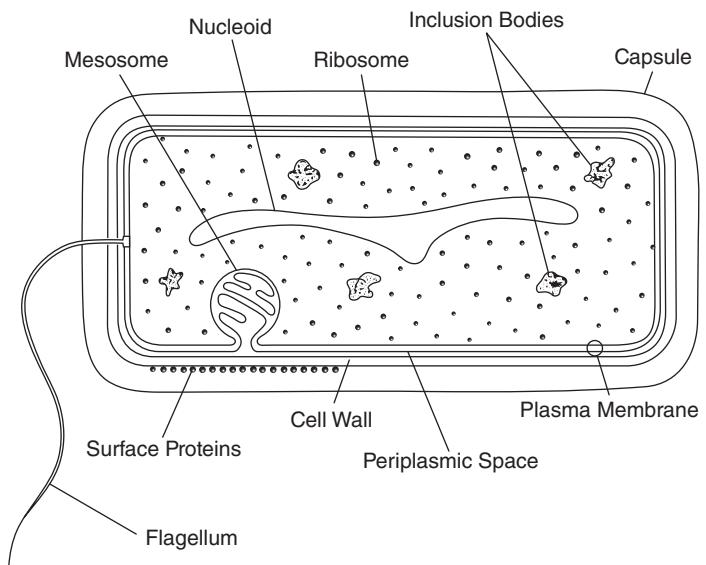
Bacteria are the largest group of organisms, most plentiful, and we often we miscategorize various phylum as bacteria. The Kingdom for bacteria is Monera.

**Table 9.1** Principal microorganisms in wastewater treatment.

Principal function of organism	Specific genus
Principal biological degradation bacteria	Psuedomonas, Achromobacter, Flavobacterium, Alcaligenes, Arthobacter, Zoogloea, Acinetobacter, Citromonas, Bacillus Bacteria: small and single-celled, come in a variety of sizes and shapes, are found in great numbers, and cause most of the diseases
<i>Nitrifying bacteria:</i> Ammonia oxidizing bacteria, and nitrite oxidizing bacteria (AOB & NOB)	Nitrosomonas, Nitrobacter, Nitrospirillum
<i>Predators:</i> protozoa, rotifers, nematodes	Vorticella, Aspicidica, Paramedium Protozoa are a large and diverse group of single-celled organisms. Most are quite mobile and swim in polluted waters. They are important indicators of treatment efficiency. Some have a branched structure similar to trees. (Most recently <i>Guardia</i> and <i>Cryptosporidium</i> are two organisms responsible for disease.) Metazoa are multicellular organism, more complex than protozoa, and it includes some of the Rotifers (which are multicellular, stalked, and have tails). Nematodes are worm-like.
<i>Nuisance bacteria:</i> Eukaryotes, bulking, forming, and overgrazing	Nocardis, Microthrix, Sphaerotilus, fungi, snails, Schistosomiasis
<i>Specialty populations</i>	Phosphate accumulating organisms, algae, cyanobacteria (blue-green algae)
<i>Other</i>	Viruses (bacteriophage), yeasts, pathogens, (E-coli, Campylobacter, various spore formers, Salmonella, Giardia, Cryptosporidium), Helmuth Ova Viruses are much smaller than bacteria and are mostly invisible without a very powerful microscope.

Bacteria are prokaryotes vs. eukaryotes (protozoa, plants and fungi, plants and animals). Bacteria have relatively simple structure and DNA, with no nuclear membrane (Figure 9.1). Bacteria also divide by binary fission.

A microorganism survives on food. Without food they self-cannibalize and, with the general exception of the spore-formers, mostly die off. In a wastewater treatment plant the microbes, unless they are predators who feed on other microorganisms, remove dissolved carbonaceous products from the wastewater to convert them into new cellular mass. Microbes have to be able



**Figure 9.1** Anatomy of a bacterial cell.

to solubilize the compounds in water before they can get them into the cell, and take them apart for their energy. This is done with extracellular polymers and enzymes which the cell produces.

Parasites are organisms that only reproduce with or within a host. Hepatitis is parasitic, but HIV (human immunodeficiency virus) is not. Parasites and pathogens can include any and all of the above, plus worms and fungi. Most if not all of the parasites can be transmitted through contact with wastewater or contaminated water.

Soil microbes and heterotrophs are bacteria, protozoans, and nematodes all found in soil in large numbers. Heterotrophs use organic material as their energy source.

Obligate aerobes are microorganisms that require oxygen in the substrate. Obligate anaerobes are organisms that find the presence of oxygen is poisonous to them, and facultative organisms can survive in aerobic and anaerobic conditions. Many of the organisms found in activated sludge are facultative and survive to aid in the anaerobic digestion of wastewater sludge.

The cell pictured in Figure 9.1 is a Gram-positive cell. There are several ways of differentiating cells using Gram staining (dye staining) techniques. The cell wall is made from long-chain polymer amino sugars. In Gram positive staining, the cell wall may comprise up to 50% of the dry weight of the cell. Gram-negative cells contain lipo-proteins and lipo-polysaccharides (fats bonded to sugars and proteins), and do not absorb the Gram dyes.

The cellular membrane is composed of phospholipids and associated embedded proteins. The head of the phospholipid is hydrophobic and the tail is hydrophilic. As a result, proteins, sugars, water and wastes pass through the cell wall by active or passive diffusion. If the cell has a long tail, it is a motile flagellum, but if it does not have the flagellum, it will probably have many pili – short, thin protruding structures (whiskers) which aid in attaching the cell to others for the purpose of reproduction. Reproduction occurs by division.

The inclusions and vacuoles in the cell are used to store energy, or in the case of cyanobacteria (blue-green algae) they store gas which makes the cell lighter than water so it can receive sunlight. Other cells have endospores, a kind of shell that helps the cell resist adverse environmental conditions. In many cells, the DNA is bound in a membrane that causes it to form a ball-like structure.

Furthermore, the cells are classified by their energy sources.

- Autotrophs and heterotrophic bacteria use CO<sub>2</sub> as their source of carbon for growth.
- Photoautotrophs use sunlight and CO<sub>2</sub>.
- Chemolithotrophs obtain energy by oxidizing inorganic nitrogen and sulfur (Nitrosomonas and Nitrobacter) and methanol and methane.
- Heterotrophs and other feeders obtain energy from organic compounds by breaking them down, and are necessary for both aerobic and anaerobic processes.

There are several important types of microbial organisms in all wastewater. This brief introduction seeks only to introduce the barest of basic facts needed to understand the basics of microbiology. All bacteria have specific environmental conditions for their survival.

Environmental conditions can play a major role in bacterial growth. Temperature Sensitive bacteria have their own ranges:

- Psychrophilic 0–20°C
- Mesophilic 25–40°C
- Thermophilic 45–50°C

Thermophilic bacteria are good for breaking down carbohydrates. Mesophilic bacteria are good in composting.

A wastewater treatment plant has several components: (i) the environment; (ii) the food source; and (iii) the operator of the plant. The environment may include type of water, concentrations of non-food chemicals in the water, oxygen supply, and temperature. The food source is the available materials in the wastewater upon which the bacteria can operate. This includes carbon compounds, nitrogen compounds, non-soluble compounds, phosphates, and other chemicals in the water. The operator tries to make the environment favorable for the bacterial populations so that they will consume the foods in

the water and produce a relatively clean effluent with biosolids that can be removed from the liquid.<sup>1</sup>

In the process of treating wastewater, there is not just one set of organisms, but several. The dynamics, number of organisms, and growth patterns are specific to each species. The general pattern for population dynamics has several stages.

- I. Adaptation to environment – during this phase the organism develops the enzymes and processes needed to feed. Think of it as tool-gathering.
- II. Log growth – competition is minimal and food is unlimited. This assumes that the rate of growth is able to outstrip the consumption of the population by predators.
- III. Stable phase – die-offs and limits of food (transport-related?) are equal.
- IV. Log Death – die-offs, lack of food, and predators overwhelm the population.
- V. Death – (at a minimal level) marginal survival.

These stages are shown in Figure 9.2.

Some of the important functions of the organisms in wastewater are reduction of the BOD/COD, and nitrification of the amines in the wastewater. Nitrification in nature is a two-step oxidation process of ammonium ( $\text{NH}_4^+$  or ammonia  $\text{NH}_3$ ) to nitrate ( $\text{NO}_3^-$ ) catalyzed by two ubiquitous bacterial groups.

*Nitrifying bacteria* are chemoautotrophic or chemolithotrophic, depending on the genera. *Nitrosomonas*, *Nitrosococcus*, *Nitrobacter*, and *Nitrococcus* are bacteria that grow by consuming inorganic nitrogen compounds. Many species of nitrifying bacteria have complex internal membrane systems that are the location for key enzymes in nitrification: ammonia monooxygenase, which oxidizes ammonia to hydroxylamine, and nitrite oxidoreductase, which oxidizes nitrite to nitrate.

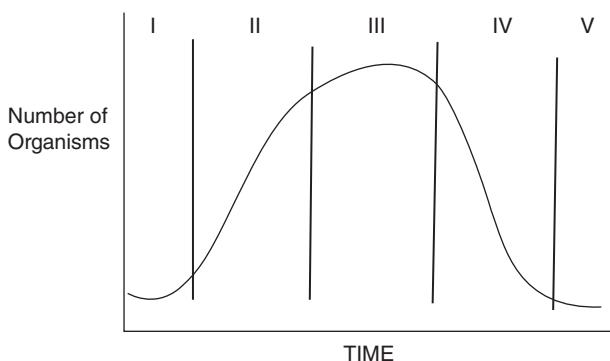
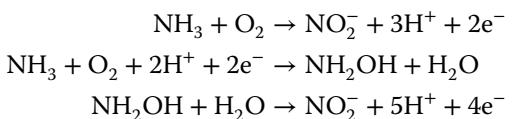


Figure 9.2 Wastewater population dynamics.

**Table 9.2** Bacteria that oxidize ammonia to nitrite.

Genus	Phylogenetic group	DNA (mol% GC)	Habitats	Characteristics
<i>Nitrosomonas</i>	Beta	45–53	Soil, sewage, freshwater, marine	Gram-negative short to long rods, motile (polar flagella) or nonmotile; peripheral membrane systems
<i>Nitrosococcus</i>	Gamma	49–50	Freshwater, marine	Large cocci, motile, vesicular or peripheral membranes
<i>Nitrosospira</i>	Beta	54	Soil	Spirals, motile (peritrichous flagella); no obvious membrane system
<i>Nitrosolobus</i>	Beta	54	Soil	Pleomorphic, lobular, compartmented cells; motile (peritrichous flagella)

The first reaction of nitrifying bacteria is the oxidation of ammonium ions to nitrite by ammonium oxidizing bacteria – primarily the *Nitrosomonas* species (Table 9.2). The second reaction is oxidation nitrite ( $\text{NO}_2^-$ ) to nitrate by nitrite-oxidizing bacteria, which are represented by *Nitrobacter* species (Table 9.3).



Aerobic metabolism involves transferring electrons from organic compounds to some oxidizer (electron acceptor) like oxygen molecules, nitrate, or sulfate. Carbon is released as carbon dioxide, hydrogen as water, and so on.

In the metabolism of aerobic organisms, nearly all of the steps are anaerobic. Combination with oxygen is the last step, and one that was apparently developed or transferred several times among prokaryotes. Eukaryotes use mitochondria for aerobic metabolism; the rest of the cell is anaerobic.

In the process of wastewater treatment, a number of different types of organisms will predominate, depending upon the length of time the wastewater is under treatment, and the length of time the biosolids are retained in the treatment system. The term for the retention time is “sludge age,” and it is an important measure of wastewater treatment plant operation success or failure.

**Table 9.3** Bacteria that oxidize nitrite to nitrate.

Genus	Phylogenetic group	DNA (mol% GC)	Habitats	Characteristics
<i>Nitrobacter</i>	Alpha	59–62	Soil, freshwater, marine	Short rods, reproduce by budding, occasionally motile (single subterminal flagella) or nonmotile; membrane system arranged as a polar cap
<i>Nitrospina</i>	Delta	58	Marine	Long, slender rods, nonmotile, no obvious membrane system
<i>Nitrococcus</i>	Gamma	61	Marine	Large cocci, motile (one or two subterminal flagellum), membrane system randomly arranged in tubes
<i>Nitrosospira</i>	Nitrospirae	50	Marine, soil	Helical to vibroid-shaped cells, nonmotile; no internal membranes

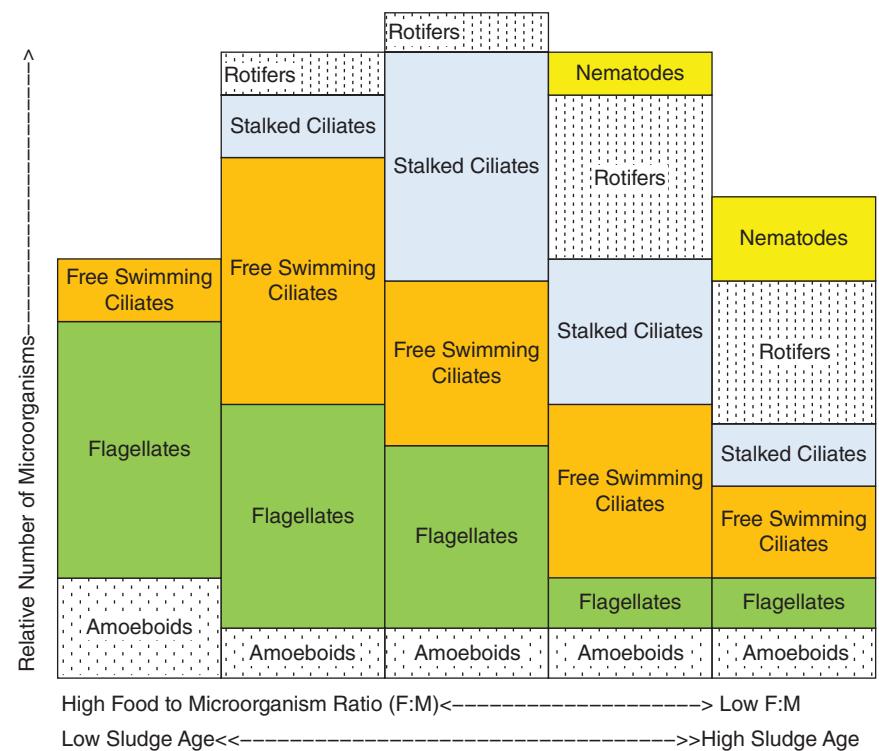
## 9.2 Order of Treatment

The development of a species is dependent upon its ability to establish a niche (metabolize the substrate (adapt to toxics?), and outgrow the predators). The principal competition is between fungi, algae, bacteria, and protozoa for the same substrate. The growth rate of an organism or genus is limited by the organism's rate of reproduction and ability to metabolize food. Note that the organism must solubilize the food and convey it into the cell before it can be used for energy. In order to accomplish that, the organism will often have to develop extracellular enzymes to help the food source penetrate the cell wall.

There is an order to microbial growth. From fastest to slowest growing, that order is: bacteria > fungi > protozoa. Bacteria generally predominate, but *if soluble substrate concentration reduces or other environmental conditions change, the population dynamics will change in response to their environment and food sources, and bacteria will no longer predominate*. If protozoa and/or filamentous organisms predominate, that may be an indication of adverse environmental conditions. For example, a pH below 6.5 may cause fungi to predominate.

If waste loadings are intermittent, primary bacteria grow and die off and *Flavobacterium* and *Alcaligenes* may predominate.

Figure 9.3 shows the relative change in microbial populations during aerobic wastewater treatment. *Sludge age* is the average length of time the biosolids remain in the aeration tank. It is computed by dividing the mass of the solids



**Figure 9.3** Population dynamics in activated sludge wastewater treatment.

under aeration by the sum of the solids in the clarifier, plus the quantity of suspended solids in the effluent.

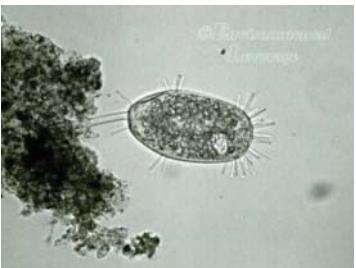
*Food to microorganism ratio (F:M)* is the mass of biodegradable material entering the plant divided by the mass of the solids in the aeration basins. Higher F:M ratios generally indicate relatively short retention times, with mixed liquor suspended solids (MLSS) concentrations of  $3000\text{ mg l}^{-1}$  or less. This might be found in a contact stabilization plant. Conversely, low F:M ratios might have an MLSS of  $6000\text{ mg l}^{-1}$  or more (with some of the newer plants running up to  $20\,000\text{ mg l}^{-1}$ ), and very thick and viscous mixed liquor with long retention times for the solids under aeration.

### 9.3 Types of Organisms

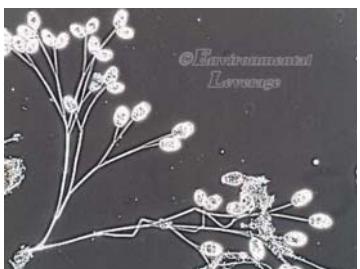
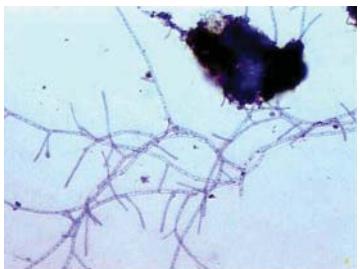
This section introduces some of the organisms you will meet when you look at wastewater under a microscope. All photomicrographs are courtesy of Environmental Leverage, Inc., North Aurora, Illinois (Figure 9.4).<sup>2</sup>

**Amoeba:****Bacteria:**

Note that bacteria have been stained for visibility.

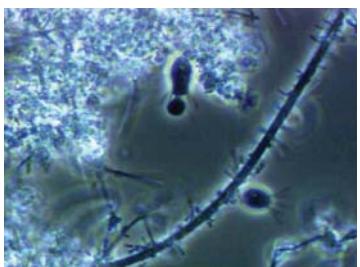
**Flagellates:****Free Swimming Ciliates:**

**Figure 9.4** Some common types of organisms found in wastewater.

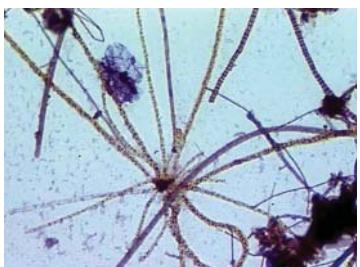
**Stalked Ciliates:****Rotifers:****Some types of Filaments:**

On21

Nocardia



0041



Thiothrix

**Figure 9.4 (Continued)**

A number of organisms grow filaments, and they are important in the final stages of wastewater treatment because they can aid in clarification of the wastewater solids by developing a natural blanket or screen to help remove the fine solids and aid in settling.

Conversely, if the population of organisms such as nocardia (pictured) grows too quickly and in too great a number, they can hinder settling in the final clarifier. There are a number of conditions that can create poor settling in the clarifier. One of the conditions is identified as “pin floc” where the floc particles are very small and do not settle (Table 9.4). We will revisit some of these issues of clarifier performance in the material on clarification and settling.

**Table 9.4** Conditions and organisms that result in poor sludge settling.

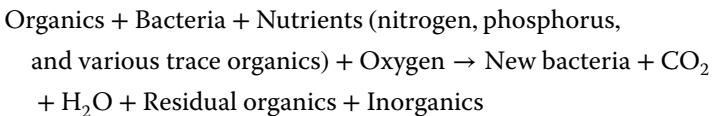
Condition causing settling problem	Organisms that may be contributing to the settling problem
Low pH	Fungi
Low F/M	Type 0041 Type 0675 Type 1851 Type 0803
Septicity (no DO in clarifier)	Type 021 N Thiothrix I and II Nostocoida limicola I, II, III Type 0914 Type 0411 Type 0961 Type 0581 Type 0092
Grease and oil	Nocardia spp. Microthrix parvicella Type 1863
Nutrient deficiency: nitrogen	Type 021 N Thiothrix I and II
Nutrient deficiency: phosphorus	Nostocoida limicola III Haliscomenobacter hydrossis Sphaerotilus natans
Low dissolved oxygen concentration in clarifier	Sphaerotilus natans Type 1701 Haliscomenobacter hydrossis

Source: *Activated Sludge Microbiology Problems and Their Control*, Michael Richard, [http://www.dec.ny.gov/docs/water\\_pdf/drrichard1.pdf](http://www.dec.ny.gov/docs/water_pdf/drrichard1.pdf). A very good discussion on control of settling problems in a clarifier.

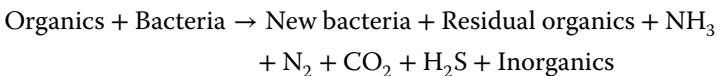
A more detailed course in microbiology is requisite for identification purposes. An excellent series of guides to microorganisms is produced by Environmental Leverage, Inc.<sup>3</sup>

## 9.4 Chemistry and Activated Sludge

A basic understanding of some of the bacterial chemistry is necessary for successful treatment of wastewater. Since most of the reactions are aerobic, and occur at approximately three times the rate of anaerobic reactions, the following general formula is applicable:



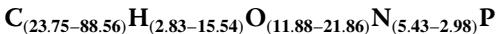
For anaerobic reactions:



If we look at the approximate formulation of bacterial cells we find that about 90% is water. The remaining 10% of the composition of the cells is approximately the following:

90% organic materials  
50–55% carbon  
25–30% oxygen  
10–15% nitrogen  
6–10% hydrogen  
1–3% phosphorus  
0.5–1.5% sulfur

The generally accepted formula for bacterial populations is  $\text{C}_5\text{H}_7\text{NO}_2$  if one excludes phosphorus. If phosphorus is included, the formula is more esoteric:  $\text{C}_{60}\text{H}_{87}\text{O}_{23}\text{N}_{12}\text{P}$  or  $\text{C}_{118}\text{H}_{170}\text{O}_{57}\text{N}_{17}\text{P}$ . Simplifying those ratios by weights, the following general formula is obtained:



If the analysis of the wastewater is expressed in terms of COD, the approximate “best” concentration of substances in wastewater is  $\text{C}_{150}:\text{N}_{20}:\text{P}$ .

For optimum biological growth, the wastewater should have the approximate nutrient ratios expressed here. If the wastewater is unbalanced, for example,

contains more phosphorus than required, some organisms, if the conditions are correct, can uptake extra phosphorus beyond what is needed for immediate respiration. Otherwise, the organism will take what it needs and leave the balance in the water. Conversely, the absence of specific nutrients will limit the growth of the population once it reaches the limits of its substrate.

## 9.5 Growth Conditions and Nitrification

One of the goals of a secondary wastewater treatment plant is to produce an effluent which is low in suspended solids, low in BOD or COD, and very low in ammonia. This is the job of the nitrifiers, principally *nitrosomonas* and *nitrobacter*. The aquatic toxicity of ammonia is well known and documented, and the limit for free ammonia in an effluent is often well below 1 mg l<sup>-1</sup>.<sup>4</sup> The elimination of ammonia is accomplished by nitrification of the wastewater.

Nitrifying bacteria are classified as obligate chemolithotrophs. This simply means that they must use inorganic salts as an energy source and generally cannot utilize organic materials. They must oxidize ammonia and nitrites for their energy needs and fix inorganic carbon dioxide (CO<sub>2</sub>) to fulfill their carbon requirements.

Species of *nitrosomonas* and *nitrobacter* are obligate aerobes and cannot multiply or convert ammonia or nitrites in the absence of oxygen. They have long generation times due to the low energy yield from their oxidation reactions. Since little energy is produced from these reactions, they have evolved to become extremely efficient at converting ammonia and nitrite. Scientific studies have shown that *nitrosomonas* bacteria devote about 80% of their energy production to fixing CO<sub>2</sub>, and consequently, they have a very slow reproductive rate. Under optimal conditions, *nitrosomonas* may double every 7 hours and *nitrobacter* every 15–20 hours. When one considers that most heterotrophic bacteria can double in as short a time as 20 minutes, the other heterotrophs vastly outgrow the nitrifiers.

All species have limited tolerance ranges and are individually sensitive to pH, dissolved oxygen levels, salt, temperature, and inhibitory chemicals. The temperature for optimum growth of nitrifying bacteria is between 25–30°C. At 4°C nitrification ceases, and cell death occurs at 0°C. At 49°C, the nitrifiers will also die. *Nitrobacter* is less tolerant of low temperatures than *nitrosomonas*.

The optimum pH range for *nitrosomonas* is between 7.8 and 8.0, and for *nitrobacter* is between 7.3 and 7.5. All nitrification is inhibited if the pH drops below 6.0. If the pH begins to drop close to 6.5, almost all of the ammonia present in the water will be in the ionized NH<sub>3</sub><sup>+</sup> state.<sup>5</sup>

According to some aquatic research, the maximum nitrification rates will occur when the DO in the aeration tank is at or above 80% of saturation, but will not occur if the DO concentration falls below  $2.0\text{ mg l}^{-1}$ . *Nitrobacter* is more strongly affected by low DO than *nitrosomonas*.

The presence of salt in the wastewater will not affect the growth of *nitrosomonas* or *nitrobacter* unless the concentration approaches  $6000\text{ mg l}^{-1}$  or 0.6%. Saltwater nitrifying bacteria will grow in salinities ranging from 0.6% to 4.4%

All species of nitrifying bacteria require a number of micronutrients. Unless the wastewater is unusually pure, it will contain sufficient micronutrients for the needs of the nitrite and nitrate forming bacteria.<sup>6</sup>

Nitrification requires alkalinity and a pH in the range of 6–8. Alkalinity and oxygen are both consumed in the nitrification process. Every gram of ammonia converted to nitrate requires 4.57 g of oxygen, and the acid produced by the bacteria consumes approximately 3.57 g of alkalinity as  $\text{CaCO}_3$  per gram of ammonia oxidized – those numbers are theoretical, and the actual values may be slightly higher. The goal in wastewater treatment is to have enough residual alkalinity to allow the nitrification, plus have some residual for buffer capacity – approximately  $50\text{--}100\text{ mg l}^{-1}$  alkalinity. In wastewater treatment operations where the ammonia concentration is high, it may be necessary to add alkalinity to get good nitrogen reductions. Nitrification in wastewater takes place when the oxidation reduction potential (ORP) is positive, above 100 mv.

Similarly, elimination of phosphate is a goal to reduce algal blooms in water bodies. If total nitrogen is in the effluent permit, the wastewater plant may also have to remove excess nitrate by biological denitrification.

## 9.6 Denitrification and Phosphate Removal

Denitrification and phosphate removal are covered in separate chapters, later in this book. Briefly here, it is important to remember that the order of nitrate and phosphorus removal is dependent upon the ORP of the wastewater. If the DO drops to zero, the bacteria in the mixed liquor will continue to respire – but they will select available sources which have oxygen in them. The two most available sources are nitrates and phosphates. When the ORP drops below +50 mV to  $-50\text{ mV}$ , denitrification begins. After the nitrate is consumed, the phosphate is consumed as an energy source in a two-step process beginning at an ORP of approximately  $-50\text{ mV}$  to  $-225\text{ mV}$ . The phosphate is then converted to fatty acids which are used by other bacteria in an aerobic process (luxury uptake). In other systems, phosphate is directly precipitated by reaction with aluminum sulfate (alum), ferric salts, or with lime. These direct precipitation processes will produce a phosphate-rich sludge.

## 9.7 Biological Growth Equation

The following are general principles that you should observe in dealing with a biological treatment system.

Before we get into the biological growth equation, we need to look at the balance of the waste stream. For ideal biological growth, the waste should be balanced.

The carbon:nitrogen:phosphorus (C:N:P) ratio of sewage is often ideal. Look closely at the C:N:P ratio of the industrial wastes, because it should be between 100:20:1 and 100:5:1 for ideal biological growth.

If the C:N:P ratio of the waste is strong in one direction or the other, poor treatment will result. This is especially true if the waste is too strong in carbon.

The waste should also be neither too weak nor too strong; although too weak is acceptable, it is difficult to treat. This is extremely hard to define. BOD is best treated in the range of 60–500. The range of the upper limit is primarily a limit on aeration ability of the system. Wastes in excess of  $500 \text{ mg l}^{-1}$  BOD have been treated very successfully if sufficient dilution is practiced in the treatment process, or if anaerobic processes are used for pretreatment. One aeration process uses high-purity oxygen in the aeration system, rather than air, because the high-purity oxygen has a greater transfer efficiency and is more suitable for treating higher strength wastes.

Biological treatment is easily effective in removing 95–98% of the BOD, but if you need to go beyond that limit, additional measures may have to be implemented.

You cannot get all the BOD removed in a biological treatment system without extremely large tankage, and that may be uneconomical.

You will not get all the COD removed from the waste treatment system for the reasons cited above; this is refractory COD which is nonbiodegradable. Biological treatment systems do not handle shock loads well. Pretreatment or equalization may be necessary if the variation in strength of the waste is more than about 150%, or if that waste at its peak concentration is in excess of  $1000 \text{ mg l}^{-1}$  BOD.

Biological systems do not like extreme variations in hydraulic loads either. Diurnal variations of greater than about 250% may be a problem primarily because they will create biomass loss in the clarifiers.

Toxic and biologically resistant materials will require special consideration and may require pretreatment before they are discharged into the wastewater treatment plant.

Oils and solids do not belong to a wastewater treatment system because they interfere with the treatment. Pretreat these wastes to remove inert solids, oils, and excessive biological solids of more than 200–300  $\text{mg l}^{-1}$ .

The capacity of the aeration system you will use is finite with regard to oxygen transfer. The capacity of the waste to use oxygen is unlimited. Consider this in the design.

The growth rate of biological organisms is highly temperature-dependent. A 10°C reduction in water temperature can cut the biological reaction rates in half. Wintertime conditions where the water is cold will virtually stop all nitrification and will slow all of the other biological processes as well. If you are dealing with cold climates, you may want to consider covering the wastewater treatment tanks to help preserve the little heat left in the system, and if the system is small enough, you may want to consider heating the wastewater.

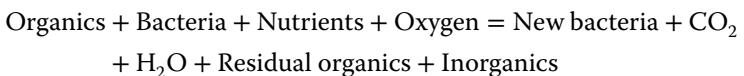
### 9.7.1 The Monod Equation

Biological growth can be described according to the Monod equation:

$$\mu = (\lambda S) / (K_s + S)$$

where  $\mu$  is the specific growth rate coefficient;  $\lambda$  is the maximum growth rate coefficient, which occurs at  $0.5 \mu_{\max}$ ;  $S$  is the concentration of limiting nutrient, that is, BOD, COD, TOC, and so forth; and  $K_s$  is the Monod coefficient. This is also called the half-saturation coefficient because it corresponds to the concentration at which the growth rate  $\mu$  is half of its maximum. This can be seen from the Monod equation by setting  $S$  equal to  $K_s$ .  $K_s$  occurs at  $0.5 \mu_{\max}$ .

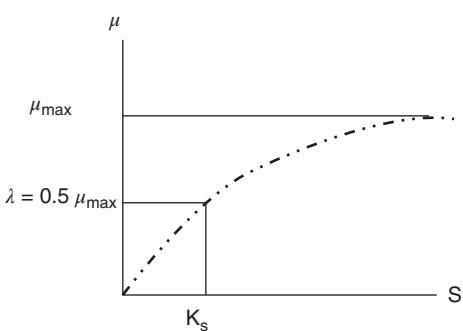
The curve in Figure 9.5 is a plot of specific growth rate coefficient versus concentration of growth-limiting substrate when there is no inhibition.



Using the Monod equation, we will consider the development of the ideas behind the reaction rates and the meanings of a few terms relating to biological decay.<sup>7</sup> Another way of looking at the overall stoichiometric rate is

$$R_g = R_e + R_s$$

where  $R_g$  is the overall growth reaction,  $R_e$  is the energy reaction, and  $R_s$  is the biosynthesis reaction. The subcomponents are as follows: one reaction for



**Figure 9.5** Determining the Monod growth rate coefficient.

biomass  $R_c$ , one for electron donor  $R_d$ , and one for the electron acceptor  $R_a$ . The reactions can be further resolved into half reactions with the following:

$$R_s = Y(R_d - R_c)$$

where  $R_s$  is the biosynthesis reaction as shown above, and  $Y$  is the yield of the reaction. From here we could go into stoichiometry and balanced chemical reactions and half reactions for various chemicals. We are *not* going to do that because it is, in a way, giving more information than you need.

If the overall reaction rate for organic growth is

$$R_o = R_e + R_s + R_{de}$$

where  $R_e$  is the energy reaction shown above, and  $R_s$  is the synthesis reaction, and  $R_{de}$  is the decay reaction,  $R_{de} = R_c - R_a$ .

Going back to the Monod equation, the change in substrate with time is:

$$\frac{dX}{dt} = \mu(SX)/(K_s + S)$$

The specific maximum substrate removal rate is defined as  $k_{max} = \mu/Y$ .

As the substrate value gets very large, the Monod curve tends to flatten out at the top and becomes a straight line, which is at  $\mu_{max}$ . This is true where  $S \gg K_s$ . At that point, the growth is essentially limited by the ability of the bacterial population to transfer food through their cell walls and reproduce. This is not the case for most activated sludge systems, because other limiting factors such as oxygen transfer and availability of other nutrients tend to govern, and have caused heavily loaded substrate systems to fail and go anaerobic.<sup>8</sup>

Where there are two wastewaters generated on an alternating basis, each is likely to have its own specific growth rate and kinetics. For treatment purposes, the substrate with the slower growth rate will govern the design. For blended wastes, look at the blend and apply the slowest growth rate accordingly.

### 9.7.2 Microbial Decay

The loss of cellular mass is microbial decay where cell death occurs. Essentially it is the degradation of endogenous mass for the generation of maintenance energy. It is the second part of a set of sequential processes where all the exogenous substrate is first used for synthesis of cell material, and later decays as the cell ages and substrate concentrations decrease. The decay process is measured by changes in particulate matter in the system, by the change in the mixed liquor volatile suspended solids, MLVSS (or simply VSS). This is shown by the rate equation

$$\frac{dX}{dt} = -k_d X$$

where  $k_d$  is the endogenous decay coefficient and  $X$  is the volatile suspended solids concentration.

VSS measures many things and not just the specific decay, and it is a very broad parameter for estimating kinetic coefficients, with an accuracy of about  $\pm 20\%$  or less.<sup>9</sup> The growth rate constants can be significantly different for similar wastewaters, and even for domestic wastes (see Table 9.5). Part of the reason for this difference is the internal differences in composition of organic matter and dissolved materials that may not show up without more extensive testing.

Industrial wastes data are also shown in Table 9.6. Typical constants are given for a variety of chemicals. The consistency is slightly greater for industrial wastewater, but not much better. The data are limited, and the fact that the values are much more consistent may have as much to do with the idea that the wastes are predominantly one product as the fact that there is a much

**Table 9.5** Various kinetic constants for domestic wastewater.

Basis for constants	$\mu$ (day $^{-1}$ )	$K_s$ (mg l $^{-1}$ )	$K_d$ (day $^{-1}$ )	$\gamma$
BOD <sub>5</sub>	0.6	12–80	0.01–0.14	0.38–0.68
BOD <sub>5</sub>	6	100	0.048–0.055	0.5–0.67
BOD <sub>5</sub>	1.43–13.2	25–120	0.04–0.075	0.42–0.75
COD	1.70	43–223	0.016–0.068	0.31–0.35
COD	3.75	22	0.07	0.67
COD	3.20–3.75	22–60	0.07–0.09	0.4–0.67

The value of  $\gamma$  is calculated from VSS data.

Source: Orhon, D. (1997). *Modeling of Activated Sludge Systems*, CRC Press. Also see the following publication for additional guidance and some kinetic constants for toxic organics: EPA 600/S2-83-073 Jan 1984, *Determination of Activated Sludge Biokinetic Constants for Chemical and Plastic Industrial Wastewaters*, and Appendix B of the same document PB 85-165 488. Appendix A contains the data and is not available except from NTIS.

**Table 9.6** Kinetic constraints for industrial wastes.

Industry	$\mu$ (day $^{-1}$ )	$K_s$ (mg l $^{-1}$ )	$\gamma$	$K$	Basis for constants
Textile	0.1–6.96	86–95	0.52–0.73	0.013–0.12	BOD <sub>5</sub> BOD <sub>5</sub>
Poultry		500	1.32	0.72	
Soybean	12	355	0.74	0.144	BOD <sub>5</sub>
Meat processing	0.57–1.09	150–362	0.34–0.42	0.03–1.0	COD
Edible oil	0.36	350	0.28	0.075	BOD <sub>5</sub>
Skim milk	2.45–2.9	100–110	0.48–0.50	0.45	BOD & COD

$\gamma$  is calculated on a VSS basis.

Source: Orhon, D. (1997). *Modeling of Activated Sludge Systems*, CRC Press.

smaller database to work with. Sometimes, you may only have one value (see Tables 9.5 and 9.6), and may have to make an educated guess.

### 9.7.3 Effect of Temperature and pH on Rate of Reactions

Temperature corrections for the rate of reaction have been simplified from the Arrhenius equation to a much more simple form, and depending upon the model you are using to look at the wastewater, you will have to correct for temperature. The standard is at 20°C. The correction for temperature is

$$r_t = r_{20} \theta^{(t-20)}$$

where  $r_t$  is the reaction rate at temperature  $t$  and  $\theta$  is the temperature coefficient. In the ranges of  $t = 10\text{--}40^\circ\text{C}$ ,  $\theta$  has a value of between 1.0 and 1.10, with a common value of 1.04.

Low pH can stop a biochemical reaction or reduce its rate to almost zero. Orhon and Artan<sup>10</sup> give the following formula for the effects of pH on growth rate:

$$\mu = \mu' K_i / (K_i + H^+)$$

where  $\mu'$  is the original uptake rate;  $K_i$  is the disassociation rate constant for the second reaction constant for the substrate, and the reactions are as follows:



where E = enzyme, S = substrate, and  $K_i$  is the disassociation constant for  $\text{ESH}^{2+}$ .

## 9.8 Principles of Biological Treatment Systems

Consider the classical representation of an activated sludge system shown in Figure 9.6. We will examine the mass balance and look at the equations for biological growth.

The first task is to set out the terms that we will use in analyzing the flows in the system.

$Q$  = Volumetric influent rate (volume/time)

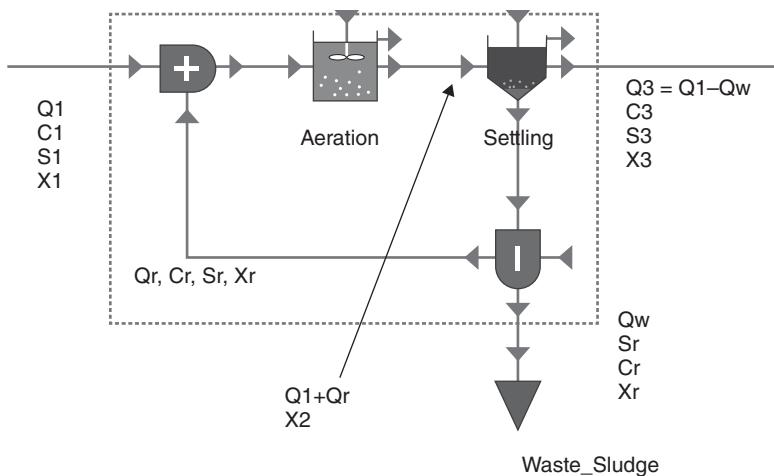
$Q_w$  = Waste sludge volumetric flow rate (volume/time)

$Q_3$  = Effluent flow rate (volume/time)

$Q_r$  = Recycle flow rate (volume/time)

$X_1$  = Microorganism influent concentration (mass/volume influent)

$X_2$  = Aeration basin microorganism concentration (mass/volume)



**Figure 9.6** Basic schematic of activated sludge system.

$X_3$  = Secondary effluent microorganism concentration (mass/volume)

$X_r$  = Recycled and wasted solids concentration

$V_2$  = Aeration basin volume

$r_{BH}$  = Reaction rate for solids (also may be written as  $dX/dt$  = rate of change of microorganisms concentration in aeration basin) (mass/volume time)

$r_s$  = Reaction rate for substrate.

Rate of bacterial growth  $r_{BH} = \mu X$ , where  $X$  is the microorganism concentration in mass/volume and  $\mu$  is the specific growth rate per unit of time

Cell yield coefficient

$$Y_{obs} = -r_s/r_s$$

where  $Y_{obs}$  is the observed yield coefficient,  $r_s$  is the substrate utilization rate, and  $r_{BH}$  is the cell growth rate:

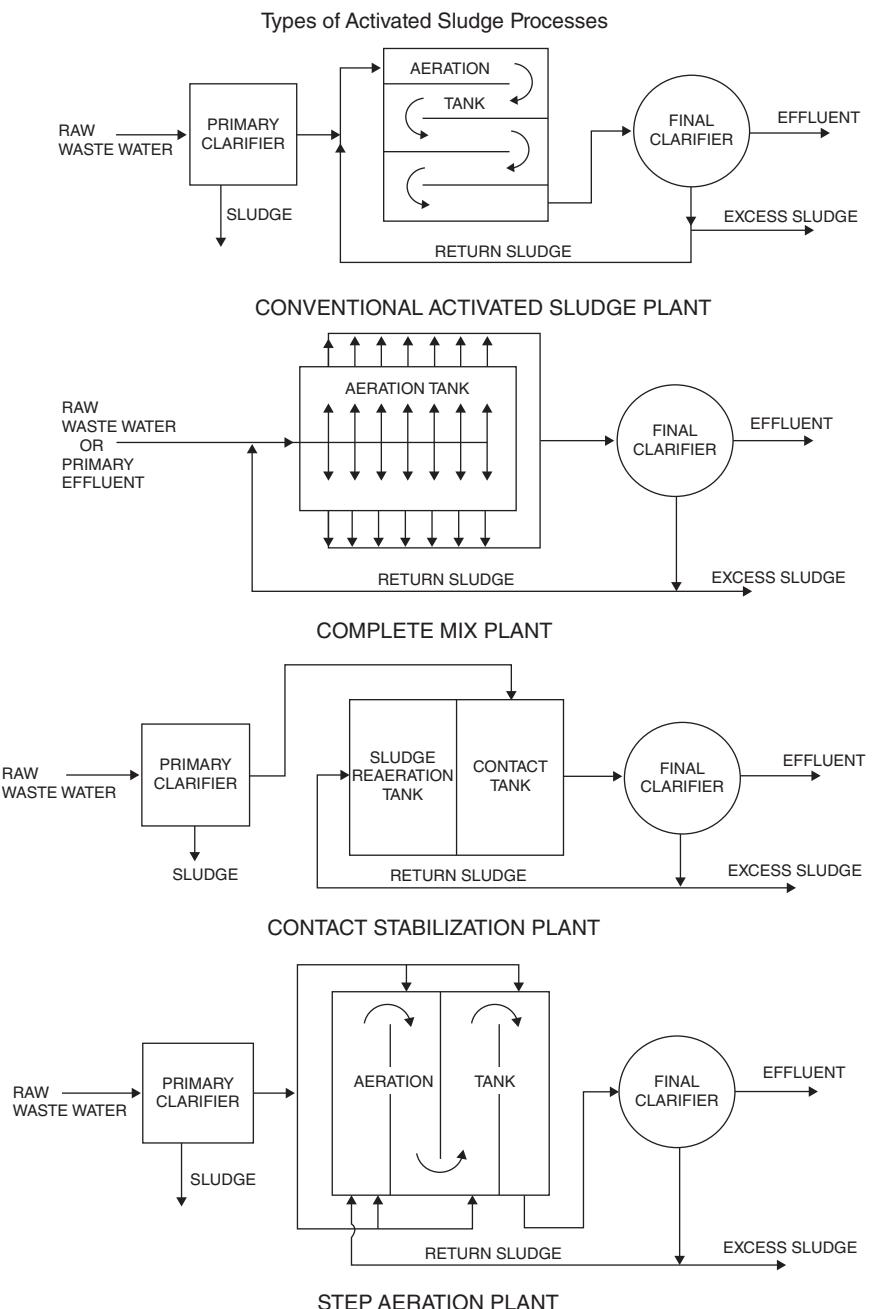
$$r_{BH} = Y_{max} r_s - bX$$

where  $Y_{max}$  is equal to  $\lambda$  and  $b$  is the specific maintenance rate, endogenous or decay coefficient in units of time.

This gives us a sample of a solution for a steady-state system.

Now, when we look at a biological treatment system, we will consider a simple system comprising a reactor or aeration tank, and a clarifier or solids removal device, as shown in Figure 9.7. Running a balance around the system we get the following:

$$Q_1 X_1 + V X_2 r_2 = Q_3 X_3 + Q_w X_r$$



**Figure 9.7** Basic wastewater treatment plant definitions.

If  $X_1$  is relatively small with respect to  $X_2$  and we assume steady-state operations, then the equation becomes

$$\mu = r_2 = \frac{Q_3 X_3 + Q_w X_r}{V_2 X_2}$$

For a bioreactor, mean cell residence time = sludge age =  $\theta_c$  = solids mass/change in solids mass =  $X / (\frac{\partial X}{\partial t})$  or

$$\theta_c = \frac{1}{\mu} = \frac{1}{r_2} \frac{V_2 X_2}{Q_3 X_3 - Q_w X_r}$$

One measure of activated sludge systems is the mean cell residence time or sludge age. The different types of systems and much of US terminology are concerned with sludge age.

Again, at steady-state conditions and making a substitution from above we get

$$Y_{\text{obs}} = \frac{\theta X}{\theta_c (S_o - S)} \quad \text{and} \quad \frac{Y_{\text{max}}}{1 + b\theta_c} = \frac{\theta X}{\theta_c (S_o - S)}$$

where the specific utilization rate is  $U = \frac{S_o - S}{\theta X}$

And the efficiency is defined in terms of the substrate removal

$$E = \frac{S_o - S}{S_o}$$

Then

$$U = F/ME \times 10^2$$

where  $F/M$  is the food to microorganism ratio or:

$$F/M = S_o/\theta X$$

The  $F/M$  ratio is one of the key parameters in designing an aerobic treatment system by conventional means in the United States. This is also called the loading rate.

## 9.9 Activated Sludge and its Variations

Table 9.7 shows the generally accepted parameters that define the various types of activated sludge plants.

Another often useful measure of the aeration system is by defining the  $X_{\text{BH}}$  in the aeration tank and the volumetric holding time or  $\theta$ . This gives us the classification scheme for types of plants and their configurations, as shown in Figure 9.7.

Typical design parameters for activated sludge process modifications are shown in Tables 9.8 and 9.9.

**Table 9.7** Aerobic wastewater treatment plant characterizations by loading rate.

Process	Loading rate <sup>a)</sup>	Removal efficiency
Extended air	0.05–0.20	85–95%
Conventional activated sludge	0.2–0.5	90–95%
Contact stabilization	0.2–0.5	85–90%
High rate stabilization	0.5–5	60–85%

a) The definition is  $QS_o = S_{V1}$ .

**Table 9.8** Typical design parameters for activated sludge process modifications.

Modification	Process loading range	MLSS, mg l <sup>-1</sup>	Aeration time (h)	R = Q (%)
Complete mix	Conventional low rate	3000–6000	3–5	25–100
Plug flow	Conventional	1500–3000	4–8	25–50
	low rate	1000–3000 <sup>a)</sup>	0.5–1.0 <sup>a</sup>	25–100
	Conventional rate	4000–10000 <sup>b)</sup>	3–6	
Step feed	Conventional rate	2000–3500	3–5	25–75
Extended aeration	Low rate	3000–6000	18–36	75–150
Oxidation ditch	Low rate	3000–5000	18–36	75–150
High purity oxygen	High conventional rate	3000–5000	1–3	25–50

a) Contact tank.

b) Stabilization tank R = Q is equivalent to  $Q_r = Q_1$ .

**Table 9.9** Formulation for parameter sensitive switches in activated sludge kinetics.

Parameter	Variable	Sample
DO	DO, $K_{DO}$	= DO/( $K_{DO} + DO$ )
Ammonia	$NH_3, K_{NH_3}$	= $NH_3 / (K_{NH_3} + NH_3)$
Nitrate	$NO_3, K_{NO_3}$	= $NO_3 / (K_{NO_3} + NO_3)$
Alkalinity and pH	ALK, $K_{pH}$ ; l	= $K_{pH} / (K_{pH} + l)$ , where $K_{pH}$ is the pH constant, and $l = 10 \exp(\text{optimum pH} - pH) - 1$

## 9.10 Substrate Removal Definitions

Water balance is:

$$Q_1 = Q_3 + Q_w$$

Running a mass balance around the system, we get

$$Q_1 C_1 - r_{vs} \times V_2 = Q_3 \times C_3 + Q_w \times C_r$$

This time, the term  $r_{vs}$  is both negative and defined in terms of the volume of the substrate in the tank. We could just as easily have defined the term as  $r_s S$ .

This is a simple way of saying that the bacterial growth removes substrate from the tank. Note that in the above equation, no specific definitions are implied, so  $C$  can be  $\text{NO}_2$ ,  $\text{NH}_3$ , COD, or anything else. However, one must define the unit of volume as well as the reaction rate. This means that the reaction rate can be  $r_{vs}$  or  $r_{xs}$  together with the unit of volume  $V_2$ , and for  $r_{sx}$  the activated sludge concentration  $X_2$ .

The units must be internally consistent. That is to say, the activated sludge concentration  $X_2$  can be measured in kg of SS/m<sup>3</sup>, kg of VSS/m<sup>3</sup>, or kg of COD/m<sup>3</sup>, but the units must be consistent in the numerator and denominator.

At steady state the materials must be all hydrolyzed before they can be accessed and consumed by the bacteria. If you have some substrate such as BOD or COD, it cannot be used until it is solubilized. That means that the basic balance will look like the following when we consider the same mass balance as in Figure 9.7, only we have now added the growth and hydrolysis terms to the equations. If we look only at the system boundaries shown in Figure 9.7:

Input + Hydrolysis + Growth = Effluent + Sludge wasting

$$Q_1 S_{s1} + K_h X_{s2} V^2 + (-1/Y) \mu [S_{s2}/(S_{sw} + K_s)] [S_{O2}/(K_{SO2} + S_{O2})] \\ \times X_{BH} V_2 = Q_3 S_3 + Q_w S_r$$

where  $X_{BH}$  is the heterotrophic biomass, and  $S_{O2}$  is the oxygen concentration, as noted earlier. Note that we are taking a balance around the system and not just around the aeration tank. The growth term removes the substrate.

When we look at specific variables in the activated sludge process, we can begin to write equations for mass balances of specific parameters. Fortunately, a number of researchers have already examined the activated sludge process and prepared a summary of critical terms and constants. These are codified in the Activated Sludge Model No. 1, which has been researched and published by the International Water Association (IWA) in London.<sup>11</sup>

Because oxygen concentration is critical for aerobic substrate removal, the Monod term has been added for dissolved oxygen. We can also add other Monod equation terms to the equations to compensate other parameters.

The Monod equation is  $S/(S + K)$ . A few of those are shown below, and several of them act as switches, because when  $S$  goes below a certain specific value, the term tends toward zero and the entire multiplier falls out of the balance equation.

Some of those terms are shown below in the following form:

$$X/(K + X)$$

where  $X$  is the parameter and  $K$  is the half saturation constant. The value and a sample formulation are shown in the table above.

Any number of switches can be included on many of the models to account for optimum performance.

The equations above are often expressed in the form of a Petersen Matrix for the ease of writing. The table is read for rate equations both down and across, and a part of the matrix is presented in Table 9.10.

This is the start of the formulation of the equations for most of the activated sludge models developed by the IWA. ASM1, ASM2, ASM2d, and ASM3 are specialty models. ASM1 is the oldest model. ASM2 and ASM2d are designed to account for denitrification and luxury phosphorus uptake in cells

**Table 9.10** The Petersen Matrix for activated sludge equations.

Process	$S_s$	$X_s$	$X_I$	$X_{BH}$	$S_{O_2}$	Reaction rater $r_v$
Aerobic heterotrophic growth	$-(1/Y)$			1	$(1-Y)/Y$	$\mu(S_s/(S_s + K_s)) (S_{O_2}/(K_{SO_2} + S_{O_2})) X_{BH}$
Heterotrophic decay		$1 - f_{XB}$	$f_{XB}$	-1		$b_H X_{BH}$
Hydrolysis	1	-1				$K_h X_s$
Units	<b>kg COD/m<sup>3</sup></b>					
					Oxygen	
					Heterotrophic biomass	
					Inert suspended organic matter	
			Slowly degradable organic matter			
			Easily degradable organic matter			

(phosphorus removals). ASM3 was designed as a later improvement to ASM1, and was designed, according to one of the developers, to be easier to calibrate.

The models address the biological processes taking place in the aeration tank of an activated sludge plant, but do not address the performance or utilization of a clarifier, nor the sludge thickening process. Separate models are required for that purpose as “add-ons” to the basic treatment model being used.

The overall purpose of using the IWA models is to design and evaluate the performance, and to “fine tune” the design or operation of a wastewater treatment plant. In that regard, the advent of the personal computer and development of dynamic models based on the IWA models has allowed designers, engineers, and operators to have a predictive model that enables the operator to adjust the operation of a wastewater treatment plant in response to variable and changing conditions.

## 9.11 Trickling Filters and Variations

A second and older type of treatment still in use is the trickling filter, or in some instances it is also used as a roughing filter for pretreatment. The filter itself is not really a filter, but an attached growth platform for microorganisms. It generally consists of large rocks, or plastic media with a large surface area, and the waste is sprayed, dumped, or poured over the filter in an intermittent fashion.<sup>12</sup> The intermittent nature of the flow is to permit the organisms to breathe.

The filter bed does not really filter at all, and can be anything from engineered plastic media to crushed rock. The entire purpose of the filter bed is to serve as a support platform for the bacteria that grow out of it and to provide them with a void space so that the surface of the liquid has an opportunity to contact the atmosphere, where it can transfer oxygen into the liquid in support of the bacteria.

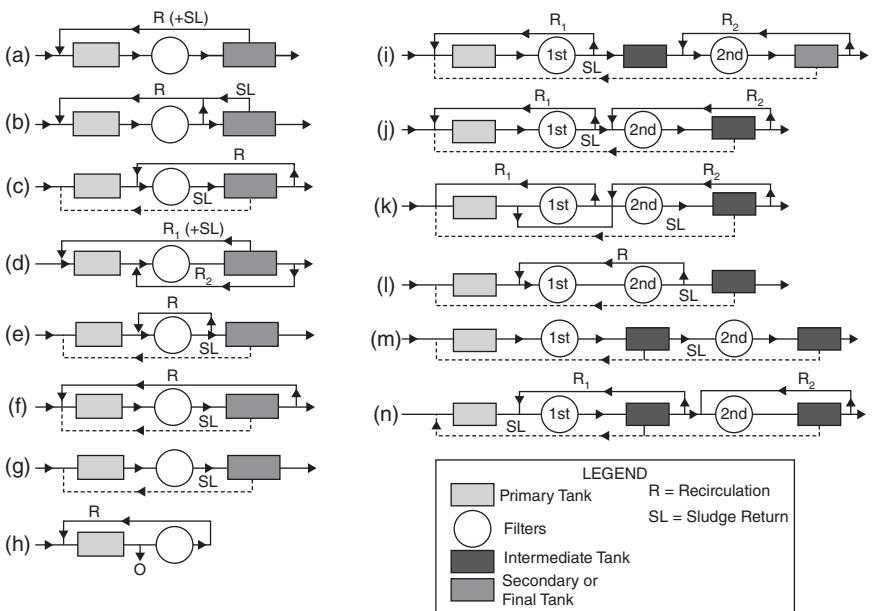
Figure 9.8 shows some typical diagrams of trickling filter systems in current use.

In the trickling filter, it is important to have a medium that has a large surface area with respect to the volume of the media. Table 9.11 illustrates some typical properties of trickling filter media.

The efficiency of trickling filters is calculated in a number of ways. The most readily understandable is the Eckenfelder formula.

$$S_e/S_o = e^{-X}/[(1 + N) - N e^{-X}]$$

where  $S_e$  and  $S_o$  are as defined above,  $N$  = hydraulic recycle ratio,  $X = K D m = Q n$ ,  $K$  = specific surface area ( $\text{ft}^2/\text{ft}^3$ )  $\times$  removal rate constant,  $D$  = depth,  $Q$  = hydraulic loading, and  $m$  and  $n$  are determined media constants. For most applications  $n = 1$ .



**Figure 9.8** Typical configurations for single and two-stage trickling filter plants. Source: *WEF MOP/8 Waste Water Treatment Plant Design Manual No. 8*, by the Water Environment Federation, Alexandria, VA.

**Table 9.11** Properties of trickling filter media.

Media/packing	Nominal size (in.)	Units per ft <sup>3</sup>	Unit weight/ft <sup>3</sup>	Surface area ft <sup>2</sup> /ft <sup>3</sup>	Void space (%)
Plastic media	20 × 48 × 2	2–3	2–6	25–35	94–97
Redwood media	47.5 × 47.5 × 1.8	2–3	10.3	14	80
Granite and stone	1–3		90	19	65
Blast furnace slag	2–3	51	68	20	49

Most trickling filters are extremely temperature-sensitive, because they rely on direct contact with air, and their performance follows the power law about biological activity and temperature, that is, the activity doubles or halves for each 10°C change in temperature.

*Comment:* The trickling filter is still in use, but inherent limitations and the great costs associated with its construction have made it a bit of a dinosaur. The other problems associated with the trickling filter include the odors arising from contact with the wastes, and psychoda flies. These

little critters are nuisance organisms that live in the trickling filter and have a development life of about two weeks. They are very tiny and can be a great source of nuisance unless the filter is flooded for about 12–24 h more often than every two weeks.

The technology that has replaced the trickling filter is the rotating biological contactor (RBC), which has its own limitations. The RBC is a series of slowly spinning disks mounted on a shaft. The RBC does have its proponents who claim that it is more flexible than activated sludge, but one of its observed principal drawbacks is the fact that the disks or rotors collect a biofilm (by design), and that adds enormous weight to the shaft. After a certain period these shafts develop stress cracks and snap, dropping the RBC into the wastewater tank.

## 9.12 Clarification for Biological Removals

Clarification will be handled in detail in the next chapter, but a few words of caution are important here.

The clarifier following an aerobic treatment process represents a separation of an active biomass from a liquid. There is a finite holding time of generally not over three hours in the clarifier, but it may be as high as five hours depending upon the quantity of the biosolids and ORP of the wastewater. After about three hours, the clarifier may become anoxic and anaerobic decomposition begins, whereby  $H_2S$  and  $N_2$  gases are produced and the clarifier is upset by gas bubbles.

The clarifier is easily overloaded by varying hydraulic conditions, especially storm flows which can cause a 3–5× surge in the dry weather flow and wash solids from the clarifier. Conservatively designed clarifiers work best with low surface overflow rates (equivalent to average vertical bulk velocity expressed in flow units such as gallons per square foot per day ( $gpd/ft^2/day$ ) or meters/hour). Clarifiers are generally built with an internal scraper arm mechanism and a surface cleaning mechanism, both of which very slowly rotate around a center shaft and sweep the settled solids, or the floating solids toward a collection point. Even this slow motion of the collector can cause horizontal currents, which upset the settling pattern in the clarifier.

Effluent weirs on clarifiers should be conservatively designed. There is some evidence that the loading rate of the effluent weir may be one of the most important features in developing good solids removal. The overflow weir is rated in terms of gallons/day/ft. of weir ( $m^3/m$ ). The weir overflow rates are often selected as 10 000–20 000 gal/linear foot of weir per day. This is equivalent to 124–250  $m^3/m$  of weir/day.

The purpose of a clarifier is threefold: (i) solids removal for recycle, (ii) sludge thickening for wasting and recycle, and (iii) removal of floating solids. The clarifiers generally have an underflow or return cycle sludge concentration of less

than 5% of the design flow (throughput or average daily flow through the plant), and this clarifier underflow is often more of the order of 1–2% of the daily design flow.

### 9.13 Other Solids Removals

In the early part of this chapter, we briefly addressed the issue of suspended material as a source of BOD or COD. The suspended solids loading to the biological treatment plant can comprise up to 50% of the total biological load applied to the treatment works. Depending upon the strength of the waste and the ability of the plant to handle the solids and maintain adequate aerobic treatment conditions, it may be necessary to have pre-clarification to remove the suspended material (and a portion of the substrate entering the plant). This is often the function of the primary clarifier, which removes the suspended material from the incoming flows and can remove up to 30–50% of the incoming biological load, leaving the aeration basin to work on the dissolved organics.

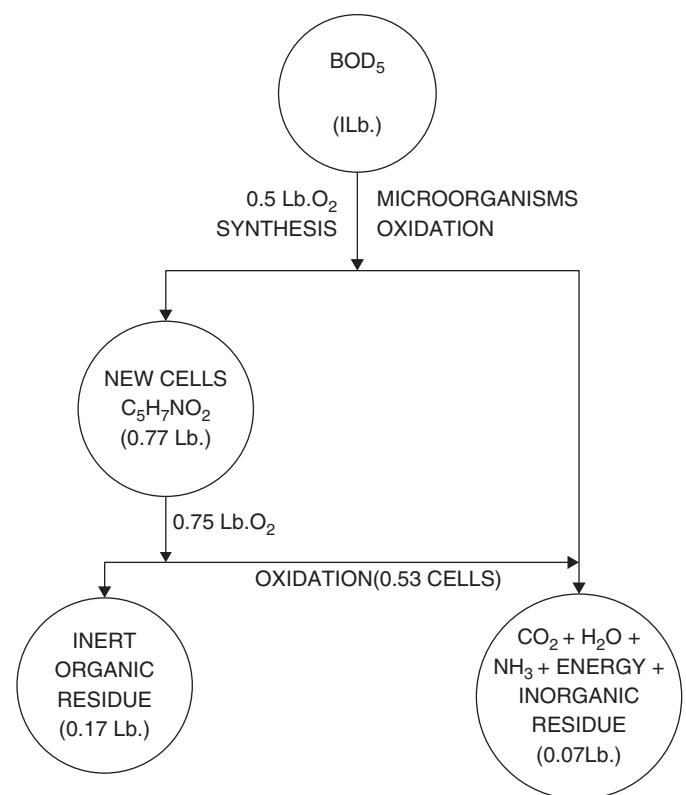
When dealing with a domestic source, one can get everything from sand and clay particles to condoms, footballs, bedsprings, and logs. In most processes, there is a provision for prescreening and solids size reduction to prevent the occurrence of a log, brick, or bedspring entering the treatment works. This is usually the function of a bar screen and grit chamber. The grit chamber is a specific device designed to remove putrescible and non-putrescible solids in a fairly quick fashion. If there is no provision for grit removal, then the sand and other coarse solids will enter either the aeration basin or the first clarifier, and play havoc with the pumps and rotating equipment. Coarse and abrasive solids should be removed from the influent stream whenever possible.

The Sutro or proportional weir mentioned in Chapter 5 is often used in a grit chamber, because it provides constant velocity through the chamber, regardless of the flow. This allows the heavier solids to settle to the chamber, where they can be removed.

### 9.14 Biological Synthesis and Oxidation

One weight unit (pounds or kilograms) of BOD or organic matter yields about 0.77 units of new cells, and that requires about 0.5 units of oxygen (Figure 9.9). As the food supply diminishes, the cells undergo a self-induced cannibalism. After some time, you will be left with 0.24 units of inert organic residue.

Thus, if you have a waste where you are looking to remove about 100 lb of BOD per day, the approximate generation of biomass will be on the order of about 77 lb of solids per day. With time and digestion, that mass of solids will be reduced to 24 units of solids. Unfortunately, those solids do not dewater well.



**Figure 9.9** Waste generation rates from biological treatment plants.

If you are very fortunate, you will be able to collect them at about 18–24% solids on a dry weight basis, so that your 24 units of solids will actually weigh about 100 weight units, give or take a bit.

The solids are collected from the underflow of a clarifier at between 1% and 3% solids. Depending upon the size of the treatment plant, the solids in the sludge may be thickened by stirring them for several hours in an anaerobic tank. The anaerobic stirring, called sludge thickening, will double the solids concentration. After that, the solids are conditioned further by the addition of all polymers and by centrifuging the sludge to concentrate it to between 10% and 15% solids.

The final solids concentration step is filtration. The sludge is processed through a belt filter press where the sludge is mechanically compressed and sheared in a traveling belt filter to attain a final solids concentration approaching 18–35%, depending upon the type of sludge and the processes used. The solids processing and disposal is one of the most costly operations

in a wastewater treatment plant, especially when the sludge must be set to a sanitary landfill or, in rare cases, a hazardous-waste landfill.

## 9.15 Biological Treatment of Toxic Wastes

Not all chemicals are easy to treat. We have discussed shock loading and temperature effects, and biologically unbalanced loads. Now let us look at some other things that may cause difficulty in biological systems. Each of these problems has a solution, but each is different.

Things that can cause toxicity include many of the following: metals such as lead, antimony, copper, zinc, chromium, cadmium, nickel, manganese (permanganate), silver; and oxidizers such as chlorine, chloramines, any of the group VII compounds in the Periodic Table, permanganates, ozone, fluorine, iodine, peroxides, and so on.

All of these compounds are direct toxins, because they directly interfere with the biological cycles in the cell and the cell enzymes.

Some organic materials are resistant because they are chlorinated, and the chlorination process makes them substantially harder to deal with. Others are toxic because they are phenolics. Phenol was one of the first major organic disinfectants.<sup>13</sup> It can be biodegraded readily, but it takes some work.<sup>14</sup>

The point is that complex organic materials have some ability to biodegrade, if the conditions are correct. Given any combination of temperature, pressure, nutrients, and substrate, the bacteria will act in a manner that promotes their survival and growth. The art is in engineering a system where the bacteria do what they will and want to do in a manner that coincides with your objectives.

One of the best sources for information on biodegradability of all organic compounds is Karl Verschueren's book, *Handbook of Environmental Data on Organic Chemicals*, published by Van Nostrand Rheinhold, NY. The book is quite complete and has excellent data on biodegradability for specific organic compounds that is unavailable elsewhere.

## 9.16 Modeling the Biological Process

There are a number of different activated sludge models available for design and evaluation. Some are very good, and some are very expensive. The designer of a wastewater system is faced with several challenges in trying to decide which way to proceed with the design of a system – static models, dynamic models, code models, or theoretical models.

If the wastewater treatment plant is being built with public money or the designer is required to obtain a permit for the design and operation of the

plant, then the code or regulatory models become very important and must be addressed. For public works, the general standard is the Ten States Standards.<sup>15</sup>

Theoretical models are based on design handbooks, such as Metcalf and Eddy.<sup>16</sup> Static models are usually computer programs that produce a specific set of design parameters under given conditions. Static models can be useful for estimating purposes using the average values for various wastewater parameters such as flow, BOD, TSS, and so on. The static models will generally follow accepted practice and can produce a preliminary workable design depending upon the amount of detail in the program.

Dynamic models are based on the IWA modeling systems, and they can provide a continuous evaluation of various aspects of the treatment plants. The dynamic models can be used to help evaluate dynamic changes in the wastewater flows and concentrations, including hydraulic surges, storm flows, and spills and slugs of biological materials – something which the other static and analytical models cannot do.

The IWA models deal with the activated sludge systems. As such, they do not address the entire plant – just the portions under aeration. Additional models are required for evaluation of clarifiers, sludge thickeners, and anaerobic digestion functions of the treatment plant. These models are generally coupled into the IWA models to provide a complete representation of the treatment plant operations.<sup>17</sup> Most, if not all, of the companies offering wastewater treatment plant models offer a number of options on the associated models. There are a number of models for clarifiers, centrifuges, filtration, pumps, tanks, chemical dosing, pipelines, and equipment, and an IWA model for anaerobic digestion (ADM1). So, the complete wastewater plant can be modeled.

Additionally, various modeling companies have developed sanitary and stormwater models, and river models. At this time, there are a few companies with complete modeling systems designed for municipalities. A few have an integrated modeling system that can use one platform for all municipal operations.

Before investing in relatively expensive wastewater treatment plant modeling software, it is recommended that one purchases and studies *Wastewater Treatment Process Modeling* (2nd ed.), a publication of the Water Environment Federation, Alexandria, Virginia. The book is an excellent guide to modeling and model calibration.

### 9.16.1 Modeling Notes Before One Starts

If you are contemplating plant design or plant operations, plan on using simulations to design the plant and to provide your plant with models for operations. As previously mentioned, design by following codes can lead to substantial overbuilding of facilities, and uneconomic designs for unrealistic conditions. Build your models carefully and evaluate them using realistic scenarios.

The first task in building a model of a wastewater treatment plant is to investigate the type of model one wishes to use. As indicated above, there are a number of IWA models plus associated models, and the selection of the wrong model can lead to unusual and inaccurate results.

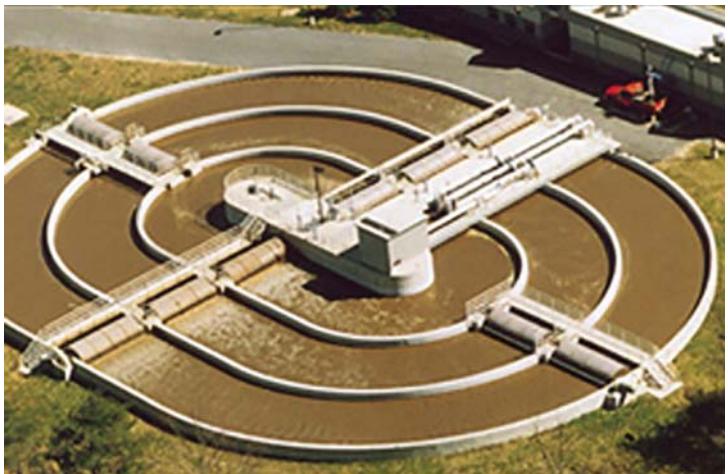
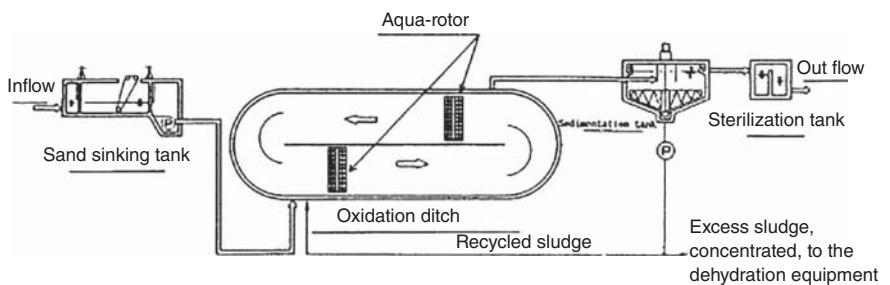
1. Sketch out the system you wish to model. Include all the flows and pathways in the system. For example, an orbal wastewater treatment plant is in some respects similar to an oxidation ditch. The aerators on the orbal are surface aerators, similar in operation to the Kessner Brush used in an oxidation ditch. The aerators impart energy to help move the wastes along the channel in both units.

Although the manufacturers of both units would scream that their systems are totally different, a moment's inspection would argue that they are similar. One of the principal differences between the two is the open partition between the paths of the orbals – as shown in Figure 9.10. The orbals resemble an oxidation ditch in concentric rings. The walls of the orbals have large openings so that the wastes can flow from the outside channels to the inside channels in response to hydraulic conditions. But the units are similar in design and the configuration of the models must accommodate the free passage of wastewater from one compartment to the next.

2. Add the appurtenances, such as pumps, clarifiers, chemical dosage, sludge recycle, and so on, to create a process flow diagram.
3. Add the instrumentation and controls – preferably on a second sheet, so that you don't confuse the process with the controls
4. Add the first estimate of the quantities of pollutants – both in mass flow, and in concentrations expected.
5. Look carefully at your particular wastewater treatment model to see what parameters you will need to define.<sup>18</sup>
6. Consider where you want to collect your samples for operation analysis.
7. Decide on the time steps you will use to collect the modeling data. This is a very big decision because of the number and cost of the analyses. Look closely at the model structure and the requirements, because the accuracy of your model can depend upon the number of samples and the interval of the data collected.<sup>19</sup>

The IWA ASTM 2D model has over two dozen parameters that need values for accurate modeling. Some programs have “splitters” – components that arbitrarily assign fractions of the influent and effluent loadings to the representative fractions for model input. While this is often suitable, it may lead to inaccuracies in the modeling.

As a practical matter, you might want to consider a maximum time-step of 30 minutes for modeling purposes. That would mean 48 samples conveyed to the laboratory daily for analysis. The sampling and modeling campaign should run for a minimum of five days to insure that you can calibrate



**Figure 9.10** Comparison between orbal and oxidation ditch wastewater treatment plants. Top drawing is an oxidation ditch plant schema from a Japanese website: [http://nett21.gec.jp/JSIM\\_DATA/WATER/WATER\\_2/html/Doc\\_231.html](http://nett21.gec.jp/JSIM_DATA/WATER/WATER_2/html/Doc_231.html). Bottom photo is an orbal wastewater treatment system: picture from <http://www.wateronline.com/doc/orbal-multichannel-oxidation-system-0001>.

the model. Optimum time might be as much as 10–15 days to insure that weekend operations and occasional storm effects have been sampled and can be modeled.

8. Collect the data on the performance of the various components such as the pumps, pump curves, aerators, aerator efficiency and power requirements, and oxygen transfer rates, pipe sizes, and so on, and set it aside for data entry as you assemble your model.
9. Build your model using the representative graphical interfaces.<sup>20</sup>
10. Apply your data to the various parts of the system.
11. Prepare your influent database.

12. You will need to make some assumptions about the biomass quantities already in the system, and distribute them accordingly.
13. Start the model at steady state and see what crashes.
14. Fix the model parameters.
15. Start at Step 12, and work until the model runs at steady state.
16. Then go to dynamic state by changing the model timescale.

If it sounds like a lot of work, it is.

The following is a partial list of some of the more popular and functional wastewater treatment plant modeling platforms. The information is as accurate as can be made at the time of writing (2018), and some of the information is gathered only from the websites of the companies offering the platforms.

### 9.16.2 Free Wastewater Treatment Modeling Platforms

#### 9.16.2.1 SSSP

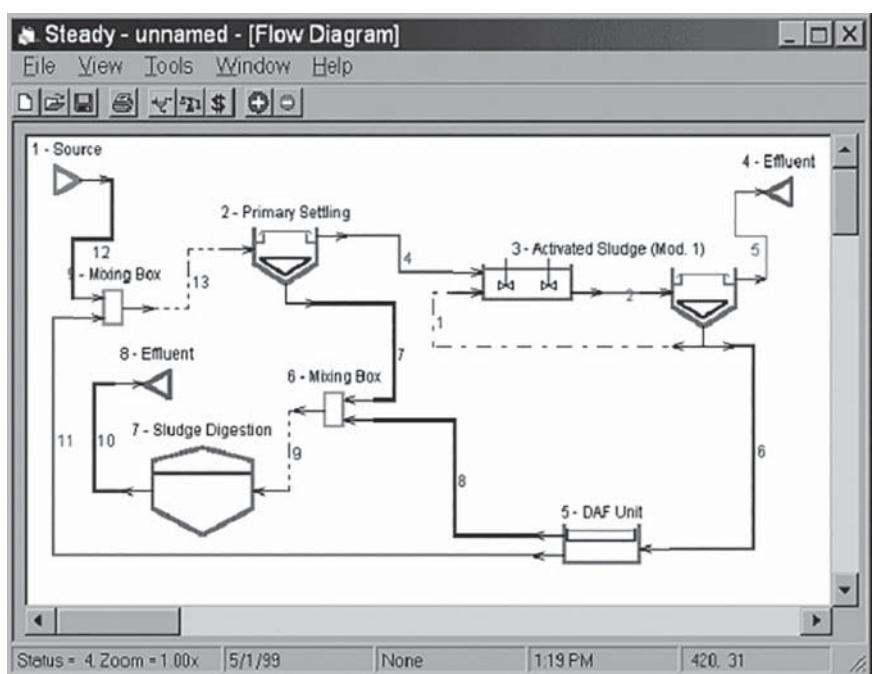
The first and oldest wastewater treatment model is the SSSP model. It was developed in 1987 by Dr Les Grady and one of his graduate students, Steven Birdrup, at Clemson, SC. It is an old DOS program but is highly flexible and runs a number of options and solves the basic equation of flow for nitrification and denitrification in wastewater systems, using the IAWQ model equations as a basis. Given the time of its development (1987), it is a very good work. The graphical interface is very rough by today's standards, but the model is free. It is also extremely difficult to locate. The model performs both static and dynamic simulations, but it uses the very old DOS platform which is generally unavailable in today's world.<sup>21</sup>

#### 9.16.2.2 STEADY

The second free model is the STEADY model. It was developed at the University of Texas, and it is a self-installing zip file of about 3.7 MB. The author, Dr Gerry Speitel, posted the model at: <http://www.ce.utexas.edu/prof/speitel/steady/steady.htm>.

The model provides a static solution to a plant design, and allows one to set up one's own simulation and run it to develop a steady-state design solution. Unfortunately it is not a dynamic model, and does not use ASM2, ASM2d, or ASM3 models.

The model will allow one to configure a wastewater treatment plant for certain limited designs and develop some data on the plant. It also has some good graphics and a well-defined adjustable interface and good screens for a manual. The principal limitation is that it does not model the clarification or the refinements of the activated sludge model very well. It is fun to play with and, considering the price, it is well worth using. Because it is simple, it can be used in Imperial or metric units. A sample of a STEADY screen shot is shown in Figure 9.11.



**Figure 9.11** Screen shot of STEADY program.

#### 9.16.2.3 JASS

A third free model is the JASS model that was developed by Uppsala University, Sweden. The model is in Java and is available on the website only. The model apparently can be used only if connected to the Uppsala University site, or their research site.

#### 9.16.2.4 Stoat

Originally, WRC plc. in the UK developed a wastewater treatment program. The principal author was Dr Jeremy Dudley. A few years ago, WRC decided to stop selling the model and released it to the public. Stoat is available on the WRC website after registration.<sup>22</sup>

The model is excellent, and has been widely used and accepted for dynamic modeling of activated sludge. The model is written in FORTRAN, but compiles and runs on all computers, has a good graphical interface, and a very useful user's manual. The software runs a variety of models including the sequencing batch reactor, a lamella model, fixed film reactors, biological phosphorus removal processes, chemical phosphorus removal processes, mesophilic and thermophilic digestion models, sand filtration models, and a very good final clarifier model. Stoat can model the effects of storm flows and can address

chemical dynamics within the modeling system, including such items as pH changes. As a final bonus, Stoat has the option of modeling on the basis of BOD and COD, so that if one only has BOD data, there is no need to make the conversion to COD – the model can handle that.

Other associated models include heat exchangers, centrifuges, rotating biological contactors, and submerged biological contactor models. The modeling platform is extremely robust and broad and easy to use, and the results of individual runs can be output both graphically and in tabular fashion.

The process descriptions and user manual are also clear and well-defined. The program is user-friendly and will run with BOD inputs as well as COD inputs. The advantage of that is that most environmental data are generated using BOD rather than COD.

### 9.16.3 Commercially Available Modeling Tools

The modeling platforms and companies listed below are commercially available, some for lease, and some for purchase. The purchase prices can be obtained from the organizations directly.

#### 9.16.3.1 GPSX

GPSX is produced by Hydromantis, Inc. in Hamilton, Ontario, and is represented in the US in Chicago. The company has a number of models for activated sludge and treatment works modeling, including ASM1, ASM2, ASM2d, ASM3, a temperature-dependent version of ASM1, and an anaerobic digester model ADM1. GPSX links directly to and from their Capdet Works program for cost estimation, and can design and model a complete works from start to finish.

The model will also perform dynamic simulations for volatile organic compounds and metals by linking with the TOXCHEM program.<sup>23</sup> TOXCHEM is often used to estimate the volatile chemical air emissions from treatment works.

A sample of a GPSX screen shot is shown in Figure 9.12. The GPSX program is complete and thorough, has good graphics and it is easy to initialize – as dynamic models go. Behind each graphical icon is a set of sophisticated models that can simulate real-time wastewater treatment works. Some of the refinements included in the modeling system are: ability to correct for elevation and types of aeration elements; ability to include chemical addition and enhanced precipitation; and the ability to model complete mix and plug flow conditions for various types of phosphorus and nitrogen removal systems.

One other useful feature of the GPSX program is that it has automated the input file functions. The input file for many programs is often a large data file with the various wastewater inputs fractionated into 16 chemical parameters

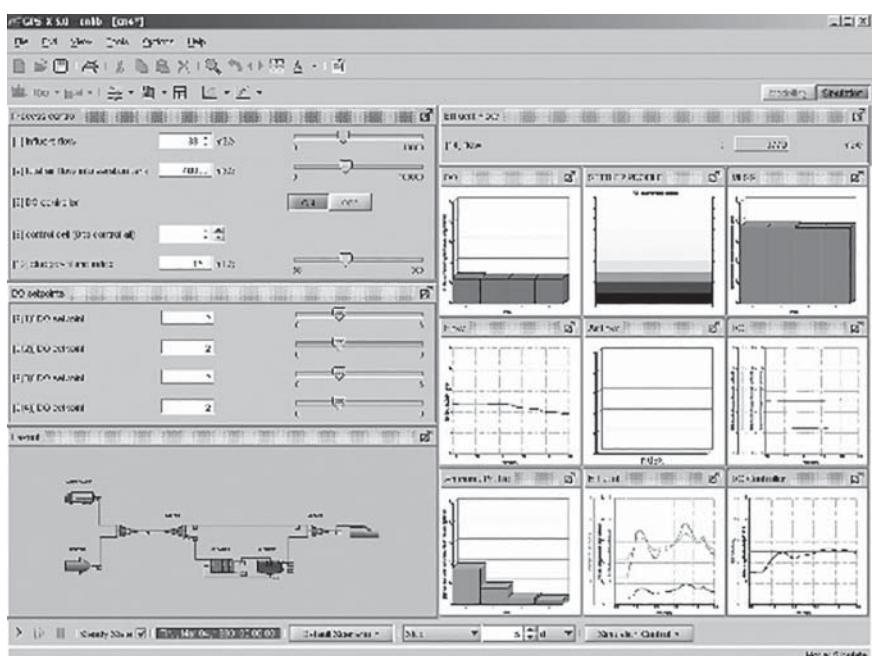


Figure 9.12 Screen shot of Hydromantis software GPSX.

as required by the IWA models. Without this assistance, creating the input file for a dynamic model can be a substantial data entry task.

In addition to GPSX, Hydromantis has CAPDEWORKS, a model that allows the estimation of the construction cost of facilities, and evaluation of their effective operational life; and SIMUWORKS, which allows one to configure a wastewater plant as if it were a flight simulator program and make modifications in real time to respond to changing concentrations and hydraulic loading conditions, and respond to the performance of the equipment.<sup>24</sup>

The GPSX software is excellent, is user-friendly, and has a wide base of use and support.

### 9.16.3.2 SUMO

SUMO is a relatively new modeling platform and the brainchild of Dr Imre Takacs.<sup>25</sup> SUMO is sold by Dynamita, which operates from Nyons, France ([www.dynamita.com](http://www.dynamita.com)).

SUMO is a powerful open process source, multipurpose simulation environment developed for environmental models, specifically for municipal and industrial wastewater treatment plants. The modeling platform will handle a wide range of biological and phosphorus removal configurations, and it uses an Excel-based open-source code called SUMOSLANG®.

SUMO can simulate traditional biokinetic models dynamically or in steady-state, mixed equilibrium–kinetic models and direct algebraic models, depending on the simulation mode.

SUMO is supplied with internally researched and developed whole plant models as well as focus models (e.g., with focus on the fate of nitrogen and greenhouse gases). The seven most widely known published models are also included in data archive known as the SUMO Museum for N and P removal, and that is a convenient set of configurations for the most advanced wastewater treatment models currently in use.

As an aside, wastewater treatment plant configurations have changed dramatically over the past 30 years, from a simple activated sludge configuration to more advanced configurations that are used for biological nitrogen and phosphorus removals. Some of the more advanced configurations are quite complex, and require a considerable effort to set up and run.

The SUMO program has the plant setup with preconfigured tank sizes, plant circulation rates, sludge wastage, and so on. The designer can use the existing configuration in a steady-state mode, or enter dynamic input data and run the model in a dynamic mode. The outputs are clear and the graphics are good. Clicking on one of the process elements gives a tabular summary of the key concentrations in a specific process unit.

SUMO is relatively easy to use, and helps the designer save time because the model is preloaded, and that cuts down on the startup time for modeling. Changing from a preloaded design to a custom design is as simple as entering data into an Excel spreadsheet.

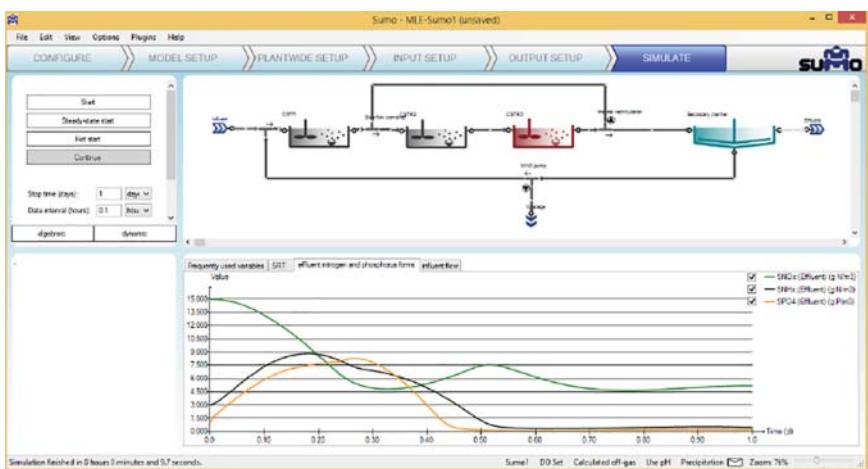
The program is quite user-friendly and the plant models are clearly illustrated. An example of a SUMO desktop modeling display is shown in Figure 9.13.

The other item that SUMO has which is unique is a graphically calculated sludge retention time (SRT). To use it, one merely drags the symbols of the process units into a window that will automatically calculate and display the SRT, as shown in Figure 9.14.

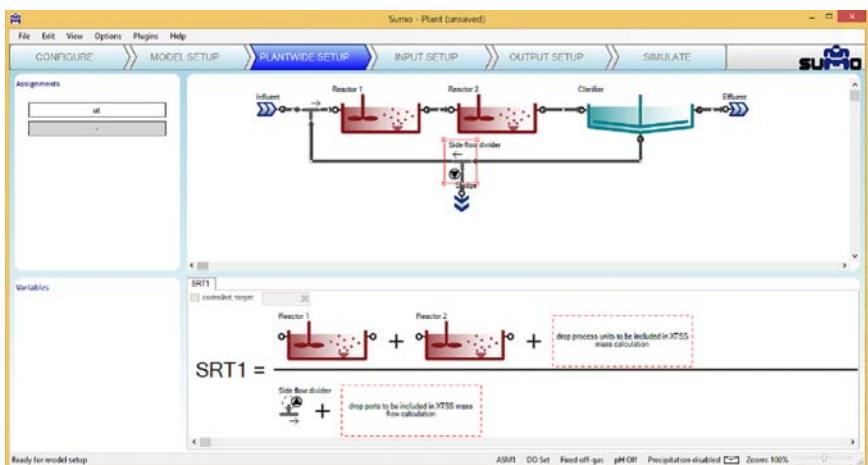
Overall, SUMO is a very easy-to-use graphical interface and modeling program with enough advanced features to accommodate almost any user.

#### 9.16.3.3 SIMBA

SIMBA was developed in Germany, and is being marketed by InCntrl in Canada. The model is highly flexible and can be focused on process details, such as friction losses from piping, and other areas in addition to running the available IWA wastewater models. The SIMBA interface comes with preconfigured designs for ease of modeling. The user has to enter tank sizes, and many



**Figure 9.13** Example of a SUMO interface window.

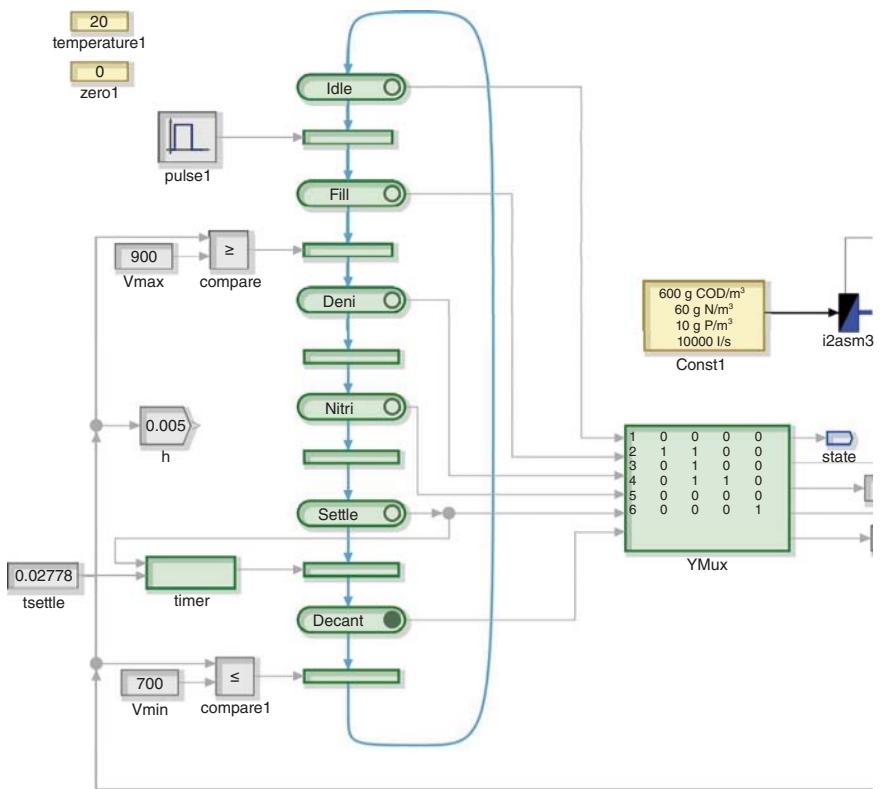


**Figure 9.14** Graphical calculation of sludge retention time (SRT) example in SUMO.

other variables, but the advantage is that the connections and configurations are pre-connected, and that makes setting up the model that much easier.

The icons are well laid out and easy to use, and part of the control panel for each of the icons displays the properties of the selected icon. The data can be changed as desired, making the model totally customizable.

SIMBA is also capable of drilling down in the model, and the calculation of process variables is well within its reach. For example, optimizing air supply is



**Figure 9.15** Partial screen shot of SIMBA control panel interface showing functional relationships and flowpaths.

often a headache, and establishing a  $k_L a$  (oxygen transfer coefficient) is often more art and experience than actual calculation. SIMBA allows the designer to estimate the pressure and head losses in piping and distribution for the airlines, and calculate the losses through the diffusers. As such it is suited for a professional who is charged with the detailed design of a wastewater treatment plant. A very good choice with a good solid interface (Figure 9.15).

#### 9.16.3.4 Biowin

Biowin is another Canadian product. It was designed by engineers and is relatively straightforward in use. The Biowin website has a lot of helpful descriptive information about the program and the technical features. Biowin is extremely popular and in wide use in a number of municipalities and consulting firms. They offer a complete line of plant models, and options including anaerobic digestion, solids processing, clarifiers, and membrane applications.

### 9.16.3.5 WEST

WEST (the World-wide Engine for Simulation Training and Automation) software is now produced by the Danish Hydraulic Institute (DHI), as a part of their overall modeling platform which is designed to model and analyze drinking water distribution systems, stormwater and sanitary water collection systems, wastewater treatment, and river modeling for biological and physical parameters. One of the advantages of this approach is that one software platform can integrate the outputs and inputs under a single operating system. Another advantage is that the models can “talk to each other” without a translator program. This makes the application able to address such things as the wet weather flow on the treatment plant, and the river.

The following comments are primarily restricted to WEST.<sup>26</sup> The interface is very good. WEST produces a dynamic model output that has a good graphical interface and true dynamic environment. Unlike some programs, the simulation can be real-time, showing the changes in the wastewater strength and the effects of those changes on the behavior of the model. WEST uses sliders to enable real-time control of input variables. As with some of the other modeling programs, one can define variables while the program is operating. With few exceptions, most of the models are open-source code, so they can be tweaked or modified as the occasion may arise.

One of the strongest criticisms of the WEST program is that it tends to be too academic. Where other programs provide one model for a clarifier, WEST has at least three, and the technical information in the accompanying manual is largely academic rather than practical.

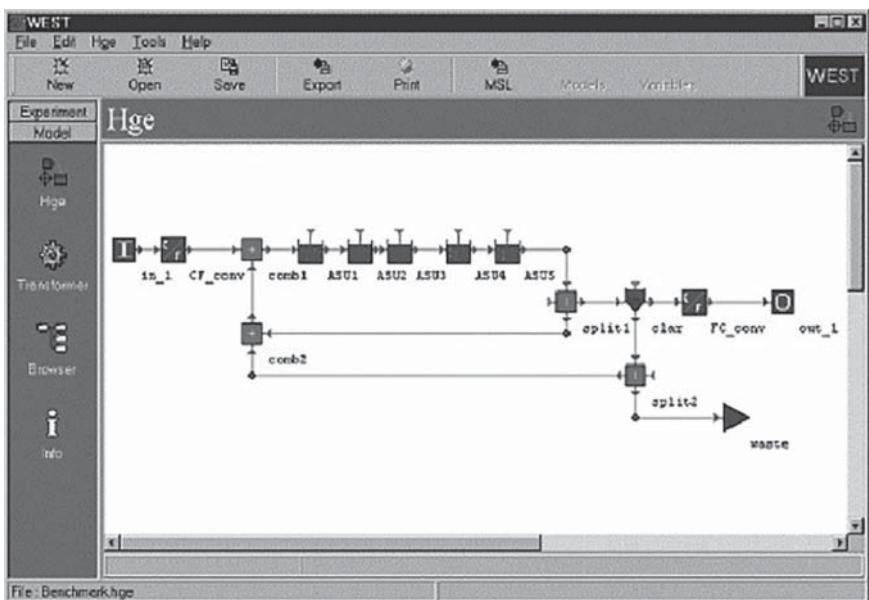
Samples of the WEST model-building screen and output screens are shown in Figures 9.16–9.18.

### 9.16.4 Modeling Summary

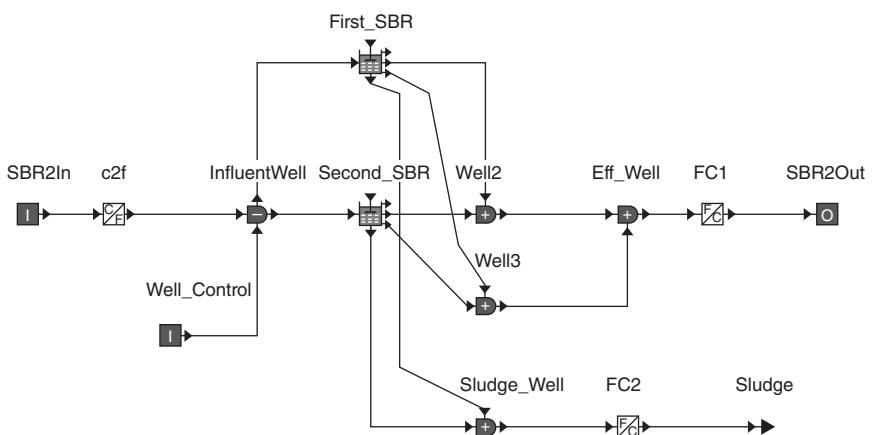
Efforts directed toward wastewater modeling can be very useful in the design, as a good model can help avoid many of the design and operational mistakes in an ever-changing environment. Modeling is not necessarily easy, but it can be worthwhile, and when the model is properly set up and calibrated, the results can be very informative.

A final word about modeling is that it is often an exercise in “matching peaks.” The fluctuations in the input can never account for the same fluctuations in the model, and one has to look at the models as an approximation of what is happening in the wastewater treatment plant.

It is often predictive, and can, under the right circumstances, be reasonably accurate in predicting behavior and changes that occur due to operational modifications, but it is seldom perfect. When one has the plant “tuned” or “calibrated” to the real world, the peaks and valleys in the parameters will occur at the same time as those that occur in the plant. The magnitude may often



**Figure 9.16** WEST software typical plant configuration.



**Figure 9.17** WEST configuration for a two-tank sequencing batch reactor system.

be different, but the duration of the internal “events” will be approximately the same in the model as in the plant. The concurrence of the “peaks and valleys” indicates that one has the basic process correct and has accounted for many of the significant influences on the real world plant.

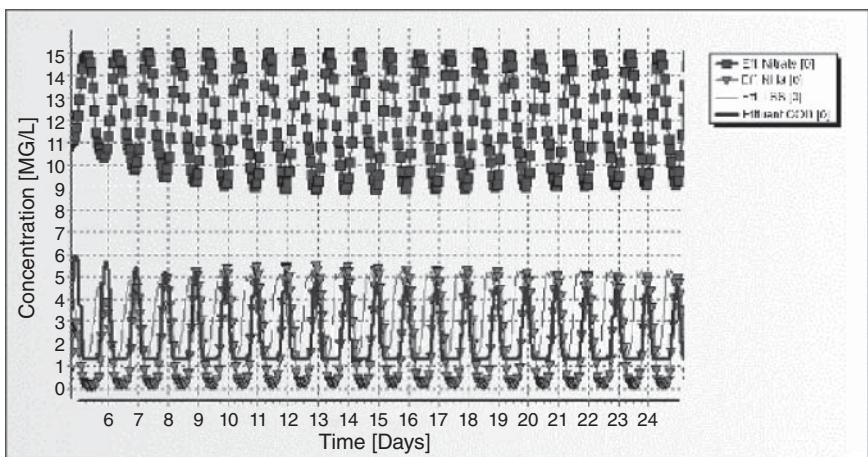


Figure 9.18 Example of WEST dynamic control output graphics.

## Notes

- 1 Mostly, the operator has a set of parameters that work to provide the effluent quality he or she is trying to achieve.
- 2 <http://EnvironmentalLeverage.com>, 812 Dogwood Drive, Suite A, North Aurora, IL, 60542.
- 3 <http://EnvironmentalLeverage.com>, 812 Dogwood Drive, Suite A, North Aurora, IL, 60542.
- 4 EPA criteria for free ammonia in rivers is  $0.035 \text{ mg l}^{-1}$ .
- 5 At  $10^\circ\text{C}$  and pH 6.5, the percent of un-ionized ammonia of the total in the water is 5.89%; at  $20^\circ\text{C}$ , it is 12.54%. See *EPA-600/3/79-091 Aqueous Ammonia Equilibrium – tabulation of percent un-ionized ammonia*.
- 6 <http://www.bioconlabs.com/nitribactfacts.html>.
- 7 The source for much of what follows is from *Activated Sludge Systems* by Orhon and Artan, published by Technomic Press, ISBN 1-56676-101-8. The book is about 600 pages of everything one would like to know about kinetic reactor modeling and activated sludge, but were afraid to ask.
- 8 There are at least two ways to determine the substrate utilization rate. One way is to use the optical density of the substrate, and compare the optical densities to determine the maximum growth rate. This technique is somewhat more approximate than actual sampling of the substrate and running suspended solids tests to determine growth rates.
- 9 The accuracy of the suspended solids test varies inversely with concentration, from 33% at  $5 \text{ mg l}^{-1}$  TSS to 0.76% at  $1707 \text{ mg l}^{-1}$  TSS. There are no published accuracy data for the VSS test.

- 10 Orhon, D. and Artan, N. *Modelling of Activated-Sludge Systems*. Technomic Publishing Co. Inc., Lancaster, PA.
- 11 Activated Sludge Model No. 1 (ASM1) is published by the International Water Association, Alliance House, 12 Caxton St., London, SWH 05Q, UK.
- 12 The media used in a trickling filter can be fixed plastic media, and with some caution, the media attached to rotating biological contactors – large disks which are partially submerged in wastewater. Bacterial films attach to the media in both types of systems, and the nutrients in wastewater are removed by the bacterial film in much the same manner as the removal occurs in a fixed film, non-rotating trickling filter.
- 13 The effectiveness of disinfectants is still measured in phenol coefficients – where the dose of a disinfectant is compared to the disinfecting power of phenol for specific organisms such as salmonella.
- 14 Phenol degradation can be accomplished by activated sludge at levels up to about  $420 \text{ mg l}^{-1}$ , if the bacterial population has been given time to acclimate to lower concentrations of phenol and develop the enzymes required for digestion. See “Review on research for removal of phenol from wastewater” by Sunil J. Kulkarni and Jayant P. Kaware. *International Journal of Scientific and Research Publications*, 3 (4). <http://www.ijsrp.org/research-paper-0413/ijsrp-p16116.pdf>
- 15 The Ten States Standards, published by the Great Lakes – Upper Mississippi River Board (GLUMRB) of State and Provincial Public Health and Environmental Managers, has published *Recommended Standards for Wastewater Facilities*, <http://10statesstandards.com/wastewaterstandards.pdf>, which has become one of the *de facto* standards for design of public treatment works. Almost every state in the US has incorporated these standards into their review process for public treatment works.
- 16 Metcalf & Eddy, *Wastewater Engineering: Treatment and Reuse*, McGraw-Hill.
- 17 A complete list of IWA models can be found at [http://www.iwapublishing.com/sites/default/files/documents/online-pdfs/IWA&percnt;202016&percnt;20brochure\\_issuu.pdf](http://www.iwapublishing.com/sites/default/files/documents/online-pdfs/IWA&percnt;202016&percnt;20brochure_issuu.pdf).
- 18 Select the model and modeling platform carefully. Be aware that there are four activated sludge models, and each is slightly different. The best source for information on the differences is *Activated Sludge Models ASM1, ASM2, ASM2D AND ASM3* by the IWA Task Group on Mathematical Modeling for Design and Operation of Biological Wastewater Treatment. The document is available at <https://www.scribd.com/document/98403051/Activated-Sludge-Models>. The different modeling platforms have preferences for the type of model being used, and there has been a debate about the comparisons between some of the models, particularly ASM2d, and ASM3.
- 19 At one time Dr M. Bruce Beck, with the University of Georgia at the time, had an automatic sampling unit consisting of two fully instrumented sampling and analytical trailers which could collect and analyze water and wastewater for a

- large number of parameters at 15-minute intervals. The results were very impressive and provided extremely good data for analyses and modeling of streams and treatment plants.
- 20 It is important to decide whether you want a complete mixed tank model aeration basin or a plug flow model aeration basin. There is a substantial difference. There is a paper that addresses the issue, entitled "Is an upgrade really necessary?" which was published in the 2002 September issue of WE&T. It is available from the downloads section at [www.globalenvironmental.biz](http://www.globalenvironmental.biz).
  - 21 See Bidstrum, SM, and Grady, CPL, Jr. (1988). SSSP simulation of single sludge processes. *Journal of the Water Pollution Control Federation* 60: 351–361. You will also want to download the revised and modified manual: <http://www.rpi.edu/dept/chem-eng/Biotech-Environ/Environmental/Clemson/sssp.html>.
  - 22 [www.wrcplc.co.uk/ps-stoat](http://www.wrcplc.co.uk/ps-stoat).
  - 23 TOXCHEM was developed by Enviromega Ltd. Company (Campbellville, Ontario), in cooperation with the Environment Canada Wastewater Technology Center. A free download of a trial version is available with registration from the Hydromantis website.
  - 24 For example, during warm weather the temperature of the wastewater increases, lowering the maximum oxygen content under saturation conditions. The warmer water also increases the activity of the microbial population in the works, at the same time that it decreases the effective oxygen transfer coefficient. The program allows one to adjust for such differences.
  - 25 Dr Takacs is a highly experienced modeler, and has developed the widely used model that simulates the performance of a clarifier.
  - 26 At one time, the author was working with the WEST program and acting as a technical and sales representative for their product. The descriptions of the WEST software are more complete because he is most familiar with their product and its performance. That does not take away from the abilities of other software manufacturers' products, and he has attempted to be impartial in looking at their software.

## 10

# Anaerobic Treatment

In the previous chapter on biological wastewater treatment, we discussed some of the elements of anoxic and anaerobic treatment for nitrate and phosphate removal. In this chapter we will focus on anaerobic activity treatment in more detail, and anaerobic digestion.

## 10.1 Basic Anaerobic Processes for Wastewater

Anaerobic processes are those that occur, by definition, without oxygen. There is some confusion between anoxic processes and anaerobic processes. Both processes are anoxic, and both can be reducing environments, but the anaerobic environment has a much more negative oxidation reduction potential (ORP).

In general, in wastewater treatment processes, the ranges shown in Table 10.1 apply. The ranges are published by Yellow Springs Instruments (YSI), makers of ORP measuring probes and Hach, Inc., who have slightly different numbers for ORP, so consider the ranges as approximate figures.

Anaerobic decomposition produces both organic acids and gas. Anaerobic processes are substantially slower than aerobic processes, but they develop about a quarter of the biomass of an aerobic process. Anaerobic treatment takes place relatively slowly, is often temperature- and toxin-sensitive, can be easily upset, and requires substantial mixing.

Anaerobic treatment is used in three areas. The first and most common is the degradation of biosolids from conventional municipal and other wastewater treatment process. The second is the reduction and treatment of high-strength wastewaters containing soluble degradable organic materials. The third is relatively recent, and includes removal of nitrogen and phosphorus from wastewater by biological means.

High-strength organic wastes where the influent biochemical oxygen demand (BOD) or chemical oxygen demand (COD) is well above  $500 \text{ mg l}^{-1}$

**Table 10.1** Biochemical reactions and corresponding oxidation reduction potential (ORP) values.

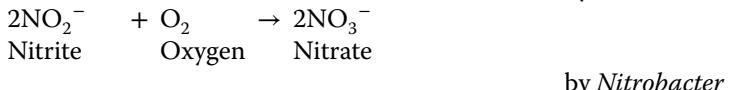
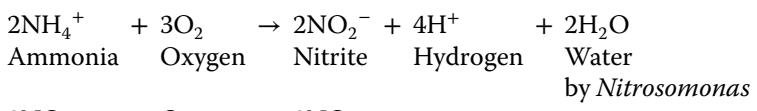
Biochemical reaction	YSI ranges (ORP, mV)	HACH ranges (ORP, mV)
Nitrification	+100 to +350	+100 to +350
Reduction of carbonaceous BOD degradation with free molecular oxygen	+0 to +250	+25 to +250
Biological phosphorus removal	+25 to +250	-100 to -250
Denitrification	+50 to -50	-50 to +50
Sulfide ( $\text{H}_2\text{S}$ ) formation	-50 to -250	-50 to -250
Biological phosphorus release	-25 to -250	-100 to -250
Acid formation (fermentation)	-100 to -225	-100 to -225
Methane production	-175 to -400	-150 to -280

The Hach range is the range recommended by Hach Chemicals, Inc.

are often very good candidates for anaerobic treatment, often because the oxygen demand is so high that it is impractical to attempt to provide enough oxygen to satisfy the demand. The wastes in this category could include animal feedlot wastes, sugar processing wastes, petroleum wastes (if the toxicity is controlled), and many canning and dyestuff wastes where water-soluble organics are used in the process. The processes are highly temperature-sensitive, and will effectively cease in cold weather operations.

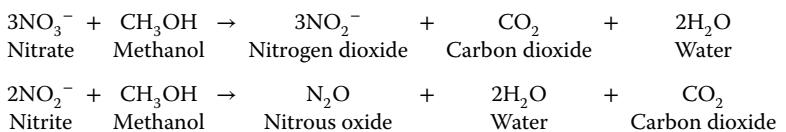
You will recall that part of the general formulation for optimum chemical composition of wastewater for biomass growth includes a carbon: nitrogen: phosphorus ratio (COD basis) of 100:5:1, as elemental C, N, and P. With some careful manipulation of the oxygen concentration for the mixed liquor suspended solids (MLSS), the bacteria will reduce nitrogen, and uptake and remove phosphorus from the wastewater.

Denitrification is accomplished by a number of bacteria – *Pseudomonas*, *Micrococcus*, *Achromobacter*, and *Bacillus*. In the process of removing carbonaceous organics from wastewater, ammonia is oxidized to nitrate. The organisms principally responsible for this transformation are *Nitrosomonas* and *Nitrobacter*. The oxidation reactions that produce nitrate are:



Nitrite does not accumulate in wastewater because the *Nitrobacter* operate at approximately three times the rate of the *Nitrosomonas*. This is detailed in Chapter 16.

The removal is slightly more complex and requires a carbon source (shown as methanol) that can be almost anything from simple sugars, to the carbon in the raw wastewater.



If organic substrates such as COD are used, the synthesis of  $\text{N}_2\text{O}$  is lower, and the consumption of COD produces around 0.25–0.30 of end-reactants.

## 10.2 Phosphorus Removal

Phosphate is reduced and absorbed only after the nitrogen has been consumed. Look at the C:N:P ratio. For every 100 units of COD removed, only about one unit of P will be removed by uptake in the cells. There is a special class of polyphosphate removing organisms (PAOs) in an anaerobic environment. According to one researcher in a *Chemical Engineering Lithograph* series, PAOs can remove P down to about  $0.4 \text{ mg l}^{-1}$ .<sup>1</sup> In order to get lower effluent results, chemical precipitation of P with aluminum or iron salts is the most practical choice. There is some evidence that the actual residual value may be down to less than  $0.1 \text{ mg l}^{-1}$ , but there are practical limits to the removal as well.

Biological P and N removals are accomplished by several different processes that involve a combination of anaerobic, anoxic, and oxidative processes in a specific order. In many cases, enhanced biological phosphorus removal (EBPR) can, through manipulation and encouragement of the growth of PAOs, obtain P removal rates of about 5% based on the weight of the organisms in the system, rather than the 1% cited above. The principal organisms are Acinetobacter and Proteobacteria, but there are a number of other organisms as well. Phosphorus is converted into a soluble form and assimilated by the PAOs.

In the first step in the conversion process, the organic matter present in the waste is converted to volatile fatty acids. Those volatile fatty acids, which are similar to acetates, are then converted to polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). These chemicals are important in the luxury uptake of phosphate by the cells. The chemistry is complex and tied into the growth of the cell, and is also dependent upon adenosine diphosphate (ADP) and adenosine triphosphate (ATP) and the Krebs cycle, also called the citric acid cycle. The Krebs cycle is important in cellular microbiology and research and is inherent to all bacterial life, but it is beyond the scope of this text.

Phosphorus removal is discussed in greater detail in Chapter 16. Briefly, however, the principal processes for removing phosphate from wastewater are (i) the A/O process; (ii) the Bardenpho process; (iii) the University of Cape Town (UCT) process; and (iv) the post-denitrification membrane bioreactor process. All of these processes utilize anoxic, anaerobic, and aerobic treatments in cycles or separate tankage as the wastewater passes through the treatment plant.

### 10.3 Basic Anaerobic Processes for Digestion and Treatment

Most anaerobic treatment (solids digestion) takes place in two specific temperature ranges – mesophilic and thermophilic. The temperature ranges are of the order of 85–100°F (30–38°C) and 120–135°F (38–50°C), respectively. From personal experience, the total gas production is about the same either way, but it is generated much faster at the thermophilic range and falls off more quickly for a given batch feed. Organisms can be brought from one temperature range to the other if the temperature conversion is performed slowly enough. It is a matter of re-growing or re-acclimatizing the existing organisms. The process often takes a week or two of gradual temperature changes. Above the thermophilic range, the temperature effects often cause partial sterilization and loss of organic growth, and at temperatures around 160°, sterilization occurs.<sup>2</sup>

In anaerobic processes there are three parts (see Figure 10.1):

*Fermentation of the wastes.* Conversion to acetates;

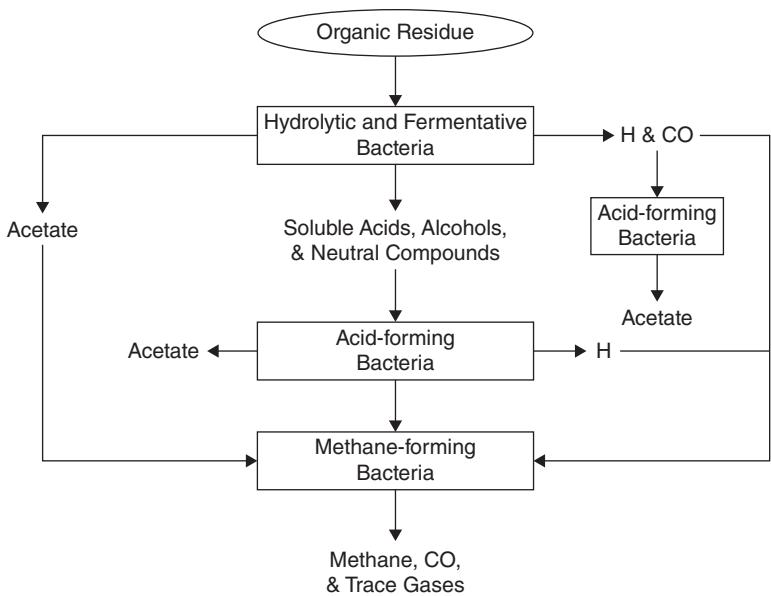
*Acetogenesis.* Conversion to acids, formaldehyde, and hydrogen; and

*Methanogenesis.* Conversion of formaldehyde, acetates, and acids to CO<sub>2</sub> and methane.

One of the principal challenges to anaerobic treatment is balancing the rates of growth. The acid-forming bacteria operate at about three times the rate of the methane-forming bacteria, and without a balanced microbial population, the wastes will turn acidic and all methane production will stop.

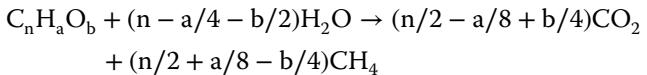
When anaerobic digesters are in “start-up” mode, this condition can occur, and it is known as a “stuck digester.” It is cured by the slow addition of alkaline buffers (dilute lime) to the mix. Strong alkalis can take the mix well out of the sludge range, where all activity stops, as can substantial changes in ionic strength of the liquor resulting from strong base addition.

Anaerobic fermentation can occur in the pH range of between 5.0 to about 9.0, while the bacterial methane operates in a much narrower range of between 6.5 and about 7.6, with the optimum point at about 7.0. General formulations for anaerobic decomposition have been provided by Buswell for



**Figure 10.1** Anaerobic digestion process. Source: *Methane Recovery for Animal Manures: The Current Opportunities Casebook*. Resource Development Associates, under contract to National Renewable Energy Laboratory; NREL/SR-580-25145, September, 1998.

carbohydrates:<sup>3</sup>



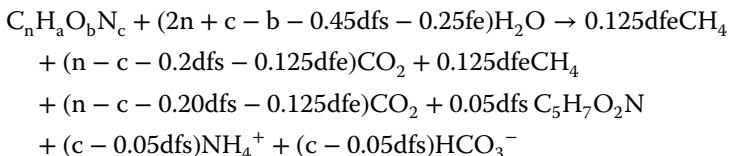
Most of the bacterial acids formed are generally propionic and acetic acids. Another researcher, McCardy and Murdoch (1963)<sup>4</sup> estimate the following:

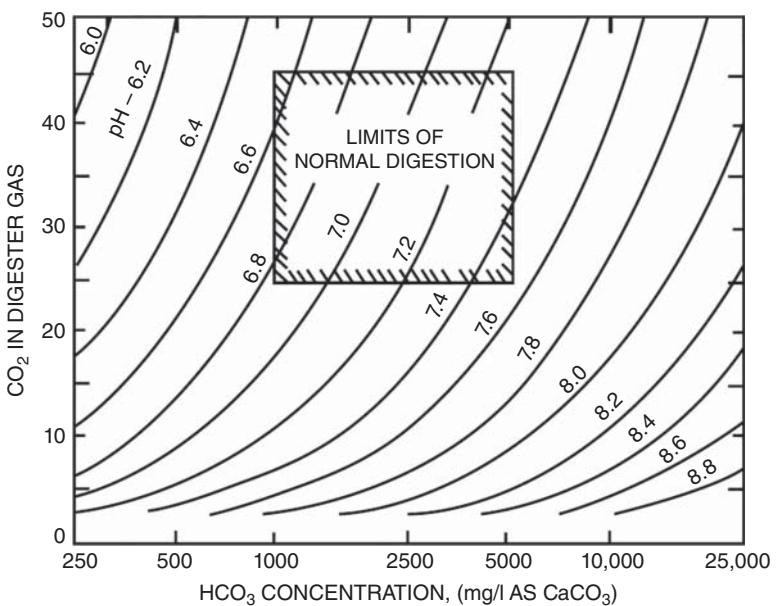
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Amino and fatty acids	$A = 0.054 F - 0.038 M$
Carbohydrates	$A = 0.46 F - 0.088 M$
Nutrient broth	$A = 0.076 F - 0.014 M$

---

where  $A$  = biological solids accumulated;  $M$  = MLVSS; and  $F$  = COD utilized. Another way of looking at the same reactions is provided by McCardy and Rittman (2001):<sup>5</sup>





**Figure 10.2** Bicarbonate and pH requirements for sludge digestion. Source: *Process Design Manual for Sludge Treatment and Disposal*. USEPA 1974.

where  $d = 4n + a - 2b - 3c$ ,  $f_s$  is the fraction of organic matter (COD or BOD) converted to cells, and  $f_e$  is the portion converted to cellular energy, such that  $f_e + f_s = 1$ . Here  $f_s$  may be estimated from cell yield, varying for different compounds. Typical values of  $f_s$  vary from 0.042 for fatty acids to 0.11 for methanol and 0.2 for carbohydrates. The value for proteins is 0.056.

The wastes must have a balanced feed, including freedom from high concentrations of salts, and relatively high levels of alkalinity must also be present to counteract the CO<sub>2</sub> generated. Figure 10.2 is taken from a sludge digestion manual, but it illustrates the point.

## 10.4 Anaerobic Pretreatment

This is performed on a number of high-strength biodegradable waste materials. Table 10.2 is taken from the study of McCarty and Eckefelder as published in *Public Works Journal* in 1964.<sup>6</sup> Note that the rates of loading are very high for the specific wastes, per unit volume of digester volume. The loading rate of 1 lb of X per 1000 of digester is equivalent to 0.0160 kg m<sup>-3</sup>.

In many instances, the completely mixed anaerobic reactor depends upon good mechanical agitation. A good reactor should have the following general elements:

**Table 10.2** Anaerobic pretreatment design parameters for contact stabilization and activated sludge processes.

Waste	Hydraulic retention time in days	Digestion temperature °F	Raw waste $\text{BOD}_5$ in $\text{mg l}^{-1}$	Pounds of VSS added per 1000 cubic feet of digester volume	Pounds of $\text{BOD}_5$ added per 1000 cubic feet of digester volume	Percentage removal on same basis as addition
Pea blanching	3.5	131		700		83
Pea blanching	6	99		400		85
Winery		97		200		87
Rye fermentation	2	130		930 total solids		54
Corn fermentation	4	130		330 total solids		76
Whey wastes	29	130		150 total solids		72
Acetic acids	30	95		1370	975	90
Maize starch	3.3	73	6820		110	88
Whiskey distillery	6.2	92	25 000		250	95
Citrus	1.3	92	4600		214	87
Wine	2.0	92	23 400 (VSS)	730		85
Molasses	3.8	92	32 800 (VSS)	546		65
Meat packing	0.5	75–92	1110–1380		131–156	92–95

A good source for feedlot and agricultural wastes design is published by the NRCS/USDA: [https://usdasearch.usda.gov/search?utf8=&percent;E2&percent;9C&percent;93&affiliate=nrcs\\_portal&dc=null&query=anaerobic+ponds&commit.x=0&commit.y=0](https://usdasearch.usda.gov/search?utf8=&percent;E2&percent;9C&percent;93&affiliate=nrcs_portal&dc=null&query=anaerobic+ponds&commit.x=0&commit.y=0).

Source: Data from McCarty and Eckenfelder, *Anaerobic Pretreatment of Industrial Wastes for Contact Stabilization and Activated Sludge Processes*; W. Eckenfelder (1966) *Anaerobic Pretreatment Before Activated Sludge Plant*, McGraw Hill.

1. provision for mixing;
2. allowance for gas handling;
3. temperature controls;
4. sampling ports;
5. solids removal system;
6. mechanical scum and hair breaking (note war story!);<sup>7</sup>
7. climatic seals to insure maintenance of anaerobic conditions;
8. provisions for odor control of gases and effluent;
9. system for breaking up accumulated fat and grease on the surface of the digester.

The design suggestions listed above are good guidance for sludge digestion as well as anaerobic treatment of wastes. Some anaerobic treatment systems

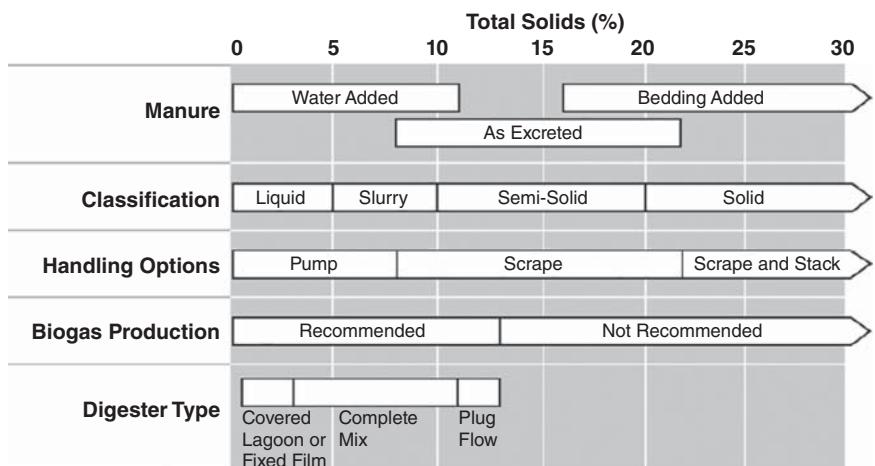
(filters) are established as attached growth or sludge blanket type units with either fluidized beds or fixed media to give a greater density of organisms. This is often met with mixed results, including various types of plugging and blinding from too much organic growth and from other materials in the waste. However, the greater surface area of a packed-bed anaerobic filter often offsets the operational difficulties and allows for greater density of organisms in a smaller reactor volume, thus saving capital costs.

The use of activated carbon as an attachment medium for the fluidized bed reactor has been a more recent trend in anaerobic reactors. The activated carbon will adsorb a number of toxic compounds such as phenols and allow the bacteria time to acclimatize to the lower relative density of the activated carbon.

One author has suggested separation of the two types of growth into an acid reactor and a methane reactor. The reactors would be of different sizes. This approach has also met with some mixed results and has not been universally adopted. This approach has been used primarily with sludge digestion, but lately is being applied to dairy manure and other feedlot wastes. The USDA has several publications on the subject of methane generation and recovery from digesters operating at feedlots and dairies.<sup>8</sup>

The focus on energy recovery and environmental control has led investigators to consider animal feedlots as potential sources of greenhouse gas prevention through energy recovery. In this regard the EPA has summarized some of the categories of successfully operated anaerobic digestion systems.

Thickening can be accomplished in a variety of ways, including gravity settling with gentle stirring (conventional thickening) and flotation. The point is to increase the solids feed and decrease the total amount of liquid stored. The



**Figure 10.3** Classification of anaerobic digesters based on solids content of digestion material.

upper limit is the ability to pump and stir the solids. The *AgSTAR Handbook*<sup>9</sup> provides some guidance on the thickening and pumping of various types of sludges, including those from feedlot operations (Figure 10.3).

## 10.5 Upflow Anaerobic Sludge Blanket Reactors

The upflow anaerobic sludge blanket reactor design (Figure 10.6) looks very much like a backwards clarifier with gas collection at the top. The anaerobic system is bottom-fed and the flow is up rather than downward in a clarifier. The sludge develops a blanket across the bottom of the clarifier, and as long as there is no significant change in the hydraulic loading (upwards velocity) to disrupt the sludge blanket, it acts as a filter as well. A modification of this design is a fluidized bed anaerobic reactor, where there is both mixing and a quiescent area for settling (Figures 10.4–10.6).

In this reactor, one option is to provide the reactor with granular materials to which the bacteria will cling. If an artificial media is employed, the reactor will

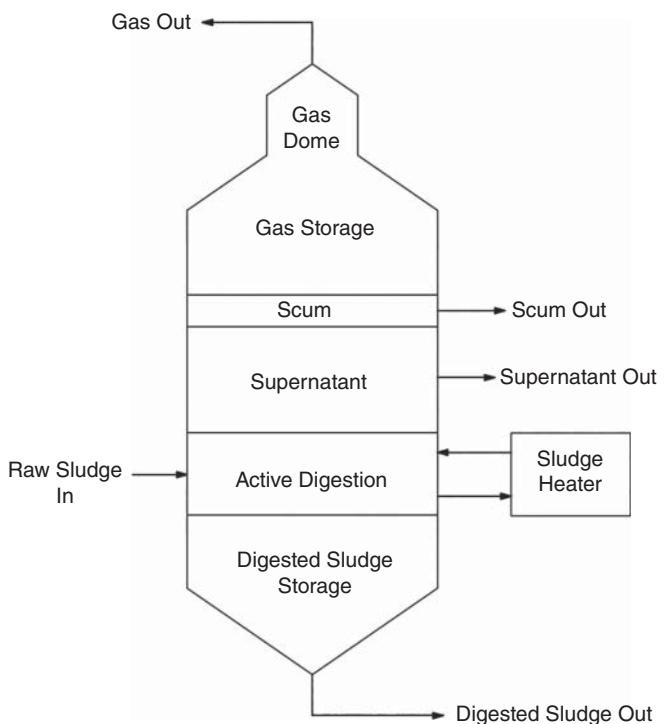


Figure 10.4 Dual compartment anaerobic digester.

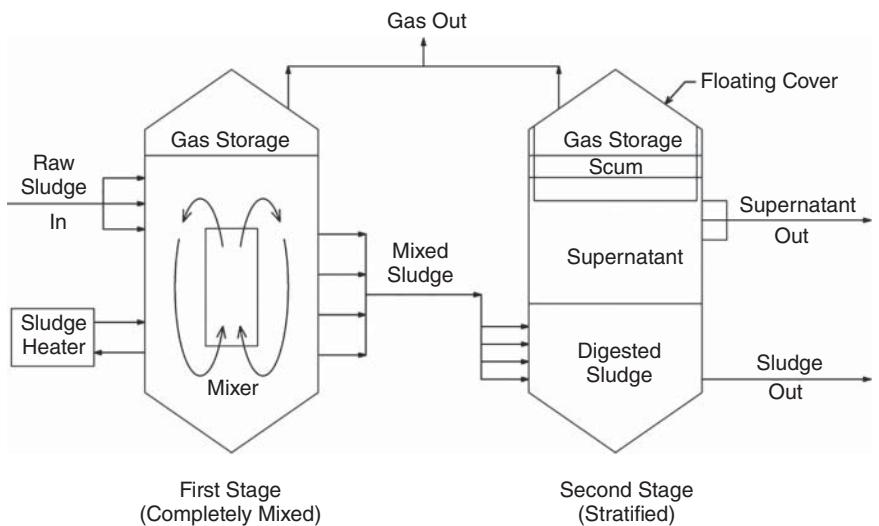


Figure 10.5 Two-stage, high-rate anaerobic digestion system.

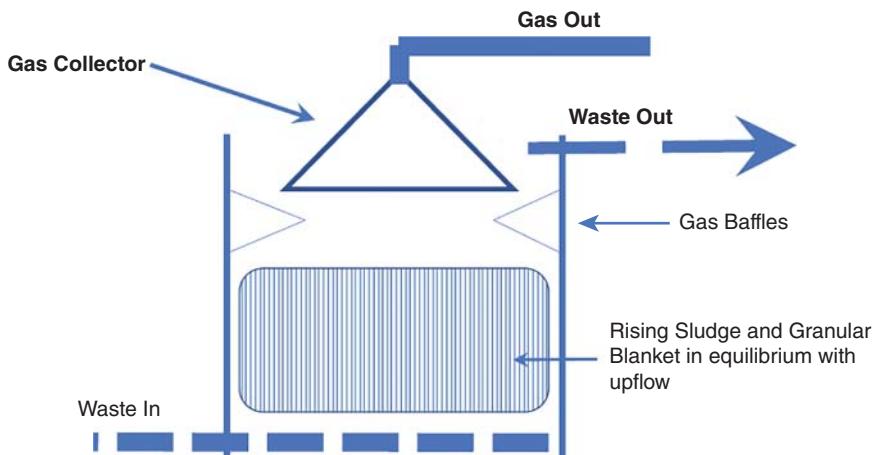


Figure 10.6 Upflow anaerobic sludge blanket reactor.

have to be stirred. If there is no additional granular material added, a sludge blanket will form and develop small granules of waste materials which should be retained in the lower compartment. The net upward velocity will be quite low, on the order of  $1 \text{ m h}^{-1}$  to keep the solids in suspension; the hydraulic retention time will probably be between 8 and 10 hours; the solids retention time will be between 30 and 60 days.<sup>10</sup>

A relatively recent development in anaerobic digestion is the development of the anaerobic sequencing batch reactor (ASBR). The treatment system is similar to that of a sequencing batch reactor, and has reasonable COD and BOD removal efficiencies – between 3.23 and 8.57 kg of COD/m<sup>3</sup>/day – but they can be difficult to operate with wide variations in strength and flow of wastes.<sup>11</sup> Of course, the organic loading to the treatment system is strongly dependent upon the type of wastes, and their biodegradability. For municipal sewage sludge, the database is extensive, but for industrial wastes, the database is much thinner, and pilot testing is strongly recommended.

## 10.6 Other Digester Configurations

Other digester configurations are also available and are becoming quite popular. Some digesters are fixed film digesters. In the fixed film mode, the digester tank is loaded with “attachable solids” which includes Rasch rings, gravel, and even pieces of bamboo. These solids form a platform for the anaerobic bacteria to attach themselves, and develop a fixed film.<sup>12</sup> The researchers considered everything from foam cubes to bricks and gravel in researching anaerobic digesters working on cattle manure. Unfortunately, the researchers did not calculate the net surface available for bacterial growth. The COD loading rate for the digester was 21 kg COD/m<sup>3</sup>/day, which is substantially higher than many digester configurations.

One other type of relatively new digestion system is from Europe. The latest technology is represented as a high solids or “dry” anaerobic digester. The digester is said to be capable of producing up to 200 m<sup>3</sup> ton<sup>-1</sup> of biogas using sorted organic wastes, and 60 m<sup>3</sup> ton<sup>-1</sup> of biogas per ton of general (mixed) waste treated. The methane produced is 0.4 and 0.13 m<sup>3</sup> of methane per ton of volatile solids treated.<sup>13</sup> Several US patents discuss a Dry Cycle Anaerobic Digester.<sup>14</sup> The patent covers a two-tank system that uses both aerobic and anaerobic digestion. Another dry anaerobic digester uses a preconditioning bacterial feed to help with the digestion of cellulosic materials. This is outlined in an e-book by Steve Last entitled, *Dry Anaerobic Digestion Secrets you will Wish you Discovered First*. Another report by a contractor for the California Integrated Waste Management Board discusses dry anaerobic treatment from a slightly different angle.<sup>15</sup>

## 10.7 Siloxane Removals

Siloxane is a group of chemical compounds with a formulation of Si=O=Si. They are relatively inert in the environment, and are essentially harmful to humans. There is conflicting evidence about the accumulation and

biotoxicity of siloxane compounds in the open environment. The principal uses for siloxanes and the way it would enter the wastewater is via the use of personal care products. The two principal compounds, D4 and D5, are octamethylcyclotetrasiloxane, with the formula  $[(\text{CH}_3)_2\text{SiO}]_4$ , and decamethylcyclopentasiloxane with the formula  $[(\text{CH}_3)_2\text{SiO}]_5$ . Both are widely used in products as diverse as hair care, personal lubricants, deodorants, sun block, and cosmetics.

The problem starts when they degrade with heat. The silicon forms a silicon–oxygen bond (sand or  $\text{SiO}_2$ ) which makes it abrasive. Because the compounds are often found in digester gas, they can render it unsuitable for use in turbines, combustion engines, and power machinery because of the accumulation of silicon dioxide, which will either cling to the walls of a combustion cylinder, the blades of a turbine, or the walls of a heat exchanger. An article in Science Direct summarizes the problem as follows:

Silica appears in the layers covering the combustion chamber, as well as silicone compound in the top cylinder zone, piston and ring grooves. Damage is associated with siloxanes (organo-silicon compounds) contained in the landfill gas, which decompose in the combustion chamber, generating silicic acid and formaldehyde under the high temperature conditions throughout the combustion processes.<sup>16</sup>

The removal of the siloxanes is accomplished in the gaseous state by adsorption on activated carbon, or by chilling the gas to make it condense as a liquid. Siloxane is moderately persistent in air and highly persistent in water, according to a Canadian Ministry of the Environment study,<sup>17</sup> and is relatively non-bioaccumulative.

## 10.8 Sludge Digestion

Most sludge digestion occurs after an aerobic biological treatment. The excess solids are loaded into an anaerobic reactor for digestion. The holding times are generally a minimum of 30 days and some, depending upon temperature and gas production, are as high as 180 days. Frequently the sludge is prethickened before it is sent to the digester. On larger systems this will increase the amount of solid in the feed from the range of 1–3% to 7–10% or more if achievable. The upper limit is the ability to pump and stir the solids, and in some cases may be as high as 15%.

The digester loading rates are low rate 40–100 lb/ft<sup>3</sup>/day or high rate 150–400 lb/ft<sup>3</sup>/day, with average solids retention times of 30–60 days for low rate and 10–20 days for high rate. Two configurations most often used for sludge digestion are shown in Figures 10.4 and 10.5.

**Table 10.3** Biogas composition and production from various sources.

Reference	Commodity	Reactor type/size	Temperature	Biogas production	Methane fraction
Bouallgui et al. 2004	Raw fruit and vegetable waste (shredded)	Tubular/18 l	Psychrophilic	0.64–1.05 l/l/d	56–58%
			Mesophilic	0.83–2.34 l/l/d	54–65%
			Thermophilic	1.7–3.17 l/l/d	58–62%
Alvarez et al. 2005	Cherry stillage	Sequencing batch reactor/1.8 l	Low mesophilic (30°C)		58–71%
Stewart et al. 1984	Bananas (fruit and stem)	Continuous/20 l	Mesophilic	497 l kg <sup>-1</sup> TS	53%
	Potatoes (peelings, rejects)			350–410 l kg <sup>-1</sup> TS	44–50%
	Oats			227–257 l kg <sup>-1</sup> TS	51–54%
Yacob et al. 2006	Palm oil mill effluent	Closed digester/500 m <sup>3</sup>	High mesophilic (37–42°C)	650–1000 kg d <sup>-1</sup>	
Tekin and Dalgiç 2000	Olive pomace	Semi-continuous/1 l	Mesophilic	0.39–0.69 l/l/d	79.5–84%
Viswanath et al. 1992	Sequential feedings: mango, orange, pineapple, tomato, processing, jackfruit and banana waste	Semi-continuous/45 l	Low mesophilic (30°C)	0.61–1.96 l/l/d	22–61.2%
Lepistö and Rintala 1997	Carrot processing wastewater. Potato and swede processing wastewater	UASB/2–3 l	Thermophilic (55°C)	7.3 l/l/d (315 cm <sup>3</sup> g <sup>-1</sup> COD)	49% (carrots)
				347 cm <sup>3</sup> g <sup>-1</sup> COD	

- Sources: The information for Table 10.3 was developed from a number of sources, including Szczegielniak, E.H. (2005–2007). Anaerobic Digestion Feasibility Protocol for Fruit and Vegetable Processing Waste. *Green Project Alternatives for Food Processor's Wastewater*. Michigan State University Biosystems and Agricultural Engineering (available at <https://www.egr.msu.edu/~steves/Arenaobic&percent;20Digester&percent;20Protocol.pdf>). Remaining references for Table 10.3 are as follows: Alvarez, P.M., Beltran, F.J., and Rodriguez, E.M. (2005). Integration of ozonation and an Anaerobic Sequencing Batch Reactor (AnSBR) for the treatment of Cherry Stillage. *Biotechnology Progress* 21 (5): 1543–1551. Bouallgui, H., Haouari, O., Touhami, Y. et al. (2004). Effect of temperature on the performance of an anaerobic tubular reactor treating fruit and vegetable waste. *Process Biochemistry* 39 (12): 2143–2178. Lepistö, S.S. and Rintala, J.A. (1997). Start-up and operation of laboratory-scale thermophilic upflow anaerobic sludge blanket reactors treating vegetable processing wastewaters. *Journal of Chemical Technology & Biotechnology* 68 (3): 331–339. Stewart, D.J., Bogue, M.J., and Badger, D.M. (1984). Biogas production from crops and organic wastes. *New Zealand Journal of Science* 27 (3): 285–294. Tekin, A.R. and Dalgiç, A.C. (2000). Biogas production from Olive Pomace. *Resources, Conservation and Recycling* 30 (4): 301–313. Viswanath, P., Devi, S.S., and Nand, K. (1992). Anaerobic digestion of fruit and vegetable processing wastes for biogas production. *Bioresource Technology* 40 (1): 43–48. Yacob, S., Hassan, M.A., Shirai, Y., Wakisaka, M., and Subash, S. (2006). Start-up and operation of laboratory-scale thermophilic upflow anaerobic sludge blanket reactors treating vegetable processing wastewaters. *Science of the Total Environment* 366: 187–196.

For a complete mathematical treatment of the sizing of an anaerobic digester, SCRIBID has a downloadable paper by V.R. Arsov, of the University of Architecture, Civil Engineering, and Geodesy in Sofia Bulgaria. The paper takes one through the mathematics of sludge digestion and thickening on an empirical basis without having to go through the torturous modeling effort associated with ADM1. The paper is easy to understand and the mathematical treatment is straightforward.<sup>18</sup> The amount of gas produced is a function of many feed and operational variables, including hydraulic retention time, as shown in Table 10.3.

## 10.9 Gas Production Emphasis

The new emphasis on the reduction of greenhouse gases has highlighted the importance of methane control from many sources including anaerobic digestion. The figures on gas production from anaerobic digestion of municipal sludges are widely varying. The gas generally contains methane ( $\text{CH}_4$ ), water vapor ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), siloxanes, and hydrogen sulfide ( $\text{H}_2\text{S}$ ). The energy released from a cubic foot of gas can range upwards from about 400 BTU per cubic foot of gas (wet basis). By comparison, methane (dry basis) has a heating value of around 1000 BTU per cubic foot of gas (37 MJ/m<sup>3</sup> of dry gas). Various studies have shown that  $\text{CH}_4$  can vary between 60% and 90% of total gas production. Studies on gas production have indicated that the gas produced can be correlated to both COD reduction and very strongly correlated to the destruction or degradation of volatile solids (VSs) in the sludge. A conservative estimate of the efficiency of the gas production reaction is that for each pound of VS reduced, the gas production can be 6.2 cubic feet or greater. Alternatively, if COD is used as a measure of gas production, each kilogram of COD reduced will generate 0.35 cubic meters of  $\text{CH}_4$  (dry basis), or about 5.63 cubic feet of dry methane per pound of COD destroyed – as indicated by Wilkes and others.<sup>19</sup>

Sludge contains both liquid and solids. The amount of VS is also correlated very strongly with the fineness of the solids. In the digester, one of the reasons for longer digestion times is that the coarser solids take time to hydrolyze, and there is some evidence developed from the US patents by Wilkes on flushed dairy wastes.

One of the reasons that sludge is digested for 20 days or longer appears to be the hydrolysis and digestion of larger solids. Based upon feedlot studies at mesophilic digestion temperatures, and with some solids reduction and segregation to insure that only very small particles enter the digester, the gas production may peak in a matter of 5–10 days in a plug flow or a fixed film reactor.

Since the hydrolysis is dependent upon size and surface area, this suggests that there may be a potentially big increase in the efficiency of the hydrolysis and gas production by reducing the particle size fed to the digester. This suggests a line of inquiry and research into the effects of micropulverizing the sludge to increase the gas production and reduce the digestion time.

## 10.10 New Technologies

There has been some new research into the possibility of using metal salts to help with the process of sludge digestion. Iron salts in particular tend to complex with sulfur and precipitate it so that it can be removed prior to digestion. The method of introducing the iron salts into the materials sent to the digester is by electrochemical means. The research looks promising and will be publicized after the concepts have been proven and the various process and other patents have been filed and the process commercialized.

Most of these digesters have been used on agricultural applications where the material fed to the digester is between 5% and 14% solids. Two types of digesters are employed. One type of digester is a fixed film digester. Similar in design to the upflow anaerobic digester, the fixed film digester uses a series of fixed media, which can be vertical pipes, configured in an upflow mode, to provide a support media for anaerobic growth (*Grant US6811701B2, Ann C. Wilkie, University Of Florida Research Foundation, Inc.*).

Plug flow digesters use two digester tanks, one for the acid formers and a second tank for the methane formers, with pH control as an intermediate step to help gas generation (*Grant US4318993A, Sambhunath Ghosh, Institute of Gas Technology*). Still other digester types have included plug flow digesters (as opposed to complete mix digesters). These digesters use internal baffles to provide some segregation of the acid-forming and gas-forming bacteria, and to control the residence time between parts of the digester (*Grant US6674243B2, Vadake R. Srinivasan, John J. Sansalone, Louisiana State University*). These are just a few of the many patents available on the subject.

One very intriguing patent uses high-pressure digestion chambers with intermediate carbon dioxide removal to produce a digester gas which is almost pure methane (*Grant US62997741B, Jack L. Ainsworth*).

All of the above digesters will produce commercial commodities of methane from feeds which are between 4% and 20% solids. Shredded and waste food-stuffs is also a good commercial source for digester feed. A recent study on energy recovery from animal feeding operations, including cows, chickens, and pigs, indicates that this type of energy recovery is feasible and it reduces the amount of methane released to the atmosphere.

## 10.11 Sludge Treatment

After digestion, municipal sludge contains substantial quantities of ammonia. It is often further processed by air-drying on sand beds, in greenhouses, and by filter pressing and with thermal and other types of treatment including composting. Indoor and warm weather sludge-drying beds are noted for growing tomatoes indoors as the seeds are unaffected by the digestion process – at least until the next batch of sludge is sent to the drying bed, when the ammonia often kills the tomatoes.

Recently the trend has been to dispose of sludges by direct soil incorporation in landfarming, composting, and with polymer treatment and filter press in landfills. This landfilling is wasteful and expensive and does little to help the landfill unless the landfill is to be converted into a large anaerobic or aerobic reactor. Most landfills are non-stirred anaerobic digesters. Enhancements to landfills where cells are opened up to recirculation of the leachate and even conversion of landfills to aerobic biological reactors have proved successful in reducing the volume in the landfill and in stabilizing the site.

## 10.12 Anaerobic Digester Model ADM1

In 2004, the IWA published an comprehensive mathematical model of the anaerobic digestion process, ADM1. Almost as soon as the model was released, there were reports about mistakes in the carbon balance, which have been corrected. Now one can model an entire wastewater treatment plant including aerobic and anaerobic treatments and the sludge digestion system. The advantage of the modeling lies in its ability to predict the characteristics of the final effluents and digestion, and to evaluate the ability to change and modify the parameters and evaluate their effects in a few hours without having long delays and the residuals of untreated or poorly treated sludge.

The ADM1 model has been upgraded and extended by various researchers to include sulfate-reducing processes and nitrate reduction processes, and other multiple reaction stoichiometry, microbial growth kinetics, conventional material balances for ideally mixed reactor, liquid–gas interactions, and liquid-phase equilibrium chemistry. As it is written, the model has at least 26 dynamic state variables, modeling 19 biokinetic chemical processes, and incorporates three gas–liquid kinetic transfer processes.

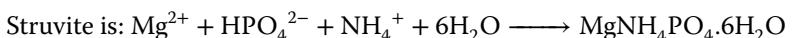
Reports from researchers using ADM1 have indicated good correlation between the model and performance in laboratory and other applications.

The plant-wide model description is available from SCRIBID as *COST Action 624 Optimal Management of Wastewater Systems*; it is a free download.

The individual models are available from the IWA. The ADM1 model is also being used to research anaerobic pretreatment for wastewater processes. As with any modeling effort, the calibration of the model to make it conform to actual plant or operational performance can be somewhat time-consuming, both in preparation and in execution.

### 10.13 Struvite and Anaerobic Processes

Struvite is a magnesium, ammonia, phosphorus compound that often gives plant operators maintenance headaches. Since the 1950s, the increasing use of phosphorus as a detergent or detergent booster has only contributed to this problem. More recently, with the advent of P limits on effluents to control algal blooms in the receiving water bodies, the P concentration in the return sludge has markedly increased. Struvite forms rock-hard coatings that can plug pipes, freeze valves, and royally mess up heat exchangers.



The manner in which one can determine whether or not there is a struvite problem involves a simple calculation based upon solubility products. According to a paper by Kazi P. Fattah,<sup>20</sup> the calculation depends upon the calculated solubility of the following:

$$\begin{aligned} \text{SSR} &= \text{Struvite Supersaturation Ratio} \\ &= [\text{Mg}^{2+}] [\text{NH}_4^+] [\text{PO}_3]/\text{PS}_{\text{equilibrium}} \end{aligned}$$

where  $\text{PS}_{\text{equilibrium}}$  is the solubility product in equilibrium under the same conditions. Calculate the total soluble orthophosphate, ammonium and magnesium in moles per liter when it is corrected for ionic activity and pH. A ratio of greater than three indicates a tendency toward struvite formation.

Struvite can be removed by application of organic or inorganic acids. The acids should be diluted so as not to attack the piping and other metallic parts. Continuous monitoring of metallic concentrations should be conducted to insure that the piping is not being attacked.

Struvite also forms at higher pH and at colder conditions. It is suggested that digester supernatant be handled separately to reduce the overall phosphate load to the treatment plant, and that would help reduce the likelihood of struvite formation.

Another author, Paul L. Bishop,<sup>21</sup> has recommended the use of magnesium hydroxide as a removal chemical for phosphate reduction and control of struvite from anaerobically digested supernatant, and possibly as a phosphate removal mechanism in the main portions of the treatment plant.

## Notes

- 1 <http://www.chemeng.lth.se/exjobb/E308.pdf> Appendix C: "Summary comparison of chemical and biological phosphorus removal in wastewater – a modelling approach." Adalbert Oneke Tanyi.
- 2 It is to be noted that the EPA has set the standard for sterilization of sewage sludge in compost (reduction of pathogens) at a sustained temperature of 55°C (132°F) for a period of 21 days.
- 3 Buswell, A.M. and Mueller, H.F. (1952). *Industrial Engineering & Chemistry* 44, pp. 550–552; Buswell, A.M. (1954). *Industrial Fermentations.*, New York: Chemical Publishing Company.
- 4 McCardy P.L. and Murdoch, W. *JWPCF* 1963, Vol. 35, pp. 1501–1516.
- 5 McCardy, P. and Rittman, B. (2001). *Environmental Technology, Principles and Application*. McGraw Hill, New York.
- 6 McCardy, P. and Eckenfelder (1964). *Public Works Journal* 85 (3).
- 7 A number of years ago, as legend has it, there was a digester somewhere in the lower central Midwest – probably Kentucky or Ohio. The anaerobic digester did not have any provision for breaking up the accumulated fats on the surface. The town also had a hide tanning plant, which contributed a substantial quantity of hair to the wastewater and sludge. The hair, solids and fats all went to the anaerobic digester. One day, after a cold winter, the gas production in the digester stopped, but the operator did nothing. Later that year, a digester wall blew out because the mat of hair and fat had gotten so thick that it trapped the digester gases under the scum layer. The story is legendary, and has the ring of truth, but I have not been able to confirm it.
- 8 *Methane Recovery from Animal Manures: the Current Opportunities Casebook*, NREL/SR-580-25145, September 1988.
- 9 *AgSTAR Handbook, A Manual for Developing Biogas Systems at Commercial Farms in the United States*. EPA-430-B-97-015.
- 10 *Wastewater Treatment for Pollution Control and Reuse*, 2. by Soli J. Arceivala & Shyam Asolekar, McGraw Hill publishers.
- 11 *The characteristic of the sequencing batch reactor (SBR), anaerobic sequencing batch reactor (ASBR) and sequencing batch biofilm reactor (SBBR)* by Koobum Kim. Available at <http://home.eng.iastate.edu/~tge/ce421-521/koobum.pdf>.
- 12 Javed Iqbal Qazi et al. (2011). Anaerobic fixed film biotreatment of dairy wastewater. *Middle East Journal of Scientific Research* 8 (3), 590–593.
- 13 Bolzonella, D., Pavan, P., Mace, S. and Cecchi, F. (2006). Dry anaerobic digestion of differently sorted organic municipal solid waste: a full-scale experience. *Water Science and Technology* 53 (8), 23–32.
- 14 US Patent 7,144,507 B2, Dec. 5, 2006, issued to Paul Baskis, Rantoul, IL.
- 15 *Current Anaerobic Digestion Technologies Used for Treatment of Produced Under Contract by Municipal Organic Solid Waste*, by the Department of Biological and Agricultural Engineering, UC Davis.

- 16 <http://www.sciencedirect.com/science/article/pii/S1350630715000321>;  
<https://www.unm.edu/~solgel/PublicationsPDF/1985-1989/BrinkerHydrolysis1988.pdf>
- 17 See [http://www.ec.gc.ca/lcpe-cepa/515887B7-AF58-45B7-ADA9-B4ADF8F204DB/CdR-BoR-D5\\_eng.pdf](http://www.ec.gc.ca/lcpe-cepa/515887B7-AF58-45B7-ADA9-B4ADF8F204DB/CdR-BoR-D5_eng.pdf), a study by the US Council on Siloxanes and the Canadian Ministry of the Environment.
- 18 R.V. Arsov, *Sizing of Wastewater Sludge Anaerobic Digesters*, University of Architecture, Civil Engineering and Geodesy, 1 Chr. Smirenensky Blvd., 1046 Sofia, Bulgaria. Available on SCRIBID.
- 19 See US Patent Number US6811701 B2 and similar works by Anne C. Wilkes at the University of Florida. Wilkes also used a fixed film reactor in digesting sludge.
- 20 Fattah, K.P. (2012). Assessing struvite formation potential at wastewater treatment plants. *International Journal of Environmental Science and Development* 3 (6).
- 21 Bishop, P.L. (2006) Control of struvite deposition in wastewater treatment plants. *Presentation at 11th Annual Central States Water Environment Association Education Conference, April 4, 2006*.

# 11

## Precipitation and Sedimentation

### 11.1 Theory of Sedimentation

The basic theory of sedimentation is a balance between gravity and drag forces.

Particle forces,  $F_1 = (\rho_s - \rho)gV$  impulse or gravity forces

Drag forces,  $F_d = C_D A \rho V^2 / 2g$

$R$  is the Reynolds number. For spheres up to  $R = 10\,000$ ,

$$C_D = 24 + \frac{3}{R} + \frac{0.34}{R}$$

At steady state,  $F_1 = F_d$  and this reduces to Stoke's law for values of  $R$  less than 1:

$$V = \frac{g}{18}(\rho_s - \rho) \frac{d^2}{\mu}$$

This is the basic formula for determining the settling rate for most discrete solids. Of course, as the size and density increase, the drag forces also increase. The keyword here is discrete. If the solids flux is too high, and/or the solids have a tendency to be "sticky" or agglomerate, settling can be hindered. Concentrations of "sewage" or organic biosolids above  $3500\text{ mg l}^{-1}$  and silt above  $6000\text{ mg l}^{-1}$  can hinder settling. Often the result is a decrease in either the bulk settling rate or zone settling rate.

One of the reasons for hindered settling is floc agglomeration and water entrapment, which leads to reduced apparent density:

$$S_m = 100 / ((100 - P) / S_s + P / S)$$

where  $S_m$  is the apparent specific gravity of a group of particles;  $p$  is the percentage of water entrained;  $S_s$  is the true specific gravity, and  $S$  is the specific gravity of liquid (Figure 11.1).

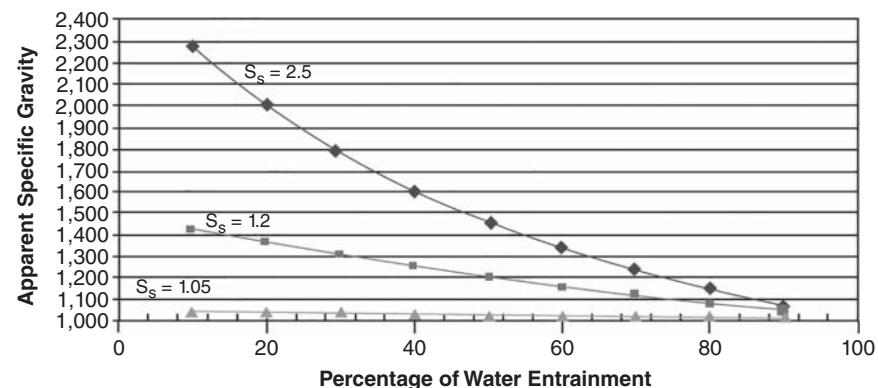


Figure 11.1 Change in specific gravity of a particle with water entrainment.

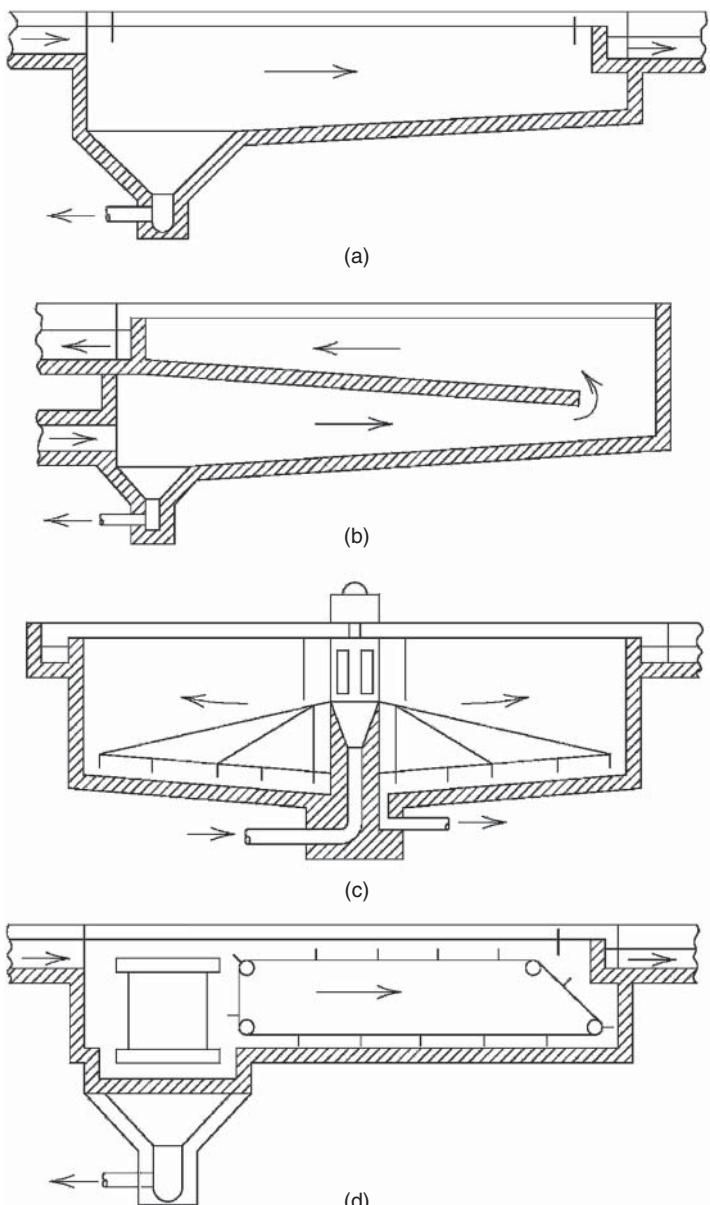
## 11.2 Clarifiers and their Design

Clarifiers are available in two shapes, round and rectangular. Depending upon specific densities, most biological flocs move at rates of  $1\text{--}2 \text{ m h}^{-1}$ . Each clarifier has an inlet zone, an exit zone, a dragout, or depending upon the design, a set of staggered sweeping squeegees as a collection device, and a sludge withdrawal area or center well. Clarifiers are moderately well understood and can be modeled, but overall there is a lot of lore and practice that is embodied in design codes and that has been established by trial and error. One year everyone will rush to put in a specific type of collector arm, the next year it will be a modification to the inlet structure or the outlet structure, or both. A typical clarifier is shown in Figure 11.2.

There are a number of good practices that have been hinted at in clarifier design, especially when one looks at biological clarifiers.

### 11.2.1 Bulk Velocity – Surface Loading Rate

Make sure that if you are using an upflow clarifier, the bulk velocity of the clarifier is not greater than the settling rate of the smallest particles you want to get out. This is often measured by overflow rate, and has been embodied in many codes, including the Ten States Standards.<sup>1</sup> Bulk loading rates are defined in terms of gallons per square foot per day. This is a velocity term – equal to about  $33 \text{ m}^3/\text{day/m}^2$  – at a maximum of  $800 \text{ gal/ft}^2/\text{day}$ . This is equivalent to about  $1.5 \text{ m h}^{-1}$  as a floc settling rate. For all intents and purposes for a biological floc, it is a good maximum rate number and should not be exceeded without good basis for the use of other criteria.



**Figure 11.2** Typical design and configuration for clarifiers. (a) Rectangular clarifier with gravity drainage for sludge. (b) Compact rectangular clarifier, which is deeper but has longer settling path. (c) Center feed circular clarifier with submerged sludge scraping mechanism. (d) Rectangular clarifier with a chain dragout and sludge scraping mechanism. Source: This figure is from Fair, G.M. and Geyer, G.C. (1964) *Water Supply and Wastewater Disposal*, John Wiley and Sons, New York.

### 11.2.2 Hydraulic Detention Time

This is often set arbitrarily at two to three hours, based upon experience with many plants. However, the optimum detention time depends upon the biological activity of the sludge and the MLSS in the clarifier feed. When one is dealing with a biologically active sludge and low to moderate dissolved oxygen entering the clarifier, it is often better to keep the detention times shorter. Again, solids concentrations, the oxygen in the water, and the oxygen uptake rate should govern the selection of this parameter. It is never a good idea to let the clarifier become anoxic or anaerobic. If the clarifier does go anaerobic, nitrogen bubbles will form and float, disrupting the sludge blanket and washing sludge solids over the clarifier effluent weir.

Conventional wisdom and guidance says that the solids loading rate to the clarifier should not exceed 20 lb/day/ft<sup>2</sup> of surface area (98 kg/m<sup>2</sup>/day). Depending upon the parameters of the sludge, a number of clarifiers have operated 50% or more over the rate. **The quantity of solids is more a function of how easily the settled solids can be moved for collection and removal from the clarifier, and that may be controlled by the clarifier manufacturer rather than by the designer.**

The concentration of the sludge is controlled by the settling characteristics and the withdrawal rate. Many settling tests and measures of sludge settleability



**Figure 11.3** Circular clarifier under construction. Observe the center baffle that is used to direct the flow downward, under the baffle, before the flow moves outward to the launder ring (scum and floatable barrier) and the overflow weir around the periphery. Source: Greeley and Hansen-Lafayette, Ind.

are conducted improperly in design and evaluation. The principal problem is that they are conducted in a graduated cylinder of relatively small diameter where edge effects occur and give false readings. The preferred cylinder should be at least 3"(7.6 cm) diameter for good readings.

Weir overflow rates should not exceed 10 000 gal/day/ft of weir or 11.54 m<sup>3</sup>/day/m. Lower rates are preferable because the local velocities can draw local solids out of the system. Do not forget that the clarifier throughput rates should include the recycle rate from the primary aeration system. Design accordingly.

Figure 11.3 shows how some of the innards of a clarifier look.

The innards and the sludge scraping arrangement from a sludge thickener are shown in Figure 11.4. Some thickener designs use vertical submerged poles attached to a rotating arm to promote the thickening by gentle stirring. The thickener concentrates the clarifier under flow by a factor between 3 and 5.

**Figure 11.4** Innards of a sludge thickener. Note the steeply sloping sides and mechanical rake which promotes sludge compaction and collection in the center well. Other manufacturers will have tanks with steeper sides and vertical poles (rakes) on the collector mechanism to promote thickening. Source: Photo courtesy Wes-Tech Engineering, Salt Lake City, UT.



## 11.3 Lamellas and Specialty Devices

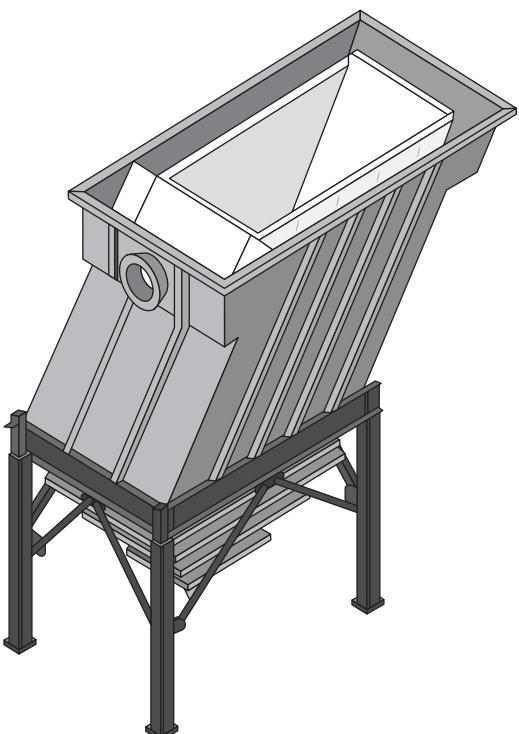
### 11.3.1 Lamellas

Lamellas are a special case for a tube clarifier. The theory of design is the same, but the internal plates give the sludge a shorter distance to travel, and they are generally more efficient. However, it may be very difficult to clean them if there are problems with the sludge. A lamella is shown in Figures 11.5 and 11.6.

Density currents can cause efficiency reductions in a clarifier. They are caused by (i) eddy currents, (ii) wind-induced currents in the settling, and (iii) convection and density currents. This is called damping.

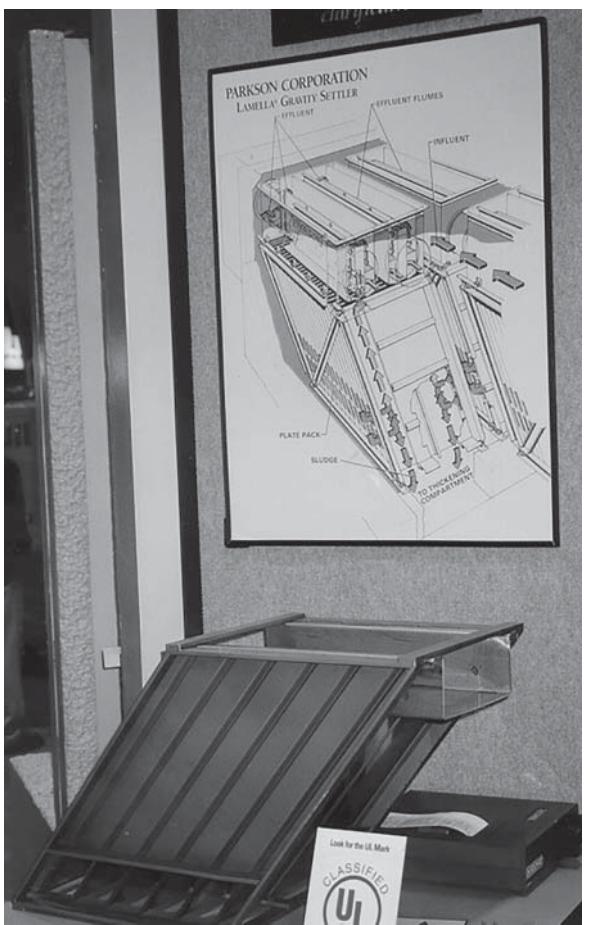
The effect of damping is shown to be reduced by increasing the number of plates and decreasing the distance the particulate materials have to settle before they encounter a plate. Damping follows the general formula given below.

If  $Y_o$  is the original settling velocity, and  $Y$  is the apparent settling velocity, then  $Y - Y_o$  is the amount of suspended matter of settling velocity



**Figure 11.5** Drawing of a lamella.  
Source: Parkson Corporation.

**Figure 11.6** Lamella model and drawing by Parkson taken at WEFTEC'03.



$V_o$  still in solution at time  $t$ . For a specific clarifier, there is the following overall relationship:

$$\frac{Y}{Y_o} = 1 - \left[ 1 + \frac{V_o}{nQA} \right]^{-n}$$

### 11.3.2 Membrane Filters

One of the most interesting developments in the past few years is the utilization of membrane filters in lieu of a clarifier. This is a unique development because, despite their higher initial cost, either in fixed or in flexible form, they have a

superior performance over clarifiers at modest head losses. The head losses are between 3 and 5 psi across the membrane, but the real advantage is that they have a long operation life of 10 years or more, and an effluent total suspended solid (TSS) of zero.

It should be noted that the definition of TSS is a laboratory measurement of the solids trapped on a membrane with 0.45 µm openings. The membranes often have an opening of 0.4 µm, which will eliminate any solids that are trapped by the TSS test. Note, too, that for mathematical modeling of activated sludge plants, the definition of fine solids is 0.2 µm.

Translated into operational terms this means that the effluent TSS is always less than  $1 \text{ mg l}^{-1}$  because the membrane only passes solids with a size of less than 0.45 µm. The other advantage is that the solids wasted are the only ones lost, at the discretion of the operator.



**Figure 11.7** Spaghetti strand hollow tube membrane filter clarifier.

The membranes tend to get caked with a slimy solid biofilm. In order to prevent this, the membranes are often installed with an “air bump”, a bubbler at the bottom of the membrane installation that bubbles air up through the membrane area to help keep the membranes (often the hollow tube type) in motion, reducing the buildup of solids.

If the membranes get plugged, for example, perhaps with either calcium solids or struvite, the operator should backwash it with acetic acid or other mild acid. A picture of one type of membrane effluent filter (hollow tube filter) is shown in Figure 11.7.

## Note

- 1 Upper Great Lakes Regional Board of Sanitary Engineers developed these standards, and they have seen almost universal application.

## 12

# Granular Filtration Theory and Practice

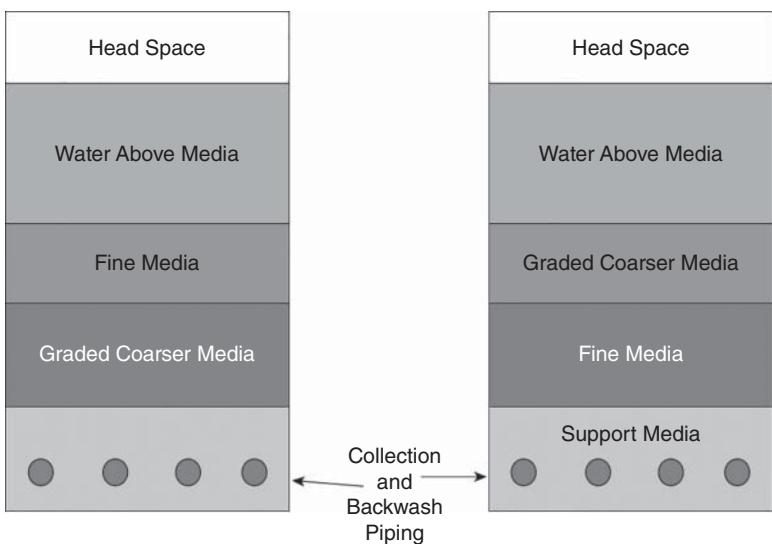
This chapter was originally intended to be inclusive of all types of filtration, including membranes and other types of skin filters. The advances in membrane manufacturing technology and efficiency coupled with price reductions have made the selection of membranes the preferred choice for many applications. There is still a wide market for granular filtration, and this chapter and the next will attempt to provide the reader with the fundamentals and applications for granular and membrane filtration.

## 12.1 Granular Media Filtration

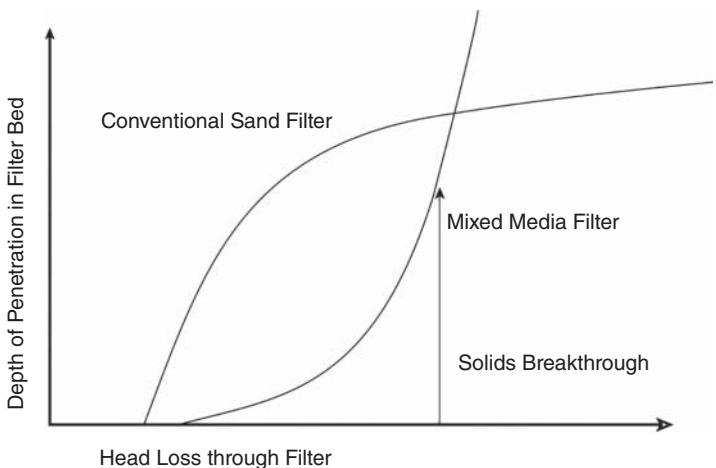
There are several types of filter in the marketplace. The most popular appear to be the “inverted” or “mixed media” filters, which employ various filter media of different densities and sizes to get the filtration, and the sand filter, which uses sand and gravel of different sizes to construct the filter. The filters are built in reverse from each other, as shown in Figure 12.1. The mixed media filters utilize varying densities and sizes of media to achieve the mixed media effect. In the conventional sand filters, the media density is about 2.65 g/cc, while in the mixed media filters, the densities range between 1.5 g/cc for plastic and artificial media and 4–4.5 g/cc for garnet sands and corundum sands. This gives the media a reverse gradient and allows deeper penetration of the solids in the filter (Figure 12.2).

### 12.1.1 Sizing of Filters by Flow Rate

There are three general classifications for sand filters: rapid sand filters, slow sand filters, and pressure sand filters. All three are built along the same general configuration for a conventional media filter shown in Figure 12.1 (left drawing). The principal difference between the three is the flow rate and the pressure drop across the filter. The slow sand filter is sometimes used in municipal water supplies and has a flow rate of under 2 gal/min/ft<sup>2</sup> (face velocity of



**Figure 12.1** Comparison of conventional and mixed media filters.



**Figure 12.2** Head loss comparison between mixed media and conventional sand filtration systems.

$4.89 \text{ m h}^{-1}$ ). The conventional sand filter has a flow rate from  $2\text{--}6 \text{ gal/min/ft}^2$  ( $4.89\text{--}29.5 \text{ m h}^{-1}$ ), and the pressure sand filter has a flow rate of greater than  $8 \text{ gal/min/ft}^2$ . The differing flow rates and pressure drops all impact upon the solids removal and the physical configuration of the filter, including the type of vessel and the backwash appurtenances used in the filter. Table 12.1 presents useful information on various types of filter in a slightly different format.

**Table 12.1** Comparison of filter types.

Filter type	Filter rate imperial (US gal/ft <sup>2</sup> /d)	Filter rate metric l/m/m <sup>2</sup>	Use	Bed depth (cm)	Grain sizes (mm)	Uniformity coefficient	Density of media	Head losses (M)
Slow sand filters	20–250	0.6–7.1	Final polishing filter after bio treatment	30 gravel 100 sand	0.25–0.35	2–3	2.65	0.2 initial 1.5 final
Rapid sand filters	3000–7500	80–250	Conventional solids removal in all types of applications	50 gravel 80–100 sand	0.45+	1.5+	2.65	0.3 initial 3–5 final
Mixed media filters	7500–22000	250–700	High rate filter applications	50 garnet sand 30 coarse sand 30 plastic media	0.45+	1.2+	4.5 2.65	Varies with flow rate 1.8–2.2
Skin filters	3000–7500	80–250	Swimming pools, commercial filtration Requires precoat media	0.3 cm max Used cloth or wire as support Has low backwash requirement	0.05+	N/A	0.256	Varies

### 12.1.2 Uniformity Coefficient and Effective Grain Size

Effective grain size is the size of 10% of the smallest media retained on a set of graded sieves, or  $D_{10}$ .  $D_{60}$  is the grain size where 60% of the filter media is retained. The uniformity coefficient ( $U_1$ ) is the ratio of  $D_{60}/D_{10}$ . The head loss through a filter is generally a function of the  $D_{10}$  grain size.

## 12.2 Filtration Hydraulics

For general hydraulic losses through a filter, the following equation holds:

$$h/L = 1 : 067(C_d v^2)/(g f^4 d)$$

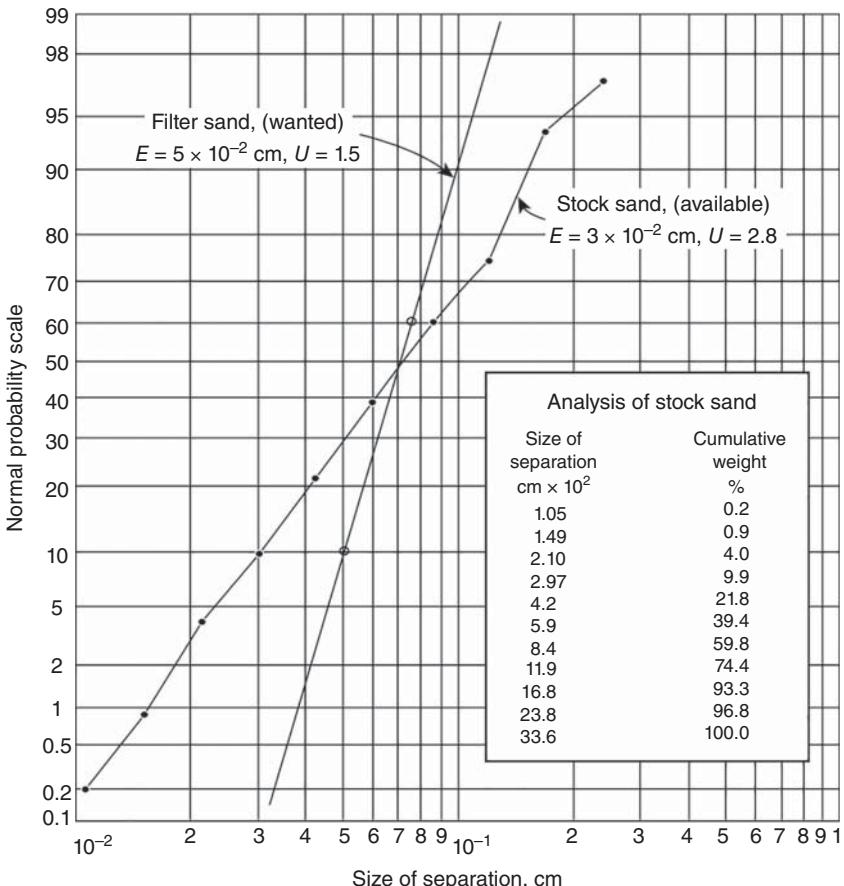


Figure 12.3 Grain size distribution of a natural sand versus desired sizing for a slow sand filter.

where  $C_d$  is the drag coefficient;  $g$  is the acceleration due to gravity;  $v$  is the face velocity of liquid; and  $f$  is the porosity of the filter bed (expressed as a decimal).

Under laminar conditions, the equation becomes  $h/L = 25.6(vv)/(gf^4d^2)$  where  $v$  is the kinematic viscosity of the working fluid. A very good granular filter, generally a slow sand filter, can achieve removals approaching 100% of particles greater than 10 µm (see Figure 12.3).

## 12.3 Particle Size Removals

All filters, except superfine reverse osmosis systems, have a particle size removal limit. In general, the smaller the grain size of the filter medium, the better the overall filtration removal. From the equations above you will also note that with finer granular media, the flow resistance to the filter increases. However, there is a limit to every type of filter, and that is controlled by the pore size. Figure 12.4 shows the relative sizes of contaminant particles, and the approximate cutoff points for various types of filtration. When we begin discussing microfiltration, ultrafiltration and reverse osmosis, the measurement scale shifts. These very small particles are measured in daltons (Das). A dalton is the standard unit of mass that quantifies atomic mass on a molecular scale.

It is important to note that many of the proteins and viruses are very, very fine, and can be absorbed directly by the skin. One rule of thumb for determining that type of molecule is something with a size of less than 500 Da.

Reverse osmosis can remove very fine molecules, including salts and metals, and can provide a very good quality water, but with the increasing removals comes increasing pressure drop across the membrane.

## 12.4 Backwash Hydraulics

Membranes, as well as filters, must be backwashed if they are to operate near peak efficiency. The backwashing process removes the particles that tend to plug the pores in the membrane.

Backwash hydraulics are substantially different in granular media, as the entire granular bed is hydraulically lifted and mechanically agitated to “scrub” the collected materials off the particles. The bulk upflow velocity through the bed and the settling rate of the particle determine which particles will be raised and by how much. Typically sand beds expand between 75% and 100% during backwash, and less with mixed media filters. However, both types must be scoured or violently agitated during backwash to break up mud balls and accumulated agglomerated material which has collected on the surface and in the filter bed.

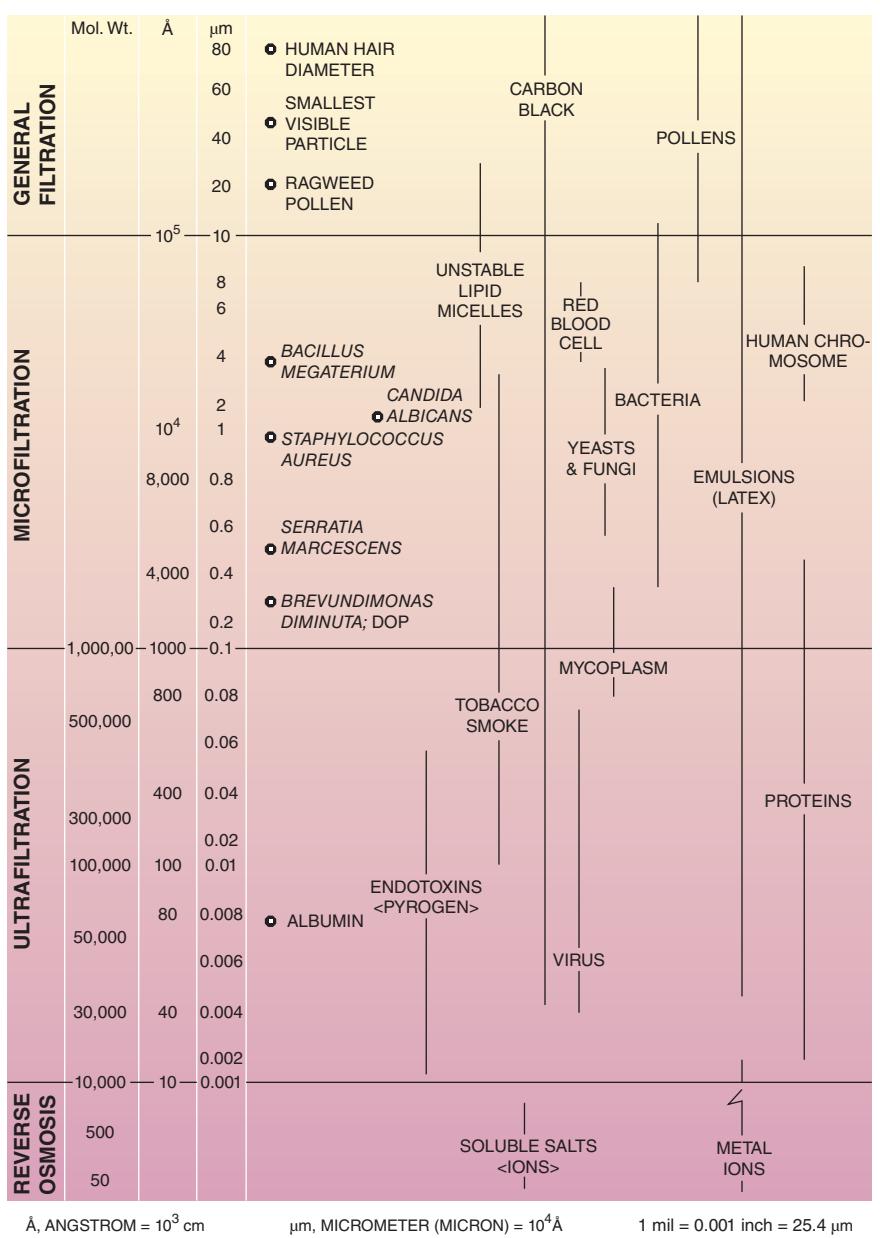


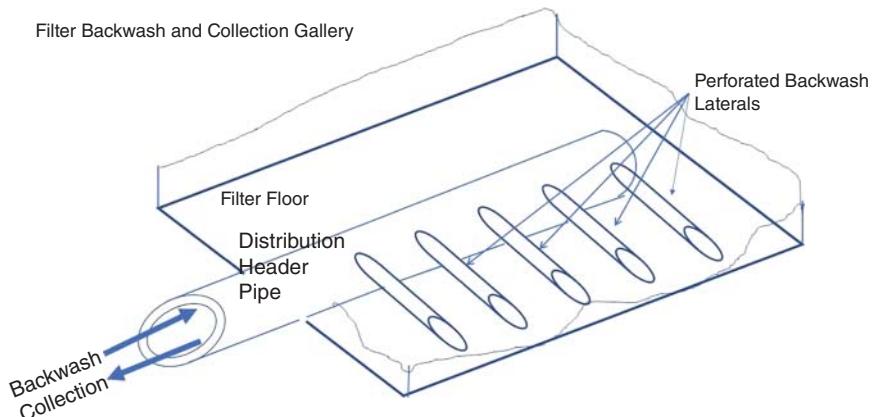
Figure 12.4 Type of filtration versus size of particles removed.

Generally this procedure is effective with many solids, but a cautionary note is in order if one is filtering oils. Some oils adhere to the granular media, and are removed only with great difficulty or with detergents or solvents. In other instances, depending upon the oil concentration in water and whether or not it is chemically emulsified, a granular filter has been able to remove up to 500 ppm of oil and produce an effluent with less than  $10 \text{ mg l}^{-1}$  of oil.

One of the most useful things encountered in backwash hydraulics for a filter is that the technique used to insure a uniform distribution of the backwash water on the underdrain system for the filter bed is also useful for many environmental problems where it is important to have uniform flow distribution over a long distance.

The problem is a curious one, but the solution is relatively simple. There are several methods for developing uniform flow along the length of a distribution header pipe. A typical example of a header pipe is shown in Figure 12.5. The objective is to have the flow be uniform to raise the filter bed uniformly. The vertical rise in the granular filter bed is generally mentioned in inches per minute or cm per minute. The filter bed is generally expanded between 20% and 50%, and air is introduced into the header pipe to provide extreme turbulence, which breaks up the mud balls. Some filters have mechanical rakes to stir the bed.

After the backwash is complete, the bed is running clear, and there are little or no suspended solids in the backwash. The flow rate is slowly reduced to allow the weight of the media to overcome the upward flow from the backwash. Gradually reducing the flow sets the filter bed in a graded fashion with the fastest settling particles settling first.



**Figure 12.5** Example of a hydraulic distribution problem for a filter bed. During the backwash cycle, water is pumped into the header and out through perforations in the laterals to expand the filter bed by 20–50%.

The distribution laterals generally have distribution fittings on them at a uniform spacing. The fittings have holes to direct the flow from the header horizontally. The fittings are also designed to prevent filter media accumulation in the distribution laterals.

The same general formulae presented below will work on any distribution that which requires uniform flow throughout the length of the pipe. This approach has also been used successfully with horizontal wells with lengths in excess of 500 m.

If the resistance across the fittings and the openings is of a greater magnitude than the head loss in the full header and the laterals, the flow will apportion evenly.

Another method suggested by the formula for energy losses through a nozzle or orifice plate is the same, but the coefficient of discharge is different. That formula is:

$$Q = C_d \times A_o \times [2gh]^{0.5} \quad (12.1)$$

where  $C_d$  is the discharge coefficient,  $A_o$  is the area of the orifice,  $g$  is the acceleration due to gravity, and  $h$  is the hydraulic head. All of it has to be in the same appropriate units. The coefficient of discharge is between 0.59 and 0.61 for most orifice plates, depending upon the Reynolds number for the fluid system. Michael Duchene and Edward A. McBean reported the head loss coefficients for a number of different piping systems as equal to 0.6–0.66, depending upon the depth of burial and the depth of flow in the distribution piping. They principally experimented on piping systems with four openings around the pipe.<sup>1</sup> They also accounted for differences in hydraulic head on the various openings due to their location on the pipe.

An old article in a textbook from the 1960s provides a good answer.<sup>2</sup> In that, they suggested that with a pipe of constant diameter, the head losses through the nozzle were approximately equal to the friction losses and equal to about a third of the frictional flow in the pipe. Put in scientific terms, the friction head or  $h_f$  is equal to the value shown in Eq. (12.1):

$$H_f = (KQ_o^2/L^2) \times (l - l^2/L + l^3/L^2) \quad (12.2)$$

where  $K$  is the hydraulic coefficient equivalent to the head losses in the total length of the pipe at full flow conditions,  $L$  is the length of the pipe,  $l$  is the fractional length of the pipe where the losses are occurring, and  $Q_o$  is the total flow in the pipe at maximum conditions. Remember that you will need to have the head greater than the hydraulic head on the outside of the pipe.

#### 12.4.1 Use of Air in the Backwash of Granular Filtration Systems

With granular filters, the backwash is also accompanied by the introduction of air into the backwash gallery. This increases turbulence and helps clean the media, often as effectively as mechanical raking. The air must be introduced

uniformly across the bottom of the filter bed, and the easiest way to accomplish that is to provide uniform air flow through the nozzle openings. Air is a compressible medium, and without proper design of the backwash air supply, the air will take the shortest route out of the piping gallery, with a consequence of providing high turbulence on the near side of the gallery at the injection point, and almost no turbulence at the far side. This leads to a partially cleaned filter, and a reduction in performance.

Compressible flow occurs in air and other gases. The formula must account for a few more variables such as the initial and final states and temperatures. As the air crosses the orifice it changes temperature, decreasing sharply as it expands from the nozzle. In order to prevent the formation from plugging into an ice flow, one must account for the change in temperature across the orifice, and preferentially keep the gas temperature above freezing to avoid ice formation.

In general, the equation for head loss across a nozzle is applicable only for incompressible flows. It can be modified by introducing an expansion factor to account for the compressibility of gases:

$$\dot{m} = \rho_1 Q = C Y A_2 \sqrt{2 \rho_1 (P_1 - P_2)} \quad (12.3)$$

The expansion factor  $Y$  is 1.0 for incompressible fluids, and can be calculated as follows for compressible gases:

$$Y = \sqrt{r^{2/k} \left( \frac{k}{k-1} \right) \left( \frac{1 - r^{(k-1)/k}}{1 - r} \right) \left( \frac{1 - \beta^4}{1 - \beta^4 r^{2/k}} \right)}$$

For values of  $\beta$  (ratio of orifice diameters) of less than 0.25,  $\beta^4$  approaches 0 and the last bracketed term in the above equation approaches 1. Thus, for the large majority of orifice plate installations:

$$Y = \sqrt{r^{2/k} \left( \frac{k}{k-1} \right) \left( \frac{1 - r^{(k-1)/k}}{1 - r} \right)}$$

where  $Y$  is a dimensionless expansion factor,  $r = P_2/P_1$  (absolute pressures), and  $k$  is the dimensionless specific heat ratio ( $c_p/c_v$ ), which for air is 1.4 and good enough for most cases, unless one has a really heavy vapor concentration in the gas.<sup>3</sup>

Substituting Eq. (12.3) into the mass flow rate Eq. (12.2), and making a few substitutions using the Gas Law, we get:

$$Q_1 = C A_2 \sqrt{\frac{2ZRT_1}{M} \left( \frac{k}{k-1} \right) \left[ \left( \frac{P_2}{P_1} \right)^{\frac{2}{k}} - \left( \frac{P_2}{P_1} \right)^{\frac{k+1}{k}} \right]} \quad (12.4)$$

and thus the final equation for the non-choked (i.e. subsonic) flow of ideal gases through an orifice for values of  $\beta$  less than 0.25, where:

- $k$  = specific heat ratio ( $c_p/c_v$ ), dimensionless  
 $m$  = mass flow rate at any section,  $\text{kg s}^{-1}$  (Eq. (12.3))  
 $Q_1$  = upstream real gas flow rate,  $\text{m}^3 \text{s}^{-1}$   
 $C$  = orifice flow coefficient, dimensionless  
 $A_2$  = cross-sectional area of the orifice hole,  $\text{m}^2$   
 $P_1$  = upstream gas pressure, Pa with dimensions of  $\text{kg} (\text{m}\cdot\text{s}^2)^{-1}$   
 $P_2$  = downstream pressure, Pa with dimensions of  $\text{kg} (\text{m}\cdot\text{s}^2)^{-1}$   
 $M$  = the gas molecular mass,  $\text{kg mol}^{-1}$  (also known as the molecular weight)  
 $R$  = the Universal Gas Law Constant =  $8.3145 \text{ J} (\text{mol}\cdot\text{K})^{-1}$   
 $T_1$  = absolute upstream gas temperature, K  
 $Z$  = the gas compressibility factor at  $P_1$  and  $T_1$  and, dimensionless – but most of the time it is 1 for air at the environmental temperatures generally encountered.

Check the velocity of the gas through the orifice, as it should not exceed the speed of sound, and it should be checked for temperature to insure that the gas vapor which contains water will remain above freezing. This is important for both vacuum extraction and vapor venting of horizontal wells (under pressure).

The entire program is easily arranged on an Excel spreadsheet, and the total orifice size and pressure drop and gas flow can be easily calculated. Then, using the same essential data, select a drill size and a spacing that is suitable to the length of the horizontal well. A brief calculation of the total orifice size and appropriate area is very straightforward and easily performed.

The procedure is a bit of trial and error to find the right quantity and orifice size, but well worth the trouble. An installation of 12 lines of 1600 ft each in the Louisiana clays successfully removed over 100 tons of chloroform and carbon tetrachloride in the ground in a period of around six months. The figures are not precise because the air permit had to be redrafted when the site started to overrun their air permit for toxics discharge. The air control equipment required 99.9% removal, and the remedial equipment was in danger of exceeding the permitted limit of toxics to the air.

## Notes

- 1 Duchene, M. and McBean, E.A. (1992) *Water Resources Bulletin* 28 (3).
- 2 Fair, G.M. and Geyer, G.C. *Water Supply and Wastewater Disposal*, John Wiley and Sons, New York, pp. 686–689.
- 3 Alternatively you can find values for  $c_v$  and  $c_p$  on sites such as: [http://www.engineeringtoolbox.com/spesific-heat-capacity-gases-d\\_159.html](http://www.engineeringtoolbox.com/spesific-heat-capacity-gases-d_159.html).

## 13

# Skin Filtration

## 13.1 Introduction

This chapter deals with the subject of skin filters as opposed to depth filters. There are numerous examples of skin filters including diatomaceous earth filters, microtrainers, cartridge filters, filter presses, and belt filters. The theory behind these filters is essentially the same whether or not there is a precoat on the filter.

The opening in the filter skin is the primary element for removing solids from the liquid.

Cloth filters generally fit into several categories: pressure, vacuum, continuous and batch or discontinuous types such as a Nutsche.

Pressure filters come in a variety of types including: continuous belt-fed, continuous and discontinuous pressure-vessel-fed, filter presses (which come in a variety of configurations), and cartridge filters.

Membrane filter systems use either cross-flow or immersed design for filtration, and the cross-flow design physically resembles the cartridge style filter.

## 13.2 Microtrainers and Screens

Microtrainers and screens serve essentially the same function. Screens have a larger opening for removal of various types of filterable solids. Microtrainers can remove solids down to the openings in the screen size. The sizes range from 0.25 in. ( $6350\text{ }\mu\text{m}$  to about  $250\text{ }\mu\text{m}$ ) for one manufacturer, and from  $100\text{ }\mu\text{m}$  down to  $15\text{ }\mu\text{m}$  for another manufacturer. Commercial screens generally have larger openings.

Most microtrainers and rotary screens are partially submerged with a relatively modest head loss across the screen. The head loss is dependent upon the flow rate and the open area of the screen. Other types of screens include

wedge-wire screens, shaker screens, and other configurations. Depending upon the shape and configuration of the screen and the backwash system, the screen wire may have up to 50% efficiency in removing suspended solids from the liquid. As an industrial pretreatment device, normal woven screens, wedge-wire screens (using triangular-shaped wires) and shaker screens (which have vibrating motors) are among the most popular, but they have a higher head loss because of their configuration and not because of the properties of the liquid passing through the screen. The parabolic screen is of particular interest because it tends to be self-cleaning, where the water pushes the collected solids removed further down the screen and into a collection trough. All these screens come in a variety of openings, but contact the manufacturer for ratings on the throughput of the screen.

Conventional or vibrating screens are often but not always circular and flat or gently sloped, and have a shaker motor installed on the frame to prevent solids blinding the screen. The horizontal screens often have a scraper or sprays to help remove the captured solids from the screen.

When using a screen, it is important to have an “away” – a place for the accumulated solids trapped by the screen to be placed pending disposal and a place for final disposal of screened solids. With many waste streams, these wastes are putrescible; with municipal wastes they not only have a high odor, but may also be a potential source for transmission of disease if they are allowed to accumulate without some type of disinfection treatment or disposal.

The microstrainer type is often used in removing detritus and street washings from stormwater flows. They have a high flow capacity of up to 25 gal/min/ft<sup>2</sup> (61.12 m<sup>3</sup>/h/m<sup>2</sup>). The screens are backwashed by a continuous spray system. Head losses across the type of screen shown in Figure 13.1 will be between 0.5 and 1 ft (0.15–0.31 m).

For industrial uses, a microstrainer is not often employed, especially where grease and oil are present. The most common types of screens are either shaker screens or parabolic screens. The parabolic screens have a vertical profile where the water flows down the screen perpendicular to the screen wire (Figure 13.2). This tends to force the solids down towards the bottom of the screen. The screens have head losses of 0.5 to 2–3 m depending upon the height of the screen.

The Nutsche filtering system has been described as a large-scale variant of the Buchner funnel, which is used in laboratory filtrations and separations. It is designed to operate in either pressure or vacuum modes, generally on a batch basis. The Nutsche filter may also contain rotary scrapers to help distribute a precoat or to provide distribution of the fluid being filtered. A picture of the Buchner funnel and the Nutsche filter is shown in Figure 13.3.

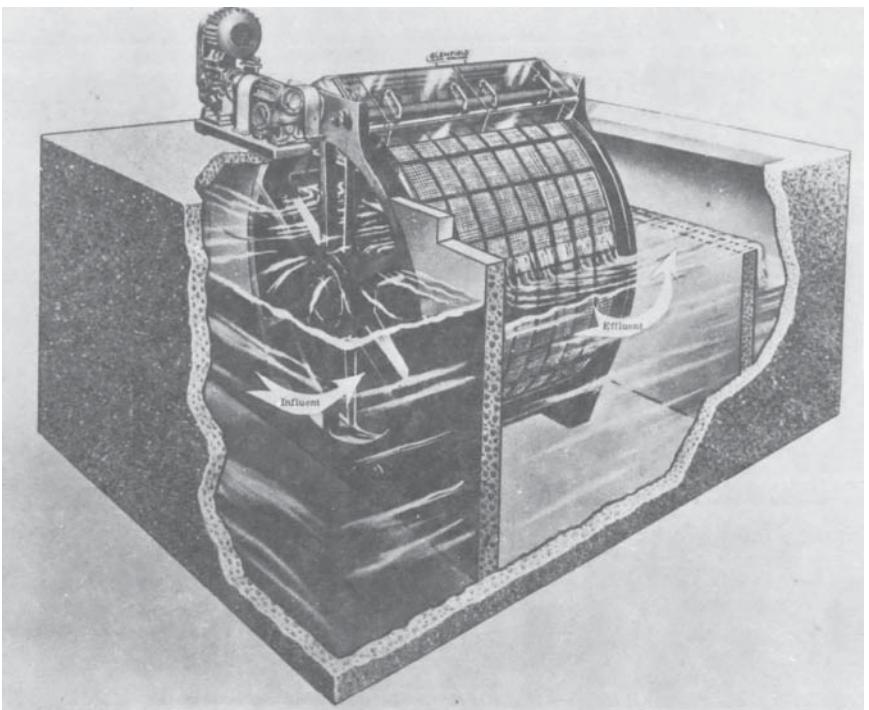


Figure 13.1 Typical drum microstainer installation. Source: USEPA.

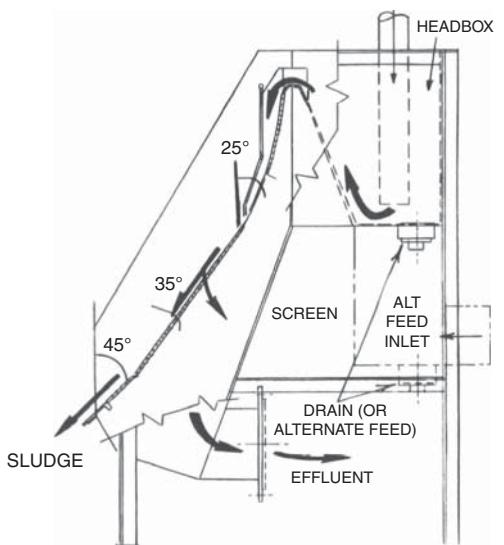
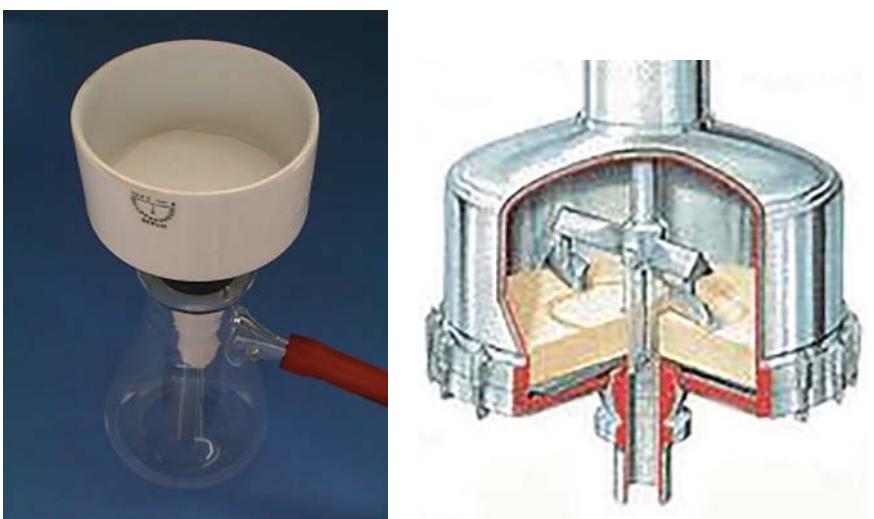


Figure 13.2 Parabolic screen. Water flow is from the top and runs along the parabolic face of the screen. Source: USEPA.



**Figure 13.3** Buchner funnel and a cutaway view of a Nutsche filter. Note the similarities and the differences.

### 13.3 Belt Filters

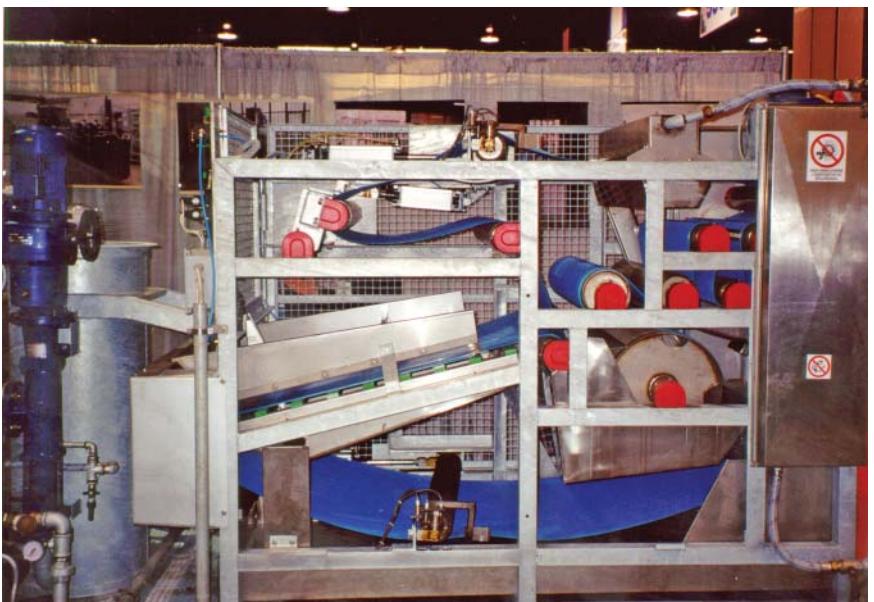
Belt filters are most commonly used for dewatering sludges in municipal operations. The sludges are deposited between two layers of high-strength filter cloth and then subjected to a tortuous path between rollers (Figures 13.4–13.6). This causes the sludge to be sheared and compressed and can achieve reasonable dewatering on municipal sludges. The ability of the belt filter to deliver a “dry” filter cake is dependent upon the amount of biosolids in the sludge. A sludge of 3–5% can often be taken up to 12–18% solids by the filter press. Higher solids concentrations can be achieved by sludge conditioning, and mixing of other materials with the sludge. However, a filter press can seldom achieve a solids concentration of greater than 22% dry weight solids basis, acting on waste-activated sludge without polymer additions. The principal reason for this is the intracellular water in the sludge. Use of steam enhancement (shown below in the filter press) raises the temperature of the cellular material and ruptures the cell wall, releasing the internal liquid. Steam-enhanced filter presses can achieve a much dryer sludge cake.

### 13.4 Plate and Frame Filters

Plate and frame filters, usually called filter presses, consist of a support plate which is grooved to support the press fabric and internal ports for filter



**Figure 13.4** Municipal belt-fed, continuous filter press. Note the tortuous path the belt takes around the rollers. Because the sludge is trapped between the belts, there is a shearing action that helps break down the sludge and increase the solids content.



**Figure 13.5** A sludge filter press with the belt tension relaxed.



Figure 13.6 A plate and frame filter press in partial disassembly.



Figure 13.7 A plate and frame filter press with steam assist. Note the similarities between Figures 13.6 and 13.7. The steam is used to heat the bacterial cells to rupture and release their internal fluids.

distribution and collection. The filter cloth is gasketed in place. The plates for the filter press are held together by a hydraulic ram. Filter presses can achieve a very dry dewatered sludge cake. The principal disadvantage of the filter press is that the press has to be disassembled and the plates cleaned manually, either with a high-pressure spray or mechanical scraping of the cloth to remove the solids. A steam-assist function in dewatering biological solids is shown in Figure 13.7.

One of the principal disadvantages of plate and frame and other type of pre-coat filters is in the cleaning cycle. The flow has to be stopped, and the filter is opened or depressurized. The filter cake is removed by mechanical cleaning or brushing, and it is a process which can be time-consuming. Even with high-pressure water sprays, cleaning a 20-element plate and frame filter can require an hour or more, plus time for handling and dewatering the filter cake.

### 13.5 Cloth vs. Paper Filters

Cloth filters and paper filters come in a variety of shapes and uses depending upon the material to be filtered. For example, General Motors used disposable inexpensive open-weave felted filter fabrics to help catch and remove emulsified paint from the wastewater in their paint spray tunnels air pollution control devices. Cloth filters have greater tensile strength than paper, and usually are preferable depending upon cost. Paper filters are commonly encountered in pleated filter cartridges that are found in automotive oil filters and other canister type applications. The pressure rating of the filter is dependent upon the spacing of the filter support frame, which gives it strength. Cloth filters are generally made from monofilament fibers because they have higher tensile strength than paper or natural fibers, are more resistant to blinding from filtration fines than natural fibers, and can be easily backwashed. These man-made fibers are also more resistant to a broad spectrum of chemical and biological attack than natural fibers.

There are also bag filters with extremely fine pore sizes. Most filtration cloths have openings of 100 µm or less. The newer generation of bag filters can reach pore sizes of 0.5 µm and less. Filtration bags can also be made from felted materials. (One manufacturer uses a felted filter fabric as a coalescer to remove oils.) Most manufacturers of bag filters post the bag sizes and the pore opening on their website. The finer the pore, the more easily it may plug, and the relative importance of precoat material addition to enhance the removal and extend the filter life by avoiding plugging. Many bag filters are made from polyester or other man-made fibers and they have high chemical resistance, but bag chemical resistance should be investigated prior to purchase.

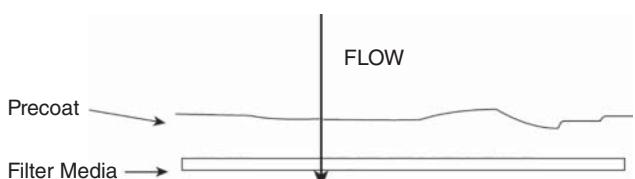
## 13.6 Precoat

Most, if not all, filters are fed a precoat material, often diatomaceous earth. The operational principle here is “dirt filtering dirt.” The precoat is added to the filter before filtration starts, and recirculated until it builds up a fine coating on the surface of the filter. The precoat then decreases the pore sizes in the filter fabric, enabling the collection of even finer materials (Figure 13.8). For most fabric filters, the amount of precoat is between 0.1 and 0.2 pounds per square foot of filter ( $0.5\text{--}1.0 \text{ kg m}^{-2}$ ). The precoat is added to the water and recirculated through the filter until the water runs clear and often at a higher rate than the design filtration rate. Once the water is clear and the precoat has been set on the filter, the entrance and exit valves to the filter are slowly opened so that the flow through the filter cloth is maintained and not dropped while filtration is begun.

Precoat material or body feed is then also added to the material to be filtered to maintain filter cake porosity. The body feed is generally prepared in a 1–2% solution and metered into the flow. The rate of addition of the body feed is determined by working conditions and trial and error during filtering operations. Some materials being filtered are highly compressible and will tend to compact and seal the filter as the filter cake gets thicker.

It is suggested that the flow rate, precoat addition rate, cake thickness, and pressure drop across the filter be recorded and used as guides to optimizing filter performance. When the flow through the filter drops below desired rates, it is time to shut down and backwash the filter. The addition of precoat to a filter can extend the length of the filter run from 20% to 50%, depending upon the size of the particulates in the fluid being filtered.

One of the most common filter aide and body feed materials is *diatomaceous earth*. The following description taken from *Material Safety Data Sheets* highlights the properties of diatomaceous earth.



**Figure 13.8** Diagram of a precoat layer on a skin filter.

## Diatomaceous Earth, DE

Synonyms: Diatomaceous silica, diatomite, de, and kieselguhr designations

Chemical Name: Diatomaceous silica chemical formula:  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$

General Description: A naturally occurring mineral derived from microscopic fossilized remains of marine diatoms. It has high absorption, low bulk density and high brightness.

Typical Chemical Purities Available: There are two basic grades available.

One grade is suitable for use as a garden insecticide (crystalline silica content is around 0.36–1.12%) and is usually approved by both the US Environmental Protection Agency and the US Food and Drug Administration.

The other grade is sold by swimming pool suppliers (crystalline silica content is close to 60%) as a filtering agent.  $\text{SiO}_2 \frac{1}{4} 86 : 30\%$ ,  $\text{Al}_2\text{O}_3 \frac{1}{4} 4 : 50\%$ ,  $\text{Fe}_2\text{O}_3 \frac{1}{4} 1 : 57\%$ , and  $\text{CaO} \frac{1}{4} 1 : 43\%$ .

Typical Granulations Available: Powder sized finer than 45  $\mu\text{m}$

Nominal Physical Constants:

Dry density ( $\text{lbs ft}^{-3}$ )	9.5–13.0 Apparent wet density ( $\text{lbs ft}^{-3}$ ), 20.0–27.5, Specific gravity, rv 2.0
G. E. brightness	64–92
Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )
Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	30
LOI (%)	4.00
Moisture (%)	rv 1.0
pH (10% slurry)	7.0–10.0
Fusion point ( $^{\circ}\text{C}$ )	1715
Color	Off-white to pink
Refractive index	1.46

Typical Applications: A silica source in the production of calcium silicates, insulation bricks and material in safes, fireproof filing cabinets, etc. Used in the paint, varnish, lacquer, and polish industries. Used as an insecticide in gardens and in swimming pools as a filtering agent.

Packaging Options: Bags, drums, and bulk bags

Precoat materials such as diatomaceous earth are crystalline dusts containing silica. As such they can pose a health risk if inhaled. At the time of writing, there

is an OSHA standard on silica-containing dusts being developed. The standard will likely be enforced fully prior to 2020.

The solution to the dust problem is, at a minimum, inhalation masks to protect the breathing zone. The masks should have an OSHA or equivalent ANSI rating. Eye protection may also be required in dusty environments.

One of the advantages of a skin filter is the relatively low volume of backwash. With plate and frame filters, the filter plates need to be separated and sprayed or brushed and washed clean. This can be time-consuming and labor-intensive. The amount of backwash water used for a skin filter is very low, sometimes as low as 1–2% of the total filter throughput.

### 13.7 Head Loss Through Cloth Filters

The head loss through a precoated filter can be almost impossible to predict and highly variable due to a number of factors that depend upon the compressibility of the solid medium being filtered out of the liquid, the quantity of body feed material, the size of the filter cake particles, and the overall porosity of the filter cake. These factors all affect the permeability of the filter cake, and the permeability of the filter cake is inversely proportional to the head loss across the filter medium.

Madan Lal Arora, in a 1970 PhD thesis for Iowa State University, ran a number of tests on skin filters using precoat materials. He offered the following general formula for head loss across a precoated skin filter.<sup>1</sup>

$$H_1 = \frac{K (1 - \varepsilon)^2 \mu L_q}{g \varphi_s^2 D_p^2 \varepsilon^3 \rho}$$

where:

$H_1$  = head loss (linear dimension – ft or m)

$K$  = determined constant

$\rho$  = density of liquid

$\mu$  = viscosity of liquid

$\varphi$  = shape factor for the particles

$g$  = gravity

$\varepsilon$  = porosity of precoat

$L$  = depth of precoat or thickness of cak

$q$  = superficial velocity of the liquid through the bed.

In certain situations, and depending upon the medium filtered and the precoat material, the precoat cake may be compressible. In that instance, the head loss across the filter would increase markedly with the apparent decrease in porosity of the cake. In fact, in some of his experiments, Arora reported that an error in measurement of the porosity of as little as 6.4% may result in an error of around 33% in the prediction of head losses through the filter. Arora also suggested that the predictive work for filtration be pilot tested rather than calculated because of better operational control and direct prediction of the head losses.<sup>2</sup>

Arora conducted his tests using Whatman filter papers and did not attempt to account for the shape of the filter septum on filtration.

### 13.8 Bag Filters

There are a number of bag filters on the marketplace. The filtration sizes vary from less than 0.5 µm (0.000 039 in.) to 1250 µm (0.049 in.) and greater. These materials are generally of manmade cloths of felted construction. They come in a variety of sizes and pore openings. Bag filters tend to be used in specialized situations as they are more difficult to regenerate than diatomaceous earth filters. Many of the bag filters have to be regenerated by turning them inside out and backwashing them with clean water and industrial cleaners: a time-consuming and labor-intensive process. In some situations, the filters cannot be backwashed to a level consistent with their initial filtration efficiency.

One manufacturer of bag filters recommends that the maximum total pressure drop across a filter not be greater than 3 psi (20.68 kPa), and the recommended pressure drop across a bag filter should be closer to 2 psi (13.79 kPa) for long bag life. The system pressure drop is the sum of the housing pressure drop plus the pressure drop across the bag. The same manufacturer also states that increasing the area of a filter bag by 2 $\times$  increases the life of the filter bag by 3–4 $\times$ .<sup>3</sup> The company produces a useful technical bulletin on filter bag sizing.

The pressure drop or head losses across these filters can be directly measured much more readily than they can be calculated, as the pressure drop is dependent upon the pore size, the fluid viscosity, fluid velocity through the filter cloth (laminar flows), and so on. One of the critical things about bag filters is their construction. Many of the commercial designs are supported on a wire screen, but some are not. The tensile strength of the filter fabric, especially at the seams, is important as many bag failures result from tensile failures at the seams joining the overlapping sections of filter fabric together.

## Notes

- 1 “*Prediction of filter cake resistance.*” PhD thesis by Madan Lal Arora, Iowa State University Digital Repository, 1970.
- 2 Op. Cit, p. 73, and the comment is made that, “... the determination of porosity of the cake is still not easy enough to be accomplished by a simple test.”
- 3 *Bag Filter System Sizing* technical bulletin by Advanced Water Engineering, Inc., Indian Harbor Beach, FL, 23937.

## 14

# Membrane Filters and Reverse Osmosis

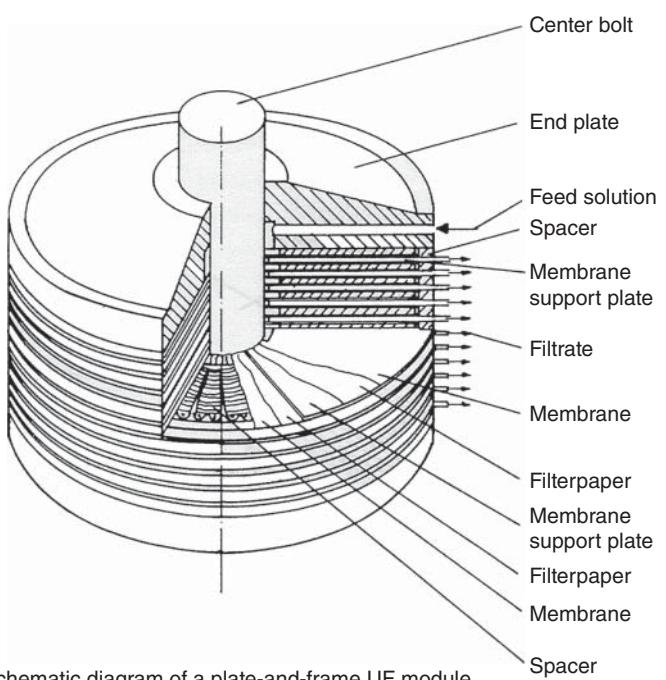
## 14.1 Introduction

This chapter will discuss membrane filtration and reverse osmosis (RO) for medium- and low-pressure applications. High-pressure RO has been well documented and commercialized on seawater applications. There are a number of large RO systems in operation in many parts of the world. The theory for high-pressure and medium- and lower-pressure RO systems is the same, but high pressure requires several extra pretreatment steps.

The commonality between these types lies in the use of permeable membranes. The membranes can be made from ceramics, foils, etched polymers, and natural and synthetic compounds. The common materials of construction include titanium or zirconium dioxides (ceramics), and cellulose acetate (CA), polyamide, polypropylene, polysulfone (PES), polytetra-fluoroethylene, polyvinylidenefluoride (PVDF), nylon 6-6, and cellulose esters. Each has its own properties and specific resistances to heat, bacterial attack, corrosion, and abrasion. The membranes themselves are thin and require a support structure to prevent tearing and rupture, and to help promote drainage. Membrane systems for wastewater applications are most commonly manufactured in cartridges (Figure 14.1) and in hollow-core spaghetti strand configurations (Figure 14.2). The cartridge systems are flat sheet membranes that are layered with support and drainage structures and wrapped around a central core, then encased in a housing which permits feed and drainage. The spaghetti strand configuration is generally used in either cartridges or in an open system where the strands are layered into a top and bottom mold, which is filled with an epoxy material. Once set, the epoxy material is then saw-cut and polished to expose the ends of the hollow core of spaghetti strands (Figure 14.3).

Consult the manufacturer of specific membranes for information on the properties and resistances of the membrane materials.

It is often helpful to think of membranes in terms of screens rather than filters because the membrane does not deliberately build up a cake in the same way



Schematic diagram of a plate-and-frame UF module

Figure 14.1 Cartridge filter system for RO systems.

Schematic diagram of a capillary membrane module.

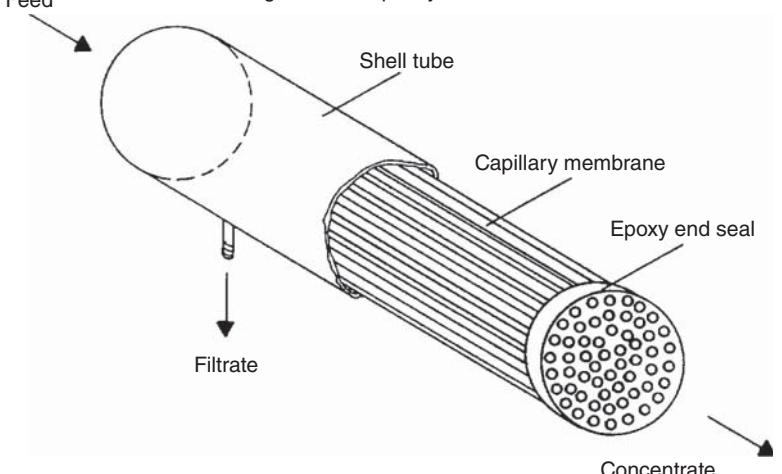


Figure 14.2 Construction of a spaghetti strand filter cartridge.

**Figure 14.3** Spaghetti strand membrane filter cartridge cutaway photograph.



that a filter does, and once the pores are plugged, the head losses across the membrane climb steeply.

The sizes of membrane pores vary greatly, as do the pressure drops. Starting with the finest sizes and working up, the following is generally applicable to all membranes.

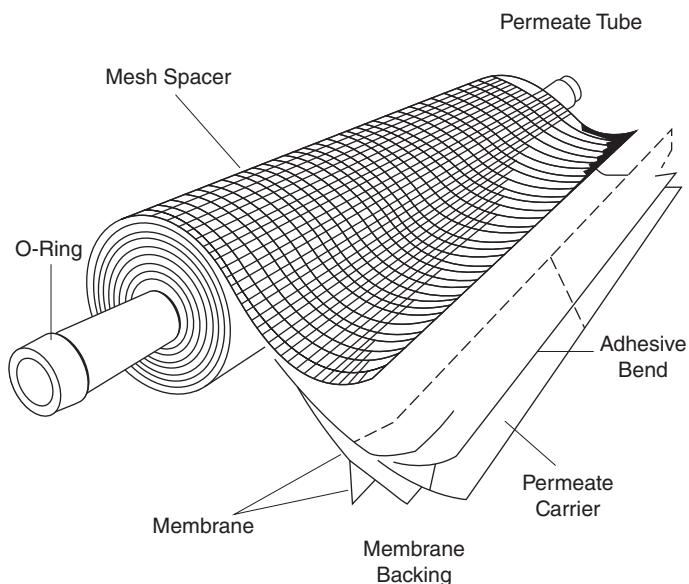
One of the measures of efficiency of a membrane is the molecular weight (MW) cutoff, which is related to pore sizing. The cutoff is rated in daltons. One Dalton (Da) is a twelfth the weight of a carbon atom, as defined by convention in 1960, and is approximately equal to  $1.660\ 538\ 73 \times 10^{-24}$  g. Table 14.1 illustrates some of the ranges of performance of various membranes.

Membranes are not always homogeneous or isentropic. Some membranes are designed to have a different density and pore gradient from one side to the other, and others are composed of layers of different materials for a very fine cleaning. Membranes often require careful cleaning or prefiltration to prevent their clogging. The finer the membrane, and the higher the pressure, the more likely that the membrane will require prefiltration and conditioning if it is to enjoy long life.

The older-style membrane tubes have a diameter between 2 and 5 cm. In the newer spaghetti strand designs, the tubes are of the order of 0.5–1 mm diameter with the same hollow core. In larger configurations, the feed is sometimes

**Table 14.1** Membrane separation properties and performance.

Type of membrane	Separation mechanism	Pore size ( $\mu\text{m}$ )	Molecular weight (amu or Da)	Operating pressures (psi)
Reverse osmosis	Screening and diffusion	<0.001	100–200	600–1500
Nanofiltration	Screening and diffusion	0.001–0.01	300–1000	50–250
Ultrafiltration	Screening	0.01–0.1	1000–100 000	3–80
Microfiltration	Screening	0.1–20	Over 100 000	1–30

**Figure 14.4** Construction of a cartridge membrane filter unit.

from the inside of the tube into a shell. The smaller diameter tubes use an outside feed and operate on pressure differential. In wastewater treatment plant configurations, the membrane tube is often in contact with the water and a vacuum is pulled over the tube. In either case the membrane is sealed into the base with an epoxy seal and a machined slot for an O-ring gasket (Figure 14.4).

Most of the time pretreatment of the water is necessary. Even in wastewater plants, prescreening to remove hair, and free fats and oils, is customary.

The design engineer does not have much control over membrane pore sizing or permeability – it is a function of how the membranes are manufactured, and the designer's only control is the selection of the membrane and the desired end results. Look at the equipment available and sift through various manufacturers' claims regarding their equipment, and then select the best equipment, trying to balance the performance guarantee against the price of the equipment and anticipated performance.<sup>1</sup>

The key to establishing long membrane life is crossflow cleaning of the membrane, coupled with frequent back-flushing or chemical cleaning, depending upon the type of membrane.

If the contaminated liquid flows across the membrane and not normal to it, the membrane filtration run is improved because the *crossflow* removes the solid buildup, which would plug the pores. For certain types of microfiltration membranes, such as those becoming more frequently used in wastewater treatment plants, the tubular hollow membrane is directly submerged in the aeration portion of the plant where it is in contact with bacteria, viruses, and protozoans in the wastewater, as well as colloidal solids and suspended materials.

For the “naked” tubular membrane applications, the manufacturers have instituted frequent back-flushing and an “air bump,” which not only shakes and scours the membrane but also promotes knocking off of the fouling layers. This, coupled with back-flushing and pulsing of the membranes, helps keep the pores open.

Other types of cleaning may be required depending upon the membrane materials, and may include: sodium hypochlorite, hydrochloric acid, ozone, oxalic acid, hydrogen peroxide, and citric acid. The acids dissolve the carbonate buildup in the membrane pores. Cleaning cycles vary from a few hours to 24 hours, depending upon the severity of the plugging. The back-flushing and back-pulsing can take from a few minutes to an hour, once per day. The chemical cleaning of the membranes is performed weekly to monthly, depending upon the need and the manufacturer's instructions.

Depending upon the application, some post-treatment may also be necessary.

Table 14.2 presents typical effluent quality from a microfiltration system.<sup>2</sup> The water may still not be safe to drink, will contain viruses and protozoan cysts, and other things with MW below 100 000 Da. In microfiltration, with a pore size of less than 0.45 µm, the filtered liquid will have no suspended solids because the 0.45 µm filter is the standard for the suspended solids test.

With RO, and the smaller pore sizes, there is a much greater statistical chance that the permeate water will be virus-free due to the smaller size, but disinfection is still recommended.

Membrane separations are usually less costly in capital and operation costs than other forms of separation, and a paper on costs of wastewater treatment brings out this point.<sup>3</sup>

**Table 14.2** Typical effluent concentration after membrane filtration.

Parameter	Units	Approximate effluent quality
BOD	$\text{mg l}^{-1}$	<2–5
Total organic carbon	$\text{mg l}^{-1}$ as C	5–25
Total Kjelldahl nitrogen	$\text{mg l}^{-1}$ as N	5–30
Total phosphorus	$\text{mg l}^{-1}$ as P	0.1–1.8
Iron	$\text{mg l}^{-1}$	0–0.2
Total suspended solids	$\text{mg l}^{-1}$	BDL
Fecal coliform	No./100 ml	2–3

## 14.2 Design Values

The design values for membrane microfilters are of the order of 30–45 l/h/m<sup>2</sup> or 16–25 gal/day/ft<sup>2</sup> for straight microfiltration on immersed activated sludge systems, and between 50 and 60 l/h/m<sup>2</sup> for relatively clean wastewater after treatment or pretreatment by a clarifier. Because many wastewater systems have a diurnal variation factor of 2.5 : 1 or more, the design for the system should be for the peak flow because the membrane systems do not take surges well. Some manufacturers recommend that backwashing of the membrane filter systems should not be scheduled for the time of day when the flow is the highest.

## 14.3 Process Selection

The following summary can help with the types of separation:

### 14.3.1 Ultrafiltration Membrane Selection

Micro/ultrafiltration membranes should have the following:

High fluxes

Sharp MW cutoff

Good mechanical, chemical, and thermal stability

High life expectancy

The most widely used polymers are CA, aromatic polyamides, PESs, and polyacrylonitrile-poly(vinyl chloride) co-polymers.

### 14.3.2 Cellulose Acetate Membranes

#### **Advantages**

Can be produced in a wide range of pore sizes  
Obtain relatively high fluxes

#### **Disadvantages**

Mechanically weak and thermally unstable  
pH operating range of 4–8  
Full temperature of 35°C  
Susceptible to bacterial attack

### 14.3.3 Polysulfone Membranes

#### **Advantages**

Excellent chemical stability  
pH range of 0–14

#### **Disadvantages**

Certain materials are adsorbed at the membrane surface  
Hard to achieve low MW cutoff characteristics

### 14.3.4 Polyamide Membranes

#### **Advantages**

Low MW cutoff and good flux can be achieved  
Excellent mechanical strength and thermal stability

#### **Disadvantages**

Sensitive to chlorine attack at low concentrations  
Adsorb certain materials at surface

### 14.3.5 Polyacrylonitrile Membranes

#### **Advantages**

Can be dried completely and re-wetted without changing filtration characteristics

#### **Disadvantages**

MW cutoffs above 30 000  
Low mechanical strength

### 14.3.6 Ultrafiltration Modules

Choice of module design is as important as the membrane material. At sufficiently high pressures a thin gel layer forms, caused by concentration polarization at the membrane surface. This gel layer can alter the properties of the ultrafiltration membrane. Flow control at the membrane surface must be taken care of.

*Tubular Module:* Pressurized feed flows into the center; the permeate flows through the membranes and is collected in the outer shell. These tubes can be installed in parallel or in series.

#### Advantages

Tolerant toward suspended solids

Easily mechanically cleaned

Control of concentration polarization effects

Adjustments over feed flow velocity over a wide range

#### Disadvantages

High investment costs and operating costs

Low membrane surface area to system volume

*Plate and Frame Module:* Some membranes are configured in a stacked array like a filter press, with the same spacers and membrane supports shown in the spiral wound membrane shown above. The feed is from inside out and is channeled across the membrane.

#### Advantages

Large membrane surface area per unit volume

Generally low operating costs

#### Disadvantages

Control of concentration polarization is more difficult

Plugging of feed flow can be problematic

*Spiral Wound:* There are limited uses of spiral wound modules in ultrafiltration; however, it is the most widely used type in RO.

#### Advantages

Membrane surface area per unit volume is high

Capital and operating costs are low

#### Disadvantages

Hard to control concentration polarization

**Capillary:** The capillary module has a large number of membrane capillaries with diameters from 0.5 to 1.5 mm. The feed is passed through the center of each capillary and the filtrate permeates the walls.

### Advantages

- Low capital costs
- Good feed flow control
- Large membrane surface area per unit volume

### Disadvantages

- Hard to control concentration polarization

**Rod Membrane:** Although they are similar to hollow fiber in RO modules, they have a grooved rod coated with an asymmetric membrane. In this module the feed runs to the outer side of the rods and the permeate is collected in the middle by grooves in the rod.

### Advantages

- High membrane surface area per unit volume

### Disadvantages

- Feed flow control is not good

## 14.4 Reverse Osmosis

RO can remove more than 99% of all dissolved minerals and organic compounds, as well as biological and colloidal suspended matter, from water.<sup>4</sup> RO is useful in wastewater and process water treatment because it can be applied to each individual process and, therefore, to each individual separation problem. Additionally, recovery is often a plausible option because there is no chemical or thermal degradation.

## 14.5 Mass Transfer Theory

RO is a process where the natural flow of fluid across a semipermeable membrane is reversed by applying pressure to the concentrated solution. Unlike many membrane filtration applications, the operating pressure is significantly higher with RO systems.

When the applied pressure is greater than the natural osmotic pressure, the solvent will flow through the membrane to form a dilute solution on the

opposite side and a more concentrated solution on the side where the pressure is applied.

The temperature of the solution, membrane properties, and differences in applied and osmotic pressures all affect the flux of water across the membrane.

To calculate the flux of component A across the membrane,  $N_A$ , the following equation is used:<sup>5</sup>

$$N_A = P_A \left( \frac{\nabla \varphi}{L} \right)$$

where  $N_A$  is the flux of A through the membrane (mass/time-length<sup>2</sup>);  $P_A$  is the permeability of A (mass-length/time-force);  $L$  is the membrane thickness (length); and  $\nabla \varphi$  is the driving force of A across the membrane. This can be either a difference in concentration or a difference in pressure (mass/length<sup>2</sup> or force/length<sup>2</sup>).

To obtain the osmotic pressure use the following equation:

$$p = C_s RT$$

where  $p$  is osmotic pressure (force/length<sup>2</sup>);  $C_s$  is the concentration of solutes in solution (moles/length<sup>3</sup>);  $R$  is the ideal gas constant (force-length/mass-temp); and  $T$  is absolute temperature (°K or °R).

## 14.6 Membrane Design Software

Membrane performance with respect to removal of certain parameters has always been an issue. Select the wrong membrane and performance suffers, or transmembrane pressures are too high, or the membrane does not clean well. Several of the membrane manufacturers have developed predictive software to assist the system designer with the selection of the membrane system based upon performance. The principal manufacturers that provide their design software are Dow, GE, Toray, KOCH, CSM, and Hydranautics. Table 14.3 is a list of the manufacturers' software and their websites.

KOCH Membrane systems did have a software package but does not offer it any longer as of 2017. A contact with the manufacturer's regional representative suggested that use of the ROSA software package should provide adequate design information for their membranes as well.

The Texas Water Quality Development Board<sup>6</sup> authorized a study on the evaluation of alternatives to membrane system pilot plant studies. In it, they evaluated several types of membrane performance predictive software programs.

The advantage of using the predictive computer models is cost. The models are free. Pilot plant testing can cost tens of thousands of dollars and may require months of evaluation. The software is reasonably predictive for removal

**Table 14.3** RO modeling software.

Software program name	Manufacturer	Website – all are prefixed with <a href="http://www">http://www</a> .
Rosa 9	Dow	<a href="http://Client.dow.com/RosaRegistration">Client.dow.com/RosaRegistration</a>
Winflows 3.3.2	GE	<a href="http://gewater.com/resources/winflows">gewater.com/resources/winflows</a>
Toray Design System	Toray	<a href="http://Ap3.toray.co.jp/toraywater">Ap3.toray.co.jp/toraywater</a>
CSMPRO5.0	CSM	<a href="http://CSMfilter.com">CSMfilter.com</a>
IMS design	Hydranautics	<a href="http://membranes.com/solutions/software">membranes.com/solutions/software</a> <sup>a)</sup>

- a) The website contains three separate downloadable programs: one for design, one for monitoring operations, and a third for simulation of the operation.

Source: Texas Water Quality Development Board (2014). Final Report No. 1448321310 “Developing Practical Alternatives to Pilot Plant Studies for Innovative Water Technologies,” Part II: Performance Evaluation of Reverse Osmosis Membrane Computer Models.

of inorganic materials, but pilot scale testing may be required when disinfection criteria govern the water use.<sup>7</sup>

Carbonate chemistry is important in determining the size and cost of the membrane system. Most models require the user to input feedwater parameters including pH, temperature, and total alkalinity (as  $\text{CaCO}_3$ ), and the software determines the concentrations of carbonate and carbon dioxide. The computer models require input of certain chemicals shown in Table 14.4. The input data should be in very close chemical equilibrium (milliequivalents per liter) with anions and cations balancing. If the input data are not in equilibrium, the program will adjust and balance the input water. If more than one stage of membrane is required, the user maybe asked to specify the pressure loss between stages.

**Table 14.4** RO model input parameters.

General	Anions	Cations
pH	$\text{Cl}^-$	$\text{Ca}^{2+}$
Temperature	$\text{SO}_4^{2-}$	$\text{Mg}^{2+}$
	$\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$	$\text{Na}^+$
	$\text{NO}_3^-$	$\text{K}^+$
	$\text{F}^-$	$\text{Ba}^{2+}$
	Boric acid ( $\text{H}_3\text{BO}_3$ ) <sup>a)</sup>	$\text{Sr}^{2+}$
	$\text{SiO}_2$	$\text{NH}_4^+$

- a) Boric acid is generally measured as B, but calculated as  $\text{BO}_3^-$ .

Over time, membranes will clog and decrease permeability due to salts depositions, the effect of cleaning chemicals, hydraulics, and abrasive forces within the membrane system. This is not a “one size fits all” system, and each system will vary, with some systems running for years without deterioration, and others fouling with months of startup. One manufacturer suggests derating the membrane flow factors by 15–25% to allow for age and unremoved deposits left over when the membranes are cleaned. This deterioration will not affect the salt rejection, but will affect the membrane throughput.

Overall, the computer models performed very well when tested against pilot plant studies. The computer models were within 6–12% of the feed pressures measured in pilot plant tests, and within 2% of the average salt rejection as compared with test cases.<sup>8</sup> The data from computer modeling runs were compared with full-scale operations at a variety of high- and low-pressure multi-stage desalination plants. In those tests, the results were generally within about –10% to +20%, with the computer models overpredicting the required pressures and underpredicting the second-stage pressures within –5% to –17%, depending upon the system and the feedwater. The salt rejection was generally within 3% of measured values.

This suggests some caution, in that the pressure system should have more than the computer-indicated design capacity, and the system should be sized overall to be between 10% and 15% larger than required for basic throughput values.

There are three membrane properties that are important for an economically successful application in the order of their importance: (i) membrane selectivity, (ii) membrane chemical stability, and (iii) membrane permeation or flux rate. Of these, the flux rate is the least important because the cost of additional membrane surface to make up for lower flux rates is a minor component of cost.

## 14.7 Membrane Materials

The ideal RO membrane has the following characteristics: (i) high water flux rates, (ii) high salt rejection, (iii) high resistance or tolerance to chlorine and oxidants, (iv) high resistance to biological attack, (v) high resistance to colloidal and suspended material fouling, (vi) inexpensiveness, (vii) ease to form into films or hollow fibers, (viii) high chemical and physical strength (resistant to high pressures), (ix) high chemical stability (ability to retain chemical properties under a variety of conditions), and (x) high thermal stability (ability to withstand high temperatures without deforming or losing shape).<sup>9</sup>

There are three main, different types of membrane materials available for RO: cellulose acetate (CA), aromatic polyamide (aramid), and thin film composites (TFCs).

CA is widely used, has low cost, and has the ability to withstand continuous exposure to low levels of chlorine. On the minus side, it tends to hydrolyze with time, has relatively poor chemical stability, requires a pH range between 4.0 and 6.5, and is subject to biological attack. The upper limit of temperature is approximately 30°C.

Aromatic polyamides have excellent chemical stability, an operating range of 0–35°C, a pH range between 4 and 11, and is resistant to biological attack. Polyamides are subject to degradation if exposed to chlorine.

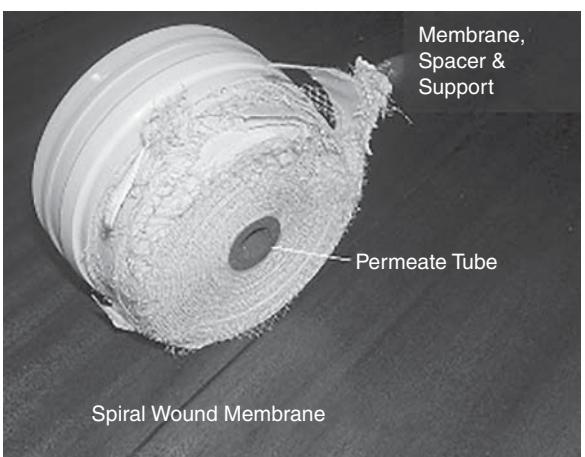
TFCs have high chemical stability, high rejection, and high flux rates at moderate pressures, in a temperature range of 0–40°C, and a pH range of 2–12. TFCs are susceptible to attack from chlorine and other oxidants.

## 14.8 Membrane Configurations

Most membrane configurations are either thin film (spiral wound) or hollow fiber, but others are used as well. The spiral-wound configuration uses layers of membranes and supports, which are wrapped around a perforated permeate tube (Figure 14.5). The spiral wound has good resistance to fouling because of relatively open feed channels, and because it is easy to clean, easy to replace, available in many varieties of membrane materials, and manufactured by a number of companies. The disadvantages of spiral wound configurations include low membrane surface area-to-volume ratio, possible concentration polarization, and difficulty in identification, isolation, and repairing individual elements in multiple-element tubes.

Hollow fiber membrane configurations are popular for a variety of reasons: (i) the hollow fiber configuration is formed by orienting the membrane fibers

**Figure 14.5** Cutaway view of a spiral wound membrane element.



parallel within cylindrical pressure vessels, (ii) pressure is applied to the fiber bundles from the outside, and the permeate flows to the interior of the bundle and through the length of the fiber, (iii) the bundle of fibers has a high membrane surface area-to-volume ratio, and (iv) it is easy to service and repair in the field. A number of manufacturers are making hollow fiber membrane bundles, and their popularity is increasing. The hollow fiber configuration is sensitive to the development of fouling by sediment and colloids and may be more difficult to clean than other types of systems.

Tubular configurations were some of the earliest RO devices ever introduced. Although not in use as often as hollow fiber and spiral wound modules, they still are used in applications with high levels of suspended solids, such as wastewater treatment. During operation with tubular modules, the high-pressure feed stream enters the tube, and the permeate passes through the membrane and supporting structure into an outer jacket where it is removed through permeate ports.

The advantages of the tubular configuration include large flow passages, which permit the high flow velocities in the tubes, a low tendency to foul, ease of cleaning, and a high temperature stability; the disadvantages include low membrane surface area-to-volume ratio, high expense, and lower selection of material choices because of the demand for high tensile strength.

## 14.9 RO Design Considerations

When designing a RO system, it is usually necessary to have both pretreatment and post-treatment of the water. The process should be viewed as a total system consisting of the following considerations: feedwater supply, pretreatment, high pressure pumps, RO membranes, post-treatment, and end use. The following parameters are an overview of the considerations that one must take into account in designing a RO process.

### 14.9.1 Feedwater Supply Considerations

Scale control, pH optimization, hardness, suspended solids content, metallic ions, organic chemical control and attack, and biological inhibition of growth

### 14.9.2 Pressure Pumping

System pressure, pump efficiency, pump flow rate and turndown rates, materials, and corrosion.

Look carefully at the pressure drop across the membrane units, and it is quite possible and probable that a booster pump may be required between subsequent stages to maintain membrane flow rates.

**Table 14.5** Summary of pretreatment methods for reverse osmosis.

Problem	Pretreatment	Purpose	Problem areas	Secondary pretreatment	Purpose
Ca/Mg/bicarbonate scale	Ion exchange softening	Replaces cations with Na	High TDS causes slip. Maximum recommended is 800 mg l <sup>-1</sup> , too expensive at flow >9000 m <sup>3</sup> d <sup>-1</sup>	Sequestrant	Causes any tendency for slip to cause precipitations
	Lime softening	Removes Ca and HCO <sub>3</sub> , precipitates Mg as Mg(OH) <sub>2</sub>	Flow greater than 5000 m <sup>3</sup> d <sup>-1</sup>	Sequestrant or acid	Prevents post-precipitation
	Acid	Replaces bicarbonates with Cl or SO <sub>4</sub>	Difficult and expensive	Sequestrant	Backup if acid dosing fails
	Sequestrant as primary conditioning	Not recommended because it delays formation of the precipitate	Other methods better suited, more reliable		
	Base exchange	See above			
Ca sulfate scale	Sequestrant	See above			
	Raise temperature	Stabilizes and increases solubility of scale	Cost of energy		
	Lime softening	See above	See above		
	Oxidize and filter	Removes precipitates	May cause problems with other materials like H <sub>2</sub> S	acid	Prevents further precipitates.

(continued)

**Table 14.5** (Continued)

Problem	Pretreatment	Purpose	Problem areas	Secondary pretreatment	Purpose
Colloids	Exclude oxidants	Keeps iron as filterable $\text{Fe}^{2+}$	Not good for intermittent Need pH < 5	acid	Prevents precipitates
	Acid	Keeps iron in solution			
	Coagulate and filter	Removes particles		Sometimes acid works	Prevents post-precipitation
	Base exchange softening	Stabilizes coagulation by changing zeta potential of colloids and discourages precipitates	Not suitable for high TDS waters where total hardness after softening is $>5 \text{ mg l}^{-1}$		
Bacteria	Sterilize with $\text{Cl}_2$ and filter	Remove with Filtration		Dose sodium metabisulfite	Removes Cl that could damage permeators
$\text{H}_2\text{S}$	Degas and add $\text{Cl}_2$	Removes $\text{H}_2\text{S}$	Hard waters need acid dose before treatment	See Bacteria above	
	Exclude oxidants	Keeps $\text{H}_2\text{S}$ in solution	Do not use if bacteria are present or if system has poor operation	Need to degas permeant	$\text{H}_2\text{S}!!!$
Chlorine of oxidants	Dose with sodium metabisulfite or remove with activated carbon	Needs good maintenance and careful operation to avoid failure	Bisulfite can fail and cause harm to system. Carbon can breed bacteria	Need to monitor and back up system	If second dose is used, helps membrane life

Source: Brandt, D., Leitner, G., and Leitner, W. (1994). Reverse osmosis membranes state of the art. In *Reverse Osmosis* (ed. Z. Amjad). Van Nostrand Publishers.

### 14.9.3 Membrane Considerations

Configuration and type of membrane, material, salt rejection, chemical resistance, and recovery.

### 14.9.4 Post-treatment

pH adjustment, demineralization, degasification, disinfection, and storage.

Rejection is a common feature of RO systems. In working with seawater it is often common to have a rejection rate of about 4 gal for every 1 gal treated. The higher the salt concentration in the system, the harder it is to get a low salt concentration in the effluent.

Table 14.5 shows the common components for a pretreatment system for RO systems.

## 14.10 Design Parameters

*Pressure.* The fluid flux is a function of the pressure differential between the applied pressure and osmotic pressure across the membrane. The higher the applied pressure, the greater the flux. Most membranes working on seawater operate at around 400–600 psig (25.7–41.4 bar).

*Temperature.* The flux increases with increasing feed liquid temperature. For water, 70°F (21°C) is a widely assumed inlet condition, but lower temperatures will lower the flux, and temperatures above 85°F (30°C) may cause long-term deterioration.

*Membrane packing density.* This is the unit area of membrane per unit volume of pressure vessel. Typical values range from 30 to 500 sq. ft./cu. ft. (100–1600 m<sup>2</sup>/m<sup>3</sup>).

*Flux.* Assuming a typical pressure of 600 psig, flux values range from 10 to 80 gallons per day per square foot (gpd/sq. ft.), with 12–35 gpd/sq. ft. being common. This flux tends to decrease with length of run, and over a period of one to two years of operation might be reduced by 10–50%.

*Recovery factor.* This consideration actually represents plant capacity and is generally in the range of 75–95%, with 80% being the practical maximum. At high recovery factors, there is a greater salt concentration in the process water as well as in the brine. At higher concentrations, salt precipitation on the membrane increases, causing a reduction in operational efficiency. Individual membranes have a recovery rate between 15% and 30%, and greater efficiency is gained by staging the membranes so that the reject water from the first stage becomes the feed for the second stage, and the second-stage reject water becomes the feed for the third stage.

Most companies will publish this information for the designer, and it is incorporated into their design software as an option. A sample of the design

guidelines for Dow's 8" Filmtec elements is shown in Table 14.6. Note that for different types of water (salt content) the element performance and recovery is different.

**Salt rejection.** Salt rejection depends on the type and character of the selected membrane and the salt concentration gradient. Generally, rejection values of 85–99.5% are obtainable, with 95% being commonly used.

**Membrane life.** Membrane life can be drastically shortened by undesirable constituents in the feedwater, such as phenols, bacteria, and fungi, as well as high temperatures and high or low pH. Generally, membranes will last up to five years with some loss in flux efficiency.

**pH.** Membranes consisting of CA are subject to hydrolysis at high and low pHs.

The optimum pH is approximately 4.7, with operating ranges between 4.5 and 5.5.

**Turbidity.** While RO units can be used to remove turbidity from feedwaters, they operate best if little or no turbidity is applied to the membrane. Generally, it is felt that turbidity should not exceed one Jackson Turbidity Unit (JTU) and the feedwater should not contain particles larger than 25 µm.

**Feedwater stream velocity.** The hydraulics of RO systems are such that velocities in the range of 0.04–2.5 feet per second are common. Plate and frame systems operate at higher velocity, while hollow fine fiber units operate at the lower velocities. High velocities and turbulent flow are necessary to minimize concentration polarization at the membrane surface.

**Power utilization.** Power requirements are generally associated with the system pumping capacity and operational pressures. Values range from 9 to 17 kWh/1000 gal, with the lower figure taking into account some power recovery from the brine stream.

**Pretreatment.** The present development of membranes limits their direct application to feedwater having a total dissolved solids not exceeding 10 000 mg l<sup>-1</sup>. Further, the presence of scale-forming constituents, such as calcium carbonate, calcium sulfate, oxides, and hydroxides of iron, manganese and silicon, and possibly barium and strontium sulfates, zinc sulfide, and calcium phosphate, must be controlled by pretreatment or they will require subsequent removal from the membrane. These constituents can be controlled by pH adjustment, chemical removal, precipitation inhibition, and filtration. Organic debris and bacteria can be controlled by filtration, carbon pretreatment, and chlorination. Oil and grease must also be removed to prevent coating and fouling of membranes.

**Cleaning.** Recognizing that under continuous use membranes will foul, provisions must be made for mechanical and/or chemical cleaning. Methods reviewed include periodic depressurizations, high-velocity water flushing, flushing with air–water mixtures, backwashing, cleaning with enzyme detergents, ethylene diamine tetra-acetic acid and sodium perborate. The control of pH during cleaning operations must be maintained to prevent

**Table 14.6** Typical (Dow) membrane performance.

RO permeate	Well water	Surface water			Wastewater			Seawater					
		Dow UF		UF/MF <sup>a)</sup>	Conventional	Dow UF		UF/MF <sup>a)</sup>	Conventional	Dow UF		UF/MF <sup>a)</sup> or Well	Conventional
		<1	<3	<2.5	<3	<5	<2.5	<3	<5	<2.5	<3	<5	
SDI													
Average flux (gfd)	21–25	16–20	16–20	13–17	12–16		11–15	10–14	8–12	9–11	8–10	7–10	
Average flux (l/m <sup>2</sup> h)	36–43	27–34	27–34	22–29	20–27		18–26	17–24	14–20	15–18	13–20	11–17	
Maximum element recovery (%)	30	19	19	17	15		14	13	12	15	14	13	

*Reverse Osmosis Design Basics* by Scott Beardsley, for the Dow Water Academy Water and Process Solutions.

a) Continuous filtration using a membrane with a pore size of < 0.5 µm.

UF, ultra-filtration; MF, membrane filtration.

**Table 14.7** Summary of operational parameters for RO systems.

Parameter	Range	Typical
Pressure (psig)	400–1000	600
Temperature (°F)	60–100	70
Packing density (ft <sup>2</sup> /ft <sup>3</sup> )	50–500	12–35
Flux (gallons/day/ft <sup>2</sup> )	10–80	
Recovery factor (%)	75–95	80
Rejection factor (%)	85–99.5	95
Membrane life (years)	–	2
pH	3–8	4.5
Turbidity	–	1 JTU
Feedwater velocity (ft/s)	0.04–2.5	–
Power utilization	9–17 kWh/1000 gal	

membrane hydrolysis. Approximately 1.0–1.5% of the process water goes to waste as a part of the cleaning operation, with the cleaning cycle being every 24–48 hours.

A summary of operational parameters is given in Table 14.7.

## Notes

- 1 In one very large plant in Gwinnett County, Georgia, a 60 million gallon per day advanced wastewater treatment plant (227 125 m<sup>3</sup> per day), the County and the design engineer arranged a side-by-side comparison of membranes from different manufacturers to select the best equipment. For large installations this approach is a very good idea.
- 2 Water Environment Federation (2005). *Membrane Systems for Wastewater Treatment*, Table 4.2. New York: McGraw Hill.
- 3 Jiang, F., Beck, M.B., Cummungs, R.G., Rowles, K., and Russell, D.L. (2005). *Estimation of Costs of Phosphorous Removal in Wastewater Treatment Facilities: Adaptation of Existing Facilities*. Water Policy Working Paper #2005-011. Available at [http://h2opolicycenter.org/pdf\\_documents/W2005011.pdf](http://h2opolicycenter.org/pdf_documents/W2005011.pdf).
- 4 Jiang, F., Beck, M.B., Cummungs, R.G., Rowles, K., and Russell, D.L. (2004). *Estimation of Costs of Phosphorous Removal in Wastewater Treatment Facilities, DeNovo*. Water Policy Working Paper #2004-10.
- 4 American Waterworks Association Staff. (2016). *Reverse Osmosis and Nanofiltration*, 2 Denver: American Waterworks Association.

- 5 *EPA Capsule Report. Reverse Osmosis Process.* Cincinnati: Center for Environmental Research Association, 1996.
- 6 Texas Water Quality Development Board (2014). Final Report No. 1448321310, "Developing Practical Alternatives to Pilot Plant Studies for Innovative Water Technologies," Part I: Performance Evaluation of Reverse Osmosis Membrane Computer Models.
- 7 Long-term bacterial water quality treatment removal standards require a 4-log reduction in measured pathogens, and that may not be achievable by some membranes; the membrane software does not evaluate pathogen or virus removal.
- 8 Texas Water Quality Development Board (2014). Final Report No. 1448321310, "Developing Practical Alternatives to Pilot Plant Studies for Innovative Water Technologies," Part I: Performance Evaluation of Reverse Osmosis Membrane Computer Models, pp. 21–22.
- 9 Brandt, D., Leitner, G., and Leitner, W. (1994). Reverse osmosis membranes state of the art. In *Reverse Osmosis* (ed. Z. Amjad). Van Nostrand Publishers.

## 15

# Disinfection

## 15.1 Introduction

The purpose of disinfection is the protection of the water quality by eliminating harmful microbial activity. The ideal disinfectant should have high bacterial toxicity, be inexpensive, not be too dangerous to handle, and should have a reliable means of detecting the presence of a residual. An additional requirement for a disinfection agent is that it should not form harmful DBPs or disinfection byproducts.<sup>1</sup>

Chlorine is one of the oldest disinfection agents used, and is one of the safest and most reliable. It has extremely good properties, which conform to many of the aspects of the ideal disinfectant as mentioned above. The principal impediment to chlorine is the formation of chloramines in a reaction with ammonia, and the formation of halo-acetic acids when chlorine reacts with humic materials. Chlorine also reacts with phenols and phenolic compounds to impart an undesirable taste and odor to the water.

Halo acid compounds had really not started to be identified until the early 1960s when the analytical tools were developed to measure low levels of DBPs and chlorinated organic compounds. Since that time, there has been a legitimate concern from public health agencies over the use of chlorine as a primary disinfectant. Chlorine is still widely used as the primary disinfection agent because of its low cost and overall effectiveness.

## 15.2 Rate of Kill – Disinfection Parameters

### 15.2.1 Chick's Law

The idea behind disinfection is to kill or to inactivate harmful bacteria and viruses.

The time-kill rate is a differential equation (Chick's Law):

$$\frac{dN}{dt} = -kN$$

where  $k$  is a rate constant, and  $N$  is the number of living organisms. The expression is specific to the type of organisms being tested.

This gives  $\ln(N_2/N_1) = -kt$  and  $t = (2.3 k^{-1}) \log(N_1/N_2)$ , where the subscripts on  $N$  refer to the number of organisms at the respective times.

The rate of disinfection  $k$  is dependent upon the concentration of the disinfectant and the coefficient of dilution. The rate constant can also be affected by the temperature, as shown in the Arrhenius equation:

$$k = Ce^{-(\Delta H_a/RT_a)}$$

where  $\Delta H_a$  is the activation energy (cal);  $R$  is the gas constant ( $1.99 \text{ cal} \cdot \text{C}^{-1}$ );  $T_a$  is the absolute temperature (K), and  $C$  is a determined constant.

The equation is evaluated by plotting  $\ln k$  versus  $1/T_a$ ; factors such as nutrient concentration, pH, and osmotic pressure all affect the constants and the rate.

The death rate of microorganisms is a first-order differential equation with respect to time.

### Problem

The following table shows the disinfection of poliomyelitis virus using hypobromite as a disinfectant.<sup>2</sup> Determine Chick's constant and the time required to reduce the concentration of viable polio virus to 1/10 000 of the original concentration.

$t(\text{s})$	$N/\text{No}$
4	0.07690
8	0.00633
12	0.00050

### Solution:

Plot  $-\ln(N/\text{No})$  against time (Figure 15.1). Execute linear regression for experimental points. This yields the slope of the line ( $k = 0.634 \text{ s}^{-1}$ ). The time required for a 10 000-fold reduction is

$$t = [-\ln(1/10\,000)/k] = -\ln(1/10\,000)/0.634 \text{ s} = 15 \text{ s}$$

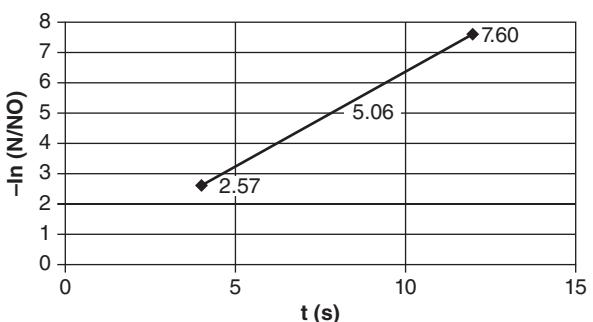
### 15.2.2 Harmful Organisms

The basic organism often used in measuring disinfection efficiency is *Escherichia coli* (*E. coli*) but the USEPA has recently begun to focus on a number of different organisms that are more resistant than *E. coli*.

We cannot get into a discussion of disinfection without some consideration of human health factors.

For a number of years, the basic problem was *E. coli* and the principal concern was and largely still is fecal contamination of drinking water, bathing water,

**Figure 15.1** Sample plot of polio virus survival ratio in disinfection experiment.



and so on. The *E. coli* organism was and still is the most frequent indicator of fecal contamination. However, in the past few years we have discovered that fecal streptococcus (*Streptococcus faecalis* and *Streptococcus faecium*; a subset of the fecal streptococci considered more feces-specific) is a better indicator of human fecal contamination.

Improperly disinfected drinking water, arising from fecal contamination, is responsible for untold deaths in the developing world. The exposure to fecal contamination can cause vomiting, diarrhea, and general dehydration, which can lead to the death of young children and adults. The threat of death from improper water treatment is so great that it outweighs the longer-term exposure to potential carcinogens arising from DBPs due to chlorination treatment of water supplies.

*Giardia lamblia* is a protozoan found in the feces of humans and animals that can cause severe gastrointestinal ailments. It is a common contaminant of surface waters. For a number of years, it went unnoticed because the principal focus was on coliform organisms. In 1981, the World Health Organization classified *Giardia* as a pathogen (capable of causing disease).

Physically, *Giardia* is a cyst-former and can survive outside the body for long periods of time. If viable cysts are ingested, *Giardia* can cause the illness known as giardiasis, an intestinal illness that can cause nausea, fever, severe diarrhea, and extreme weight loss. The symptoms usually last for several days only and the body can naturally rid itself of the parasite in one to two months. However, for individuals with weakened immune systems the body often cannot rid itself of the parasite without medical treatment.<sup>3</sup>

In the United States, *Giardia* is the most commonly identified pathogen in waterborne disease outbreaks – but that may be because of the attention given to *E. coli*.

*Giardia* is not host-specific, in contrast to some forms of coliform organisms. *Giardia* can jump species, and the viable cysts excreted by animals can infect and cause illness in humans if it enters their drinking water. There are two ways in which *Giardia* can infect humans. Both involve inadequately treated (inadequately disinfected) drinking water. One way is through animal feces in the

watershed entering the drinking water, and the second way is through human sewage entering the drinking water. In both the cases, the control mechanism is adequate disinfection.

The effective control of *Giardia* is accomplished by chlorine and ozone, combined with filtration. Filtration may be sufficient by itself, but that assumes that the filtration will be sufficient to remove all the *Giardia* cysts. The USEPA has focused on the inactivation of *Giardia* as being one key to safe drinking water.<sup>4</sup>

Another important bacterial drinking water contaminant is *Legionella pneumophila*. It survives and is often found in improperly disinfected cooling water systems. The first contamination caused by *L. pneumophila* was the deaths of several attendees at an American Legion convention in Philadelphia, in 1976.<sup>5</sup>

The Center for Disease Control (CDC) tracks waterborne diseases and provides quality and timely information on the routes of exposures. According to the CDC, the US has one of the safest drinking water systems in the world. The CDC has classified and listed the incidence of outbreaks of waterborne diseases in the US.<sup>6</sup> Because it takes time to determine the causes of disease outbreaks, the CDC is frequently several years behind in summarizing the incidences of waterborne disease outbreaks. The CDC does list the following diseases as the most prevalent waterborne diseases: *Giardia*, *Legionella*, *Norovirus*, *Shigella*, *Campylobacter*, *Salmonella*, hepatitis A, *Cryptosporidium*, and *E. coli*.<sup>7</sup>

Some organisms are harder to inactivate than others. This is especially true of the spore-formers and the protozoans. An example of the relative resistance of various organisms is shown in Table 15.1.

The effectiveness of the inactivation power of several disinfectants depends upon the organism and the type of disinfectant. The organisms commonly found in water include vegetative bacteria, viruses, protozoan cysts, spores, and eggs. The disinfectants ranked from best to worst would be: O<sub>3</sub>; ClO<sub>2</sub>; iodine; free chlorine; chloramines.

**Table 15.1** Comparison of bacterial disinfection rates – the relative ease of disinfection depends on heat.

Organism	Relative resistance
<i>E. coli</i>	1
Bacterial spores	3 000 000
Mold spores	2–10
Viruses and bacteriophages	1–5

Source: Rahn, O. (1945). Physical methods of sterilization of micro-organisms. *Bacteriological Reviews* 9, pp. 1–7.

The effectiveness of the disinfectant varies with the type of microbe and chemical and environmental factors. There are many large municipal water supplies that use a combination of disinfectants for both bacteriological control and taste and odor control. Often selected chemicals include ozone and chlorine dioxide, to disinfect the water and oxidize many of the organics and tannins, followed by enough chlorine to provide a detectable residual and insure distribution system water quality.

Some of the common challenges to any disinfection system include the following:

*Microbial aggregation.* Protects interior microbes from inactivation.

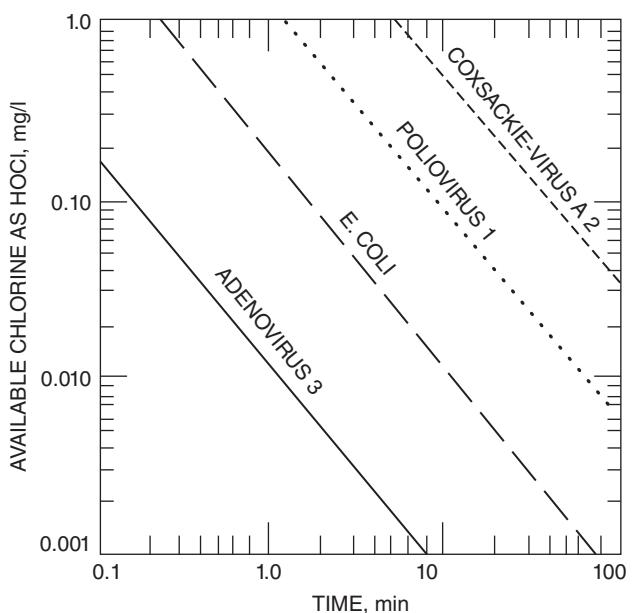
*Water quality: particulates.* Protect microbes from inactivation.

*Dissolved organics.* Protects; consumes disinfectant; coats microbes.

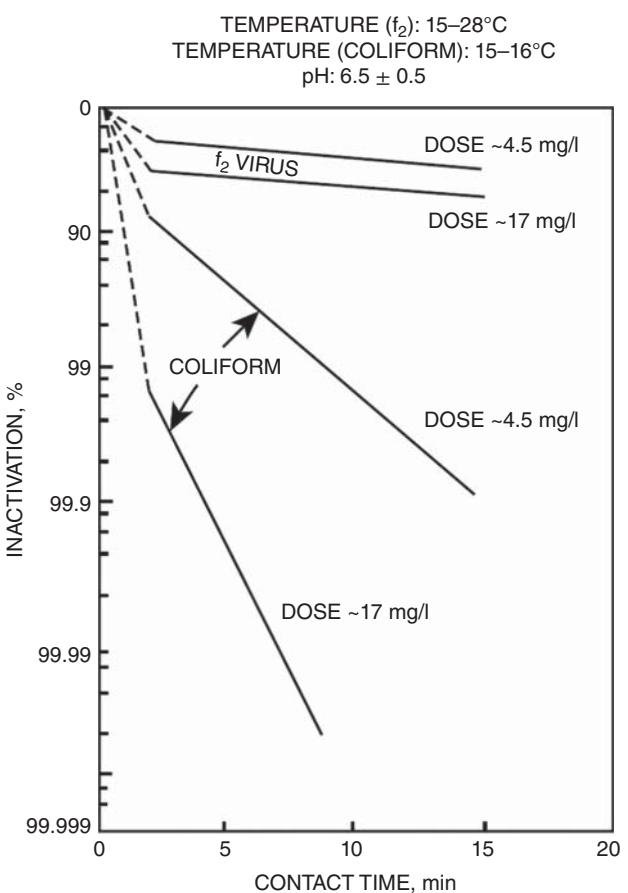
*Inorganic compounds and ions.* Effects vary with disinfectant pH, and effects depend on disinfectant. Free chlorine is more biocidal at low pH where HOCl predominates, but low pH can corrode pipes and equipment.

Chlorine dioxide is more microbiocidal at high pH. Free chlorine is still the most commonly used disinfectant.

See Figures 15.2 and 15.3 on virus and bacterial inactivation.



**Figure 15.2** Time vs. concentration for 99% kill of *E. coli* and three viruses by hypochlorous acid at 0–6°C. Source: Water Environment Federation (WEF) (2017). *Design of Water Resource Recovery Facilities, Manual of Practice 8*. Alexandria, VA: WEF.

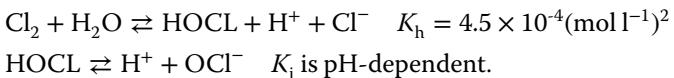


Viral and bacterial inactivation at a 5700 m<sup>3</sup>/day (1.5 mgd) conventional activated sludge plant conditions. The  $f_2$  bacterial virus was seeded in the secondary settling basin at a titer of approximately  $10^6$  plaque forming units/ml. Chlorine dosages were approximately 4.5 and 17 mg/l.

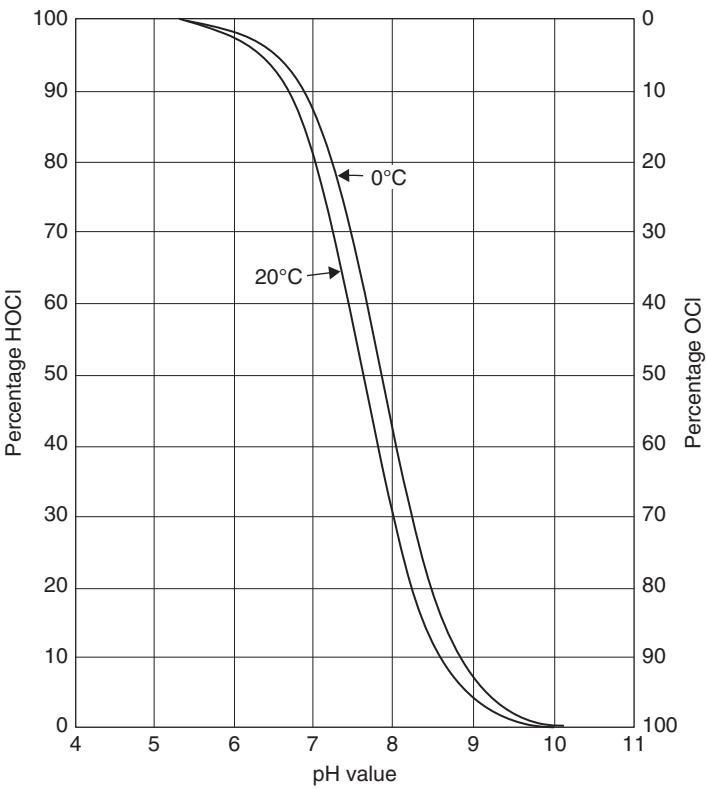
**Figure 15.3**  $f_2$  virus and coliform inactivation in a chlorine contact tank under controlled conditions. Viruses are often more difficult to kill than are coliform and non-spore-forming organisms. Source: Water Environment Federation (WEF) (2017). *Design of Water Resource Recovery Facilities, Manual of Practice 8*. Alexandria, VA: WEF.

## 15.3 Chlorine

Silver and heat are probably the oldest disinfectants, but chlorine has got the most acceptance. Chlorine dissociates in water. The reactions are as follows (see Figure 15.4):



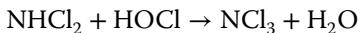
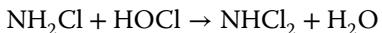
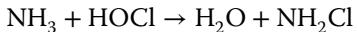
The most cost-effective form of disinfectant is the HOCl form. By applying the pH and speciating the OCl and HOCl forms, it is possible to calculate the required dose of chlorine for a specific kill based upon pH (Figure 15.3).



**Figure 15.4** Distributions of hypochlorous ( $\text{HOCl}^-$ ) and hypochlorite ( $\text{OCl}^-$ ) ions in water at various pH levels.

### 15.3.1 Ammonia, Chlorine, and Chloramines

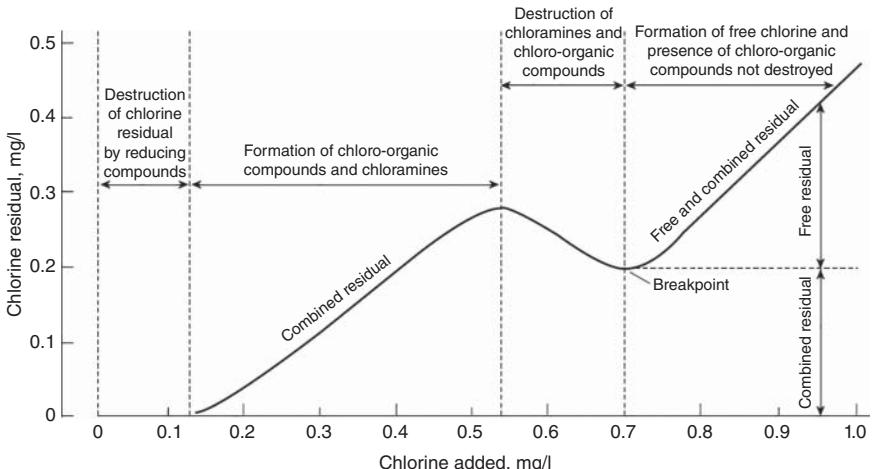
Free ammonia combines with the HOCl form of chlorine to form chloramines in a three-step reaction:



When the pH > 6 and  $[\text{HOCl}]/[\text{NH}_3]$  is around 1, monochloramine predominates. The reason for the detailed explanation is that chloramines are also a form of disinfectant – not as effective as HOCl, but as a disinfectant nonetheless.

When the molar ratio of chlorine to ammonia is substantially above 2, dechlorination of the hypochlorite/hypochlorous ions occurs because of the formation of chloramines. The concentration of residual chlorine first rises, then falls, then rises again, as shown in Figure 15.5.

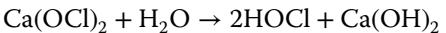
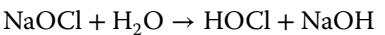
Chloramines have some disinfecting power, but their ability to inactivate viruses and especially spore-formers such as *Giardia* is quite limited. Chloramines have been in use as disinfectants since the early 1900s, but the use is limited because of the expense of generation and relatively poor effectiveness against several common types of pathogens.



**Figure 15.5** Break point chlorination by the formation of chloramines. The free chlorine residual levels first rise, then fall until the reaction with ammonia have been completed. As additional chlorine is applied and ammonia is consumed, the chlorine residual again rises.

### 15.3.2 Other Types of Chlorine

Chlorine comes in a variety of forms. The most common are calcium hypochlorite (tablet and powder) and sodium hypochlorite (liquid). Both compounds are basic. The disassociation reactions are as follows:



Sodium hypochlorite (concentrated liquid bleach) and calcium hypochlorite tablet and powder (dry bleach and disinfecting tablets and powders) can react violently with organics and fuels, and are corrosive to clothing.

When reacted with acids, violent explosions have been known to occur. The resulting gas is chlorine gas and hydrogen. Because it is a powerful oxidizer, it must be properly stored away from any potential fuels or reactive metals, including aluminum. There have been situations when people have been killed from the explosion resulting from the accidental mixing of drain cleaner (usually a sodium salt of sulfuric acid ( $\text{NaH}(\text{SO}_4)$ ) or the acid itself ( $\text{H}_2\text{SO}_4$ )) and powdered bleach ( $\text{Ca(OCl)}_2$ ) in trying to clean out a toilet bowl. There are an equally large number of cases of reported fires when a homeowner attempts to store oily rags in a container of calcium hypochlorite disinfecting powder, which has not been properly cleaned out and still contains powder residues.

### 15.3.3 Other Reactions with Chlorine

Chlorine in water will oxidize iron, manganese, chromium, arsenic, and a variety of other elements. In the case of the latter two elements the higher valence is the more toxic. It is extremely effective in oxidizing these compounds, especially at pH less than 7. It will also react with natural organic compounds such as tannins from leaves and will form trihalomethanes, chloroform, and other probable human carcinogens.<sup>8</sup> However, the use of the word “probable” is subject to interpretation. Various lobby groups are against the use of chlorine for a variety of reasons, and while some of the halomethanes are actual carcinogens, there is scant evidence that chlorinated drinking water will cause cancer from halomethanes, especially when the risk of not using chlorine is considered.

Chlorine forms chlorate ions that are also “suspect” compounds. The EPA is currently regulating DBPs in municipal water supplies.

### 15.3.4 Chlorine Safety

Chlorine gas is corrosive, oxidizing, toxic, and denser than air and should be handled accordingly, with extreme caution. It can react violently with a number of compounds.

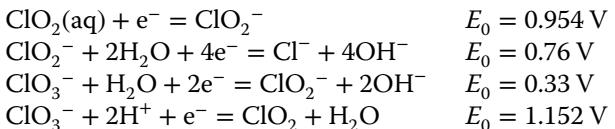
The EPA has designated chlorine as a toxic gas under Section 313 of SARA and Section 112r of the Clean Air Act. As such, anyone handling quantities in excess of 200 lb may have to fulfill special notification requirements under Section 313, and if the total quantity stored is in excess of 2500 lb, special evacuation and community notification plans will be mandatory under US law. It is important to note that in the United States a one-ton cylinder of chlorine may create a “theoretical” evacuation distance around the source of almost 2 miles.<sup>9</sup> Since the RMP Rule was published, many municipalities have converted to liquid forms of chlorine.

### 15.3.5 Chlorine Dioxide

Chlorine dioxide ( $\text{ClO}_2$ ) is a neutral compound of chlorine in the +IV oxidation state. It disinfects by oxidation; however, it does not chlorinate. It is a relatively small, volatile, and highly energetic molecule, and a free radical even while in dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, it is stable in dilute solution in a closed container in the absence of light.

Chlorine dioxide functions as a highly selective oxidant owing to its unique, one-electron transfer mechanism where it is reduced to chlorite ( $\text{ClO}_2^-$ ).

The  $pK_a$  for the chlorite ion, chlorous acid equilibrium, is extremely low at pH 1.8. This is remarkably different from the hypochlorous acid/hypochlorite base ion pair equilibrium found near-neutrality, and indicates that the chlorite ion will exist as the dominant species in drinking water. The oxidation–reduction of some key reactions are as follows:



Chlorine dioxide is always generated on-site because it is explosive when compressed. It also reacts violently with sunlight and/or UV light with explosive decomposition. It is generated from sodium chlorite and sodium chlorate.

Chlorine dioxide is less pH-sensitive than chlorine and may be equally as effective as a disinfectant. However, it costs substantially more than chlorine. Because of the air hazards associated with chlorine, and the problems associated with the treatment of various byproducts of disinfection and concerns about the formation of dioxins from chlorination, chlorine dioxide<sup>10</sup> has seen a resurgence in the paper industry in the pulp bleaching area. However, it is still not as economical as chlorine.

## 15.4 Ozone

Ozone exists as a gas at room temperature. The gas is colorless with a pungent odor readily detectable at concentrations as low as 0.02–1.5 ppm (by volume), which is below concentrations of health concern. Ozone gas is highly corrosive and toxic.

Ozone is a powerful oxidant, second only to the hydroxyl free radical, among chemicals typically used in water treatment. Therefore, it is capable of oxidizing many organic and inorganic compounds in water. These reactions with organic and inorganic compounds cause an ozone demand in the water treated, which should be satisfied during water ozonation prior to developing a measurable residual.

Ozone is slightly soluble in water. At 20°C, the solubility of 100% ozone is only 570 mg l<sup>-1</sup>, compared with about 11.3 mg l<sup>-1</sup> for oxygen. Typical concentrations of ozone found during drinking water treatment range from <0.1 to 1 mg l<sup>-1</sup>, although higher concentrations can be attained under optimum conditions.

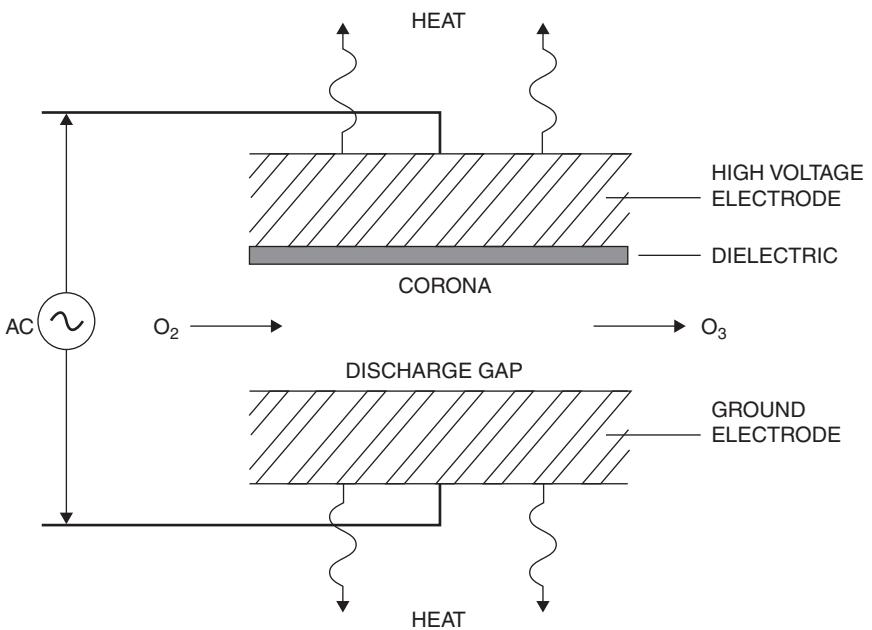
Ozone decomposes spontaneously during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals. The hydroxyl free radicals are among the most reactive oxidizing agents in water, with reaction rates of the order of 10<sup>10</sup>–10<sup>13</sup> M s<sup>-1</sup>. The half-life of hydroxyl free radicals is of the order of microseconds; therefore, concentrations of hydroxyl free radicals can never reach levels above 10<sup>-12</sup> M.

- In the presence of many compounds commonly encountered in water treatment, ozone decomposition forms hydroxyl free radicals. The oxidation of many types of naturally occurring organic matter leads to the formation of aldehydes, organic acids, and aldo- and ketoacids.
- Ozone can mineralize some organic materials if the pathway is predominantly one of hydroxyl radical oxidation.
- Oxidation of bromide ions leads to the formation of hypobromous acid, hypobromite ions, bromate ions, brominated organics, and bromamines.
- Bicarbonate or carbonate ions, commonly measured as alkalinity, will scavenge the hydroxyl radicals and form carbonate radicals.

Because ozone is an unstable molecule, it should be generated at the point of application for use in water treatment. It is generally formed by recombination of oxygen molecules (O<sub>2</sub>):



This reaction is endothermic and requires a considerable input of energy. Ozone was first discovered by the electrolysis of sulfuric acid. Ozone can be



**Figure 15.6** Schematic drawing of corona discharge method for making ozone.

produced by several ways, although one method, corona discharge, predominates in the ozone generation industry. Ozone can also be produced by irradiating an oxygen-containing gas with ultraviolet light and electrolytic reaction.

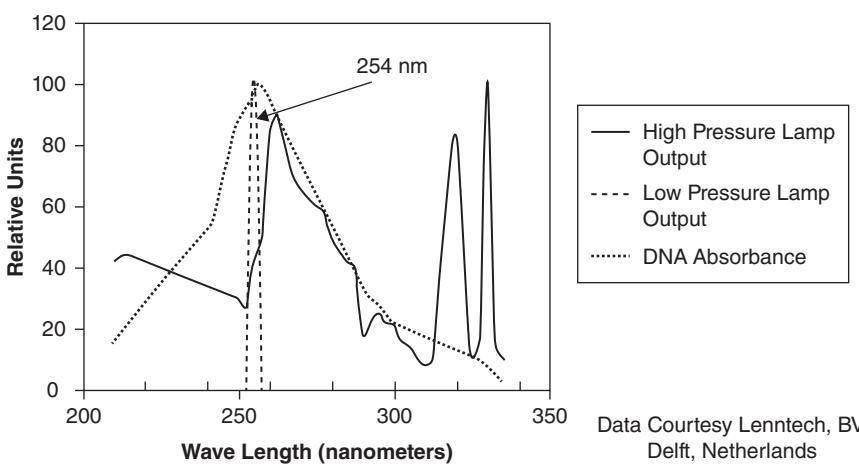
Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and a discharge gap. Voltage is applied to the electrodes, causing an electron flow across the discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone. Figure 15.6 shows a basic ozone generator.

## 15.5 Ultraviolet Light

Ultraviolet or UV light is a bacterial disinfectant. It carries no residual. It requires clear, nonturbid, and noncolored water for its use. Most commercial disinfection systems operate low- to medium-powered UV lamps, and the technology currently in use focuses on a wavelength of about 254 nm (Figures 15.7 and 15.8).

The UV dosage is calculated as

$$D = I \times t$$



Data Courtesy Lenntech, BV.  
Delft, Netherlands

**Figure 15.7** UV spectra for various types of lamps. A low pressure lamp has the spectra almost precisely at the 257 nm range where UV disinfection is most effective.



**Figure 15.8** UV lamp disinfection unit with horizontal configuration. Vertical configurations are also used. In both cases, the flow path is along the length of the lamp because it gives the greatest time in contact.

where  $D$  is the UV dose ( $\text{mW}\cdot\text{s cm}^{-2}$ );  $I$  is the intensity ( $\text{mW cm}^{-2}$ ); and  $t$  is the exposure time (s).

Research indicates that when microorganisms are exposed to UV radiation, a constant fraction of the living population is inactivated during each progressive increment in time. This dose–response relationship for germicidal effect indicates that high-intensity UV energy over a short period of time would provide the same kill as a lower-intensity UV energy for a proportionally longer period of time.

The UV dose required for effective inactivation is determined by site-specific data relating to the water quality required. On the basis of first-order kinetics, the survival of microorganisms can be calculated as a function of dose and contact time.

The advantage of UV is that, for waters with high transmittance, it is directly effective against the DNA of many organisms, is not reactive with other forms of carbonaceous demand, and can give good bactericidal kill values while not leaving any residue, chlorites, or trihalomethanes.

The advantage is often the disadvantage, because power fluctuations, variations in hydraulic flow rates, and color or turbidity can cause the treatment to be ineffective. Also recently some discussion of cell recovery and repair from UV exposure, with a consequent rapid recovery and regrowth of the damaged organisms because of the inactivation of their predators and competitors, has come to light.

### 15.5.1 LED Lighting

Light-emitting diodes (LEDs) can emit UV light. Unfortunately, the emission spectra of gallium/indium LED lights are very narrow (approximately 10 nm), and in the 257 nm range the efficiency of the lighting is very low. That, coupled with the high expense of LEDs, makes their use as disinfecting lighting questionable for large installations at this time. However, small flow commercial units are available on the market, but the disinfection spectra of these units is not at optimum conditions (265 nm range for Ga/I/N lights gives very low efficiency at the 257 range).

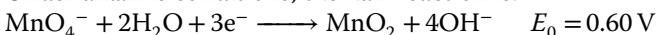
## 15.6 Other Disinfecting Compounds

### 15.6.1 Potassium Permanganate

Potassium permanganate is highly reactive under conditions found in the water industry. It will oxidize a wide variety of inorganic and organic substances. Potassium permanganate ( $\text{Mn}^{7+}$ ) is reduced to manganese dioxide ( $\text{MnO}_2$ ) ( $\text{Mn}^{4+}$ ), which precipitates out of solution. All reactions are exothermic. Under acidic conditions the oxidation half-reactions are:



Under alkaline conditions, the half-reaction is:



Reaction rates for the oxidation of constituents found in natural waters are relatively rapid and depend upon temperature, pH, and dosage.

Potassium permanganate is a good oxidant but not a very good disinfectant. Its primary uses are taste and odor control, and like HOCl it is more effective as a disinfectant under acidic conditions down to a pH of about 5.9. Under alkaline conditions, it is very powerful as an oxidant but less so as a disinfectant.

### 15.6.2 Hydrogen Peroxide and Ozone

Hydrogen peroxide is a liquid with the formulation  $\text{H}_2\text{O}_2$ . There is a bit of a debate over the exact mechanism of disinfection. Hydrogen peroxide is not much of a disinfectant by itself, but in combination with ozone it has powerful disinfection properties. The combination is called peroxone. Until recently there was a big debate on whether or not peroxones even existed. That debate has largely been settled. However, peroxone is very short-lived, and one must combine ozone and hydrogen peroxide to get the proper disinfection reactions.

Hydrogen peroxide or ultraviolet radiation accelerates the decomposition of ozone and increases the hydroxyl radical concentration. By adding hydrogen peroxide, the net production of hydroxyl free radicals is 1.0 mol hydroxyl radical per mole ozone. The two principal methods of disinfection are (1) direct oxidation of compounds by aqueous ozone ( $\text{O}_{3(\text{aq})}$ ) and (2) oxidation of compounds by hydroxyl radicals produced by the decomposition of ozone. Dosage levels for peroxide and ozone are generally of the order of  $5 \text{ mg l}^{-1}$  each, with ratios of peroxide/ozone between 0.5 and 0.8 and detention times greater than 5 minutes but less than 20 minutes.

The two oxidation reactions compete for substrate (i.e., compounds to oxidize). The ratio of direct oxidation with molecular ozone is relatively slow ( $10^{-5}\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) compared with hydroxyl radical oxidation ( $10^{12}\text{--}10^{14} \text{ M}^{-1} \text{ s}^{-1}$ ). The hydroxyl radical reactions are very fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively small.

A key difference between the ozone and peroxone processes is that the ozone process relies heavily on the direct oxidation of aqueous ozone, while peroxone relies primarily on oxidation with the hydroxyl radical, which is a powerful oxidant in its own right. In the peroxone process, the ozone residual is short-lived because the added peroxide greatly accelerates the ozone decomposition. The oxidation by the hydroxyl radical more than compensates for the reduction in direct ozone oxidation because the hydroxyl radical is much more reactive. The net result is that oxidation is more reactive and much faster in the peroxone process compared with the ozone molecular process. However, because

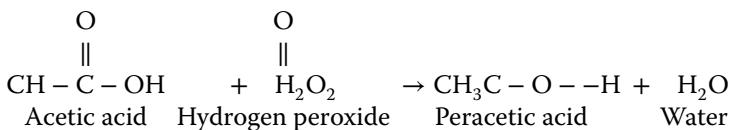
an ozone residual is required for determining disinfection contact-time credit, peroxone may not be appropriate as a pre-disinfectant. Because the ozone peroxide radical oxidation is much more vigorous and effective than with ozone oxidation alone, it is being used to treat organics, which are difficult to oxidize, such as taste and odor compounds and chlorinated organics (PERC and TCE) and reactive materials including explosives in the groundwater.

Neither ozone nor peroxone significantly destroys total organic carbon (TOC). Peroxone will oxidize the saturated hydrocarbons and produce byproducts such as aldehydes, ketones, peroxides, bromate ion, and biodegradable organics. However, because the peroxone is a “more powerful and rigorous oxidant,” the organic material is subsequently rendered more amenable to hydrolysis and subsequent oxidation by bacterial compounds and can be biodegraded. pH and bicarbonate alkalinity play a major role in peroxone effectiveness because the carbonate/bicarbonate system competes for hydroxyl radicals at high alkalinity and at high pH levels. The presence of fine particulate solids causing turbidity does not affect the effectiveness of peroxone treatment, and the presence of peroxones will not necessarily reduce turbidity.

Table 15.2 summarizes the key differences between ozone and peroxone as they relate to their application in drinking water treatment.<sup>11</sup> The comparisons are similar for wastewater treatment.

### 15.6.3 PAA: Peracetic Acid

Peracetic acid (PAA) is acetone mixed with hydrogen peroxide in solutions to produce 5–15% peracetic acid. The acid has a sharp vinegar-like odor and will cause burns to exposed skin. As a disinfectant it is quite powerful, but generally less effective than ozone or chlorine dioxide, but safer to handle than either. Commercial solutions are widely used for disinfecting hospital implements and surfaces, in the food industry for equipment disinfection. It has the advantage of not creating any DBPs, but adds a little bit to the COD of the wastewater after it is reacted. The equation for PAA creation is:



The reason for its popularity as a disinfectant is that it has a high oxidation capacity as measured by electron voltage.

Ozone: 2.07 EV

Peracetic acid 1.81 EV

Chlorine dioxide: 1.57 EV

Sodium hypochlorite 1.36 EV.

**Table 15.2** Comparison between ozone and peroxone oxidation.

Process	Ozone	Peroxone
Ozone decomposition rate	Normal decomposition producing hydroxyl radical as an intermediate product	Accelerated ozone decomposition increases the hydroxyl radical concentration above that of ozone alone
Ozone residual	5–10 minutes	Very short-lived due to rapid reaction.
Oxidation path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation
Ability to oxidize iron and manganese	Excellent	Less effective
Ability to oxidize taste and odor compounds	Variable	Good, hydroxyl radical more reactive than ozone
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical more reactive than ozone
Disinfection ability	Excellent	Good, but systems can only receive CT credit if they have a measurable ozone residual
Ability to detect residual for disinfection monitoring	Good	Poor. Cannot calculate CT value for disinfection credit.

USEPA Guidance Manual on Alternative Disinfectants and Oxidants, 1999, Chapter 7:

[https://www.discountpdhunlimited.com/pdhcourse/pdf/disinfecting\\_the\\_water\\_using\\_peroxone.pdf](https://www.discountpdhunlimited.com/pdhcourse/pdf/disinfecting_the_water_using_peroxone.pdf).

The method of attack is that PAA oxidizes the outer cell wall of bacterial organisms, effectively killing them. PAA is becoming more accepted as a wastewater disinfection mechanism because it is so powerful, and doses are low, enabling it to compete with chlorine and other disinfectants. From various literature sources, it appears that application rates for disinfection of wastewater is  $1.0 \text{ mg l}^{-1}$  or less, but above a floor of about  $0.4 \text{ mg l}^{-1}$ . The USEPA performed a side-by-side comparison of disinfectants to test their effectiveness on porous surfaces such as concrete. The comparison is shown below. The PAA concentration was  $25 \text{ mg l}^{-1}$  as applied, and in all cases, the disinfectant was washed off with a  $1 \text{ ft s}^{-1}$  ( $0.3 \text{ m s}^{-1}$ ) water hose at the end of the test cycle.<sup>12</sup>

The results of the test showed that free chlorine at pH 7 reduced the spores to undetectable levels after 6 hours with a  $25 \text{ mg l}^{-1}$  dose. Chlorine dioxide reduced the spore count to undetectable levels at a  $5 \text{ mg l}^{-1}$  dose after 2 hours.

Monochloramine reduced the spore count to zero after 18 hours; ozone at  $2\text{ mg l}^{-1}$  dose reduced the spore count to non-detectable after 1 hour, and PAA at a  $25\text{ mg l}^{-1}$  dose reduced the spore count by between 1 and  $1.2 \log_{10}$  factor after 22 hours. On corroded iron a  $25\text{ mg l}^{-1}$  dose of chlorine dioxide was the only disinfectant that totally reduced the spore count to zero after six hours. Under the test conditions PAA and another compound tested (acidified nitrate) were ineffective in reducing spores to undetectable levels.

#### 15.6.4 Bromine

Bromine has been used as a disinfectant in a number of applications. It has good toxicity, is a liquid at room temperatures (while chlorine is a gas at room temperature), and is somewhat easier to handle than chlorine.

The chemistry of bromine is similar in many respects to the chemistry of chlorine; however, bromine cannot be used for shock treating (high-dose disinfection) in the same manner as chlorine is used.

Bromine has a pH of 4.0–4.5. When bromine is added to water and an oxidizer is present, the bromine forms hypobromous acid ( $\text{HOBr}$ ) and hypobromite ions ( $\text{OBr}^-$ ). Like chlorine, the percentage of each is affected by pH. However, the effect is not as strong as it is with chlorine. Like chlorine, bromine combines with organic impurities to form combined bromine or bromamines. However, combined bromine is still an effective sanitizer, and it does not smell as strongly as chlorine. Bromine is substantially more expensive than chlorine. Consequently, it has fallen out of use as a commercial disinfectant except in swimming pools where it is still used, because it reportedly has less eye irritation than chlorine, but it has seen a resurgence in popularity because of the perceived hazards associated with chlorine gas. Bromine's disinfectant power is also dependent upon pH, as shown in Table 15.3.

**Table 15.3** Ion species of bromine with pH (compare with Figure 15.4 for chlorine).

HOBr Hypobromous acid % bromine as HOBr	pH	$\text{OBr}^-$ Hypobromite ion % bromine as $\text{OBr}^-$
100.0	6.0	0.0
99.4	6.5	0.6
98.0	7.0	2.0
94.0	7.5	6.0
83.0	8.0	17.0
57.0	8.5	43.0

### 15.6.5 Iodine

Iodine kills bacteria and disease-causing organisms. Iodine is, however, ineffective as an algicide. Iodine has been in use to disinfect water since the early 1900s. In its natural state, iodine is a solid black crystal. The simplest method of disinfecting water with iodine is by dissolving iodine in water to form a saturated solution and then injecting the iodine solution into a water system.

Iodine does not kill bacteria on contact; a holding time of at least 20 minutes is needed depending on the iodine concentration. An iodine residual of  $0.5\text{--}1.0\text{ mg l}^{-1}$  should be maintained, and iodine at this level gives the water little or no iodide taste or odor. Iodine can be removed from water with a carbon filter just before drinking.<sup>13</sup>

Iodine dosage is highly temperature-dependent – iodine crystals are more soluble at higher temperatures. Iodine remains effective over a wide range of pH and does not lose effectiveness until the pH of water reaches 10. Iodine residuals in water can easily be measured using a test kit that indicates a color change.

Iodine tablets were developed during World War II to disinfect small amounts of water for emergency or temporary use. A few drops of tincture of iodine or iodine tablets are popular with campers and the military for disinfecting water. Globaline™ is one of the most common compounds commercially available.

#### 15.6.5.1 Types of Iodinators

Iodinators are in-line systems that are sized to treat all the water used in a household. Iodine solutions are injected into a water system using bypass saturator systems or injection pumps. A holding tank or coil of pipe is used after iodine injection to provide the necessary holding time. There is substantial interest and application of iodinators in southeast Asia, particularly Malaysia (see Figure 15.9).<sup>14</sup>

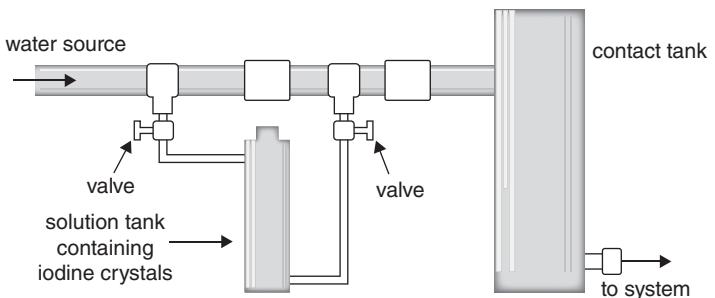
The most common type of iodinator is called a bypass saturator and consists of a solution tank containing iodine crystals. Bypass saturators do not require any electrical connections. The solution tank is connected to the water system and diverts a small amount of water through it and back into the water line. Valves are placed on either side of the iodinator to control the iodine dose. Fluctuation in water temperature affects the solubility of iodine. Adjustments in the bypass rate are needed if water temperature changes.

Chemical injection pumps can also be used to inject iodine solutions for individual water treatment. These are the same injection systems that are used for chlorine.

#### 15.6.5.2 Careful Use of Iodine

The question of possible health effects of iodine is still unanswered. No adverse health effects have been shown, yet continuous consumption of iodine-treated

### A TYPICAL IODINE TREATMENT SYSTEM



**Figure 15.9** Schematic drawing of a bypass iodinator – United States patent 4 555 347.

water is not recommended. Carbon filters can be used to remove excess iodine in the drinking water.

Iodine is also appropriate for occasional use in vacation homes, campgrounds, and restaurants. Iodine treatment of drinking water supplies to dairy cattle is also a concern, because dairy cattle can drink from 15 to 30 gal of water a day, and normal levels of iodine used for disinfection may cause iodine carryover into milk.

## 15.7 Disinfection by Ultra Filtration

In recent years, the development of membrane cartridges with very small pore sizes has proven to be a popular disinfectant item with outdoors men and women. The concept is simple: filtration through a porous medium with pore sizes of  $0.1\text{ }\mu\text{m}$  or less will catch viruses and bacteria. However, there is a slight catch. This filtered water does not contain any residual compound to prevent re-infection, should it occur. Another catch is that the filtration systems require some pre-filtration if they are to have a substantial life. Recommendations from manufacturers indicate that a  $5\text{ }\mu\text{m}$  pre-filter will remove many substances which will rapidly blind the finer filter. Once the filters are clogged they can be backwashed to remove the contaminants. Some commercial units are available, principally in Europe.<sup>15</sup> The cost is relatively modest, with a 25 gal per minute system costing around US\$ 40 000.00, according to the Fertinnova website. Another good reference on the performance of membranes for disinfection is the USEPA publication on *Low Pressure Membrane Filtration for Pathogen Removal*.<sup>16</sup>

## Notes

- 1 DBPs are generally formed by the reaction of chlorine and bromine with naturally occurring organic substances, such as tannic acid, which is a byproduct of the decay of leaves and bark, especially in the fall. These DBPs are carcinogenic and, while present in very low concentrations, are believed to have a cumulative effect, possibly leading to cancers.
- 2 <http://www.nbif.org/course/env-engr/index.html>.
- 3 <http://www.ladwp.com/bizserv/water/quality/topics/giardia/giardia.htm>.
- 4 <http://www.fc.net/rvtdeagan/water/one.html#GIARDIASIS>.
- 5 <http://emedicine.medscape.com/article/965492-overview>.
- 6 <https://www.cdc.gov/healthywater/surveillance/drinking-surveillance-reports.html>.
- 7 [https://www.cdc.gov/healthywater/drinking/public/water\\_diseases.html](https://www.cdc.gov/healthywater/drinking/public/water_diseases.html). It is observed that copper is not a waterborne disease but a naturally occurring metal most commonly found in plumbing. The recommended maximum drinking water concentration for copper is  $1.3 \text{ mg l}^{-1}$ , and the application of any disinfectant to a water supply containing copper will not be effective.
- 8 EPA/600/R-02/068 September 2002 *The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study*.
- 9 See ALOHA (program) by the USEPA, and Risk Management Plan (RMP) program by EPA. <https://www.epa.gov/rmp/risk-management-plan-rmp-rule-overview>. At one time, when first published, the probable evacuation distance around a 1 ton (2000 lb) chlorine gas cylinder was set at 5 miles based upon toxicity considerations. After the regulation was issued, the Risk Management Plan requirements were quickly altered when it was discovered that the potentially affected populations were so large as to be unmanageable and hostile to cities, should the RMPs ever be taken seriously by the public. The recommended evacuation distance was quickly reduced to about 2.2 miles, *without any supporting documentation* – indicating that it was a political decision. No further research has been performed on this issue.
- 10 See 40 CFR 68 for requirements.
- 11 See USEPA *Alternative Disinfectants and Oxidants Guidance Manual* EPA 815-R-99-014, April 1999.
- 12 USEPA Technical Brief: *Decontamination of Drinking Water Infrastructure Contaminated with Bacillus Spores on Iron and Cement-mortar Surfaces*, EPA/600/S-15/168, November 2016.
- 13 <https://phc.amedd.army.mil/PHC%20Resource%20Library/Iodine%20Disinfection%20in%20the%20Use%20of%20Individual%20Water%20Purification%20Devices.pdf>

- percent;20Library/Iodine&percent;20Disinfection&percent;20in&percent;20the&percent;20Use&percent;20of&percent;20Individual&percent;20Water&percent;20Purification&percent;20Devices.pdf.
- 14 Supriya Punyani, et al. (2006). "Iodine based water disinfection: A review." *Journal of Scientific & Industrial Research* 65, pp. 116–120.
  - 15 <http://www.fertinnowa.com/technologies/disinfection-water-ultrafiltration> and <https://www.environmental-expert.com/articles/feasibility-assessment-of-surface-water-disinfection-by-ultrafiltration-439879>.
  - 16 *Low Pressure Membrane Filtration for Pathogen Removal: Application, Implementation, and Regulatory Issues*, Office of Water EPA 815-C-01-001, April 2001.

## 16

# Phosphorus and Nitrogen Removal

## 16.1 General

Phosphate in effluents from a wastewater treatment plant is responsible for growths of unicellular blue-green algae and many other types of algae. Phosphate has been determined to be the principal limiting nutrient in controlling algae growths. The most prevalent source of phosphates was detergents, but now, feedlot operations (cattle, swine, and chicken) and other excessive fertilization beyond agronomic uptake rates are also major contributors; the wastewater treatment plants are point sources and tend to be more easily controlled, but the runoff from a field or a farm requires control of the application rate. The detergent industry voluntarily phased out the use of phosphate detergent boosters in laundry products in around 1994.<sup>1</sup>

Feedlot operations are often regulated as point sources, but the agricultural fertilizer applications are considered an area source and are much more difficult to regulate.<sup>2</sup> The presence of natural deposits of phosphates in some rock formations (parts of Tennessee and Florida) can also contribute to the overall phosphate loading for a stream, but the phosphate is generally in the calcium phosphate form and is less bioavailable.

According to a US Geological Survey water quality study report in 2002, the concentration of phosphates in major lakes in the United States is  $0.0464 \text{ mg l}^{-1}$ , the total nitrogen level is  $0.805 \text{ mg l}^{-1}$ , and the ratio of N:P is 22.893. Many rivers in the United States are currently above  $4 \text{ mg l}^{-1}$  phosphate and thus are ripe candidates for eutrophication. Algal blooms generally do not occur at phosphate concentrations of less than  $0.018 \text{ mg l}^{-1}$ .<sup>3</sup> Much of the phosphate in lakes and rivers is in the form of fine particulate material, which is either washed from the soil during rainfall or discharged from various point sources including wastewater treatment plants and feedlots.

Phosphate removed in the wastewater treatment plant is often re-released when the biosolids (sludge) is land-applied for disposal. Because of the adoption of the ban on phosphates in laundry detergents, other chemicals have been substituted.<sup>4</sup> The quantity of phosphate has been reduced, but the

European Chemical Council makes a persuasive case for partially lifting the ban on phosphates because they are better for the environment and biosolids management when all factors are considered.<sup>5</sup> This includes sludge volume and chemicals remaining in the sludge.

The largest current source of phosphate in the environment appears to be from agricultural applications, including concentrated animal feeding operations (CAFOs). The regulatory response to agricultural and feedlot applications of phosphate appears to focus on the control of phosphorus in animal feed to concentrations utilized by the animals, and agronomic application of phosphate in crops, limiting the phosphate application to the amount required by the specific crops.

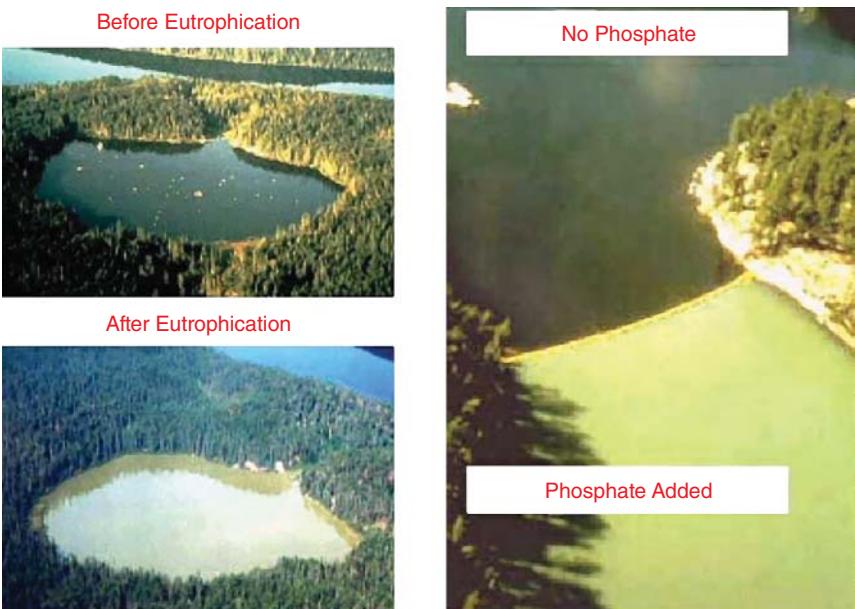
In many communities the water quality limits dictate the maximum daily load of phosphate discharged to the stream either by concentration or by total load. The current trend is to regulate on a watershed basis and develop a TMDL (total maximum daily load) for that watershed, considering all sources within the watershed. In many communities that are now instituting phosphate limits, it is not uncommon to find discharge water quality limits of the order of  $0.2 \text{ mg l}^{-1}$  total phosphate. This is often a difficult goal to attain without advanced treatment.

The principal form of phosphate is polyphosphate, a compound that is incorporated into the adenosine diphosphate (ADP) in cells and as phospholipids in cellular materials. Domestic wastewaters contain between 6 and  $20 \text{ mg l}^{-1}$  total phosphate, of which only 10–15% is organic phosphate. The balance is inorganic phosphate that is generally derived from detergents and other fertilizer sources.

To understand the effects of phosphate contamination, look at the two sets of illustrations given in Figure 16.1. The photographs illustrate the point about phosphate control and algal blooms.

There are two principal methods of removing phosphates: biological and chemical. The chemical method is through precipitation with metallic ions. The biological method is discussed in the following section, followed by the chemical method. The USEPA has issued a nutrient control design manual with a State of Technology Review.<sup>6</sup>

Revisiting the C : N : P ratio discussion from earlier tells us that it takes about 100 units of carbon to remove one unit of phosphorus. The secret to natural phosphorus removal appears to be the same method used in total ammonia and nitrogen control – anoxic treatment. The principal organism for this removal is the ubiquitous bacterium *acinetobacter*. There is uncertainty whether the bacterium is stressed by an anoxic period, or whether the anoxic period allows it to utilize other carbon sources and then store up excess phosphate for future growth. The consensus is that the organisms use acetate and short-chain fatty acids to store polyphosphates as poly-*b*-hydroxybutyrate (an acid polymer). The exact mechanism is tied up with the production and regeneration of ADP



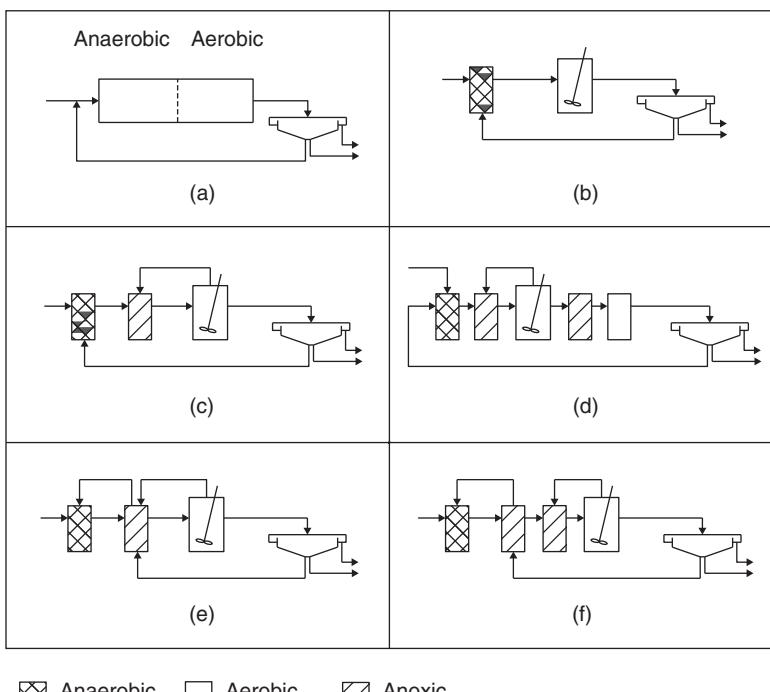
**Figure 16.1** Photographs showing the effects of algal blooms in lakes due to phosphorus levels. The lighter colors indicate algal blooms. Source: [www.nhm.ac.uk/mineralogy/phos/index.htm](http://www.nhm.ac.uk/mineralogy/phos/index.htm), now no longer available.

within the cellular material, and it involves the ADP/adenosine triphosphate (ATP) chain within the bacteria – it is an extremely complex subject, which will add little to this discussion. This uptake phenomenon was also known as “luxuriant uptake of phosphorus” in some of the earlier literature because the bacteria involved actually acquire more phosphorus than they require for growth. This is done principally through extracellular enzymes, and the bacteria store the phosphorus until it is required for growth or respiration.

In a wastewater treatment plant, phosphorus and nitrogen removal do not occur simultaneously. Nitrate appears to interfere with phosphorus uptake, and phosphorus will not be removed until the nitrate is gone. Phosphate removal requires true anaerobic conditions, which occur only when there is no other oxygen donor.

If nitrate reduction and phosphorus uptake are to take place, then an additional source of carbon is required. As was discussed previously, the carbon source can be an added sugar, an alcohol, or the carbon in the entering waste stream. In the anaerobic process, the bacteria first release their extracellular phosphorus and then uptake more than they release.

As shown in Figure 16.2, there are a number of configurations possible for phosphorus uptake streams. There are even several modifications of the



☒ Anaerobic    □ Aerobic    ☐ Anoxic

**Figure 16.2** Principal phosphorus removal systems: (a) modified activated sludge system; (b) “Phoredox” two-stage system; (c) “Phoredox” three-stage system; (d) BardenPho system (modified by “Phoredox”); (e) system developed by University of Cape Town (South Africa); and (f) UCT process modified for biological P and N removal.

BardenPho<sup>®</sup> process that will allow a variety of options and adaptations. Perhaps the simplest one is the first one shown in Figure 16.2, where the aeration at the head of the main tank is turned off and the initial oxygen content decreases through bacterial respiration. When the oxygen concentration approaches zero, the bacterial population will look for other oxygen sources, and will start to use nitrates and phosphates as a source. This may occur at an oxidation reduction potential (ORP) which is negative to about  $-150\text{ mV}$ .

If the oxygen supply was turned off in the entire basin, the system would go fully anaerobic, and the oxidation reduction potential could go as low as  $-350\text{ mV}$ , the nitrogen oxides, phosphorus oxides, and sulfur oxides would be reduced, and the system might begin to develop the “rotten egg” odor from the release of hydrogen sulfide ( $\text{H}_2\text{S}$ ).

There are several variations on this process with some interesting caveats. Recycled sludge from an aerobic tank contains dissolved oxygen generally between  $2\text{ mg l}^{-1}$  and about  $6\text{ mg l}^{-1}$ , although the latter figure represents poor practice because it is wasteful. It will require some time for the bacteria in

the entering waste to consume the oxygen in the return sludge and recycled aeration return. Thus the initial mixing will not be anaerobic for some time. That is highly dependent upon the amount of dissolved oxygen in the recycle lines, as well as the biosolids in those lines, and achieving anaerobic or fermentation conditions may require between 2 and 5 hours. If the wastewater treatment plant is designed with long narrow tanks, it is comparable to plug flow and it will be possible to attain anaerobic conditions if the aeration can be adequately controlled. By comparison, use of circular tanks for aeration will require separate tankage.

Work by Jiang et al. (2005) indicates that there is an optimum detention size for the anaerobic tankage to minimize total plant cost.<sup>7</sup> That size is approximately 3 hours, and is independent of the size of the aeration tankage with regard to the performance of the phosphorus removal of the system.

## 16.2 BardenPho<sup>©</sup> Processes

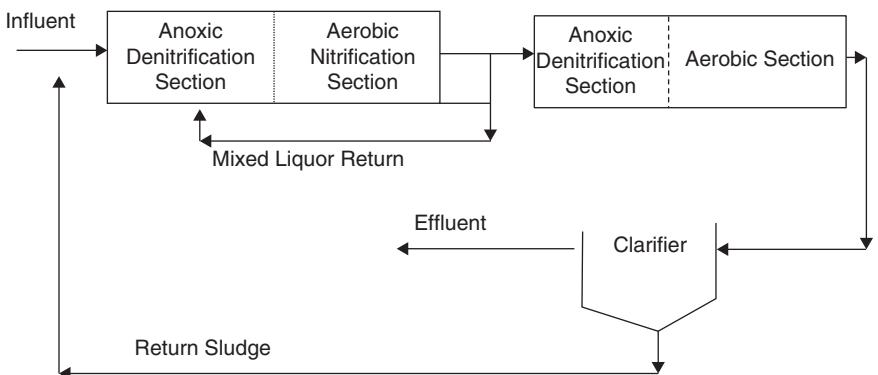
While working on bench-scale nitrogen removal systems in South Africa in the early 1970s, Barnard observed phosphorus removal when the initial zone of the bioreactor was anaerobic (no dissolved oxygen and no nitrate oxygen present). This finding convinced Barnard to work further on the application and develop several biological nitrogen and phosphorus removal systems in South Africa. The largest of these systems are in Pretoria, Cape Town, and Johannesburg. These systems were designed to operate at relatively long hydraulic retention times (18 to 24 hours) and high sludge retention times (SRT or sludge age) (~16 days).

The process was introduced to the United States in the early 1980s, at Palmetto. Cold-weather adaptations of the process were installed at a 23 000 m<sup>3</sup> per day plant in Kelowna, British Columbia. It should be noted that cold-weather application is a significant accomplishment because of the severe effects of cold weather in decreasing the rate of nitrification and denitrification. Since then there has been an incorporation of a number of modifications in the technology to make the process more cost-effective and adaptable to a wide variety of applications and climates.

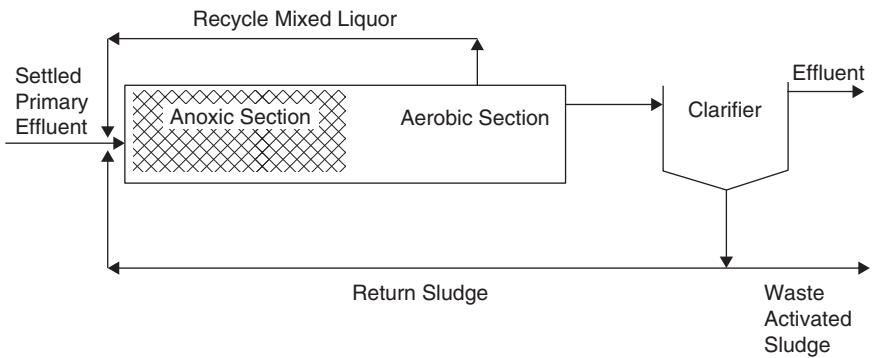
The BardenPho<sup>©</sup> process and other similar processes start with high SRT-extended aeration systems, which generate a highly nitrified effluent. The effluent is then stirred in an anoxic tank followed by an anaerobic stirred tankage. The process removes both nitrogen and phosphorus. The design is somewhat complex, and there are a number of variations of the process.

A schematic of the BardenPho process is shown in Figure 16.3. Note that the influent is from a secondary treatment process.

The modified Ludzak–Ettinger process also relies on a secondary treatment system before it is applied. As an adapted system, the piping is generally



**Figure 16.3** BardenPho process using two tanks. Note that the tanks need to be long and narrow, approaching plug flow.

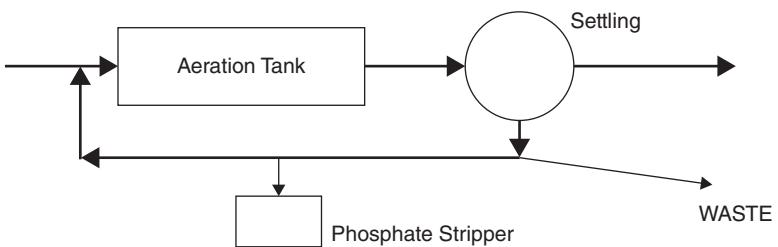


**Figure 16.4** Modified Ludzak-Ettinger process for phosphate removal. Requires long, narrow tanks for maintenance of plug flow, and in the anoxic section the waste activated sludge is returned from the clarifier as well as recycled mixed liquor from the aerobic section. The latter needs to be closely controlled if anaerobic conditions are to be maintained.

re-routed so that the existing clarifier can be used for the final solids removal (Figure 16.4).

Another process for removal of phosphorus is the Phostrip process. The Phostrip system receives the effluent from the activated sludge system. A small portion of the settled sludge from the activated sludge clarifiers is diverted to an anoxic phosphorus strip tank where it will be held for several hours in an anaerobic condition and enhanced with acetic acid to induce the sludge to release its phosphorus.

The low phosphorus sludge is then washed with a portion of the clarifier effluent. The elutriate from the washing process contains 60–80 mg l<sup>-1</sup> of phosphorus, and it is reacted with lime to remove the phosphorus. The



**Figure 16.5** Schematic of the Phostrip process. The sludge is treated chemically to remove phosphorus before it is returned to the aeration tank.

stripper overflow after treatment is very low in phosphorus, and it, along with the phosphorus-poor sludge, is returned to the aeration tank. This process is shown in Figure 16.5.

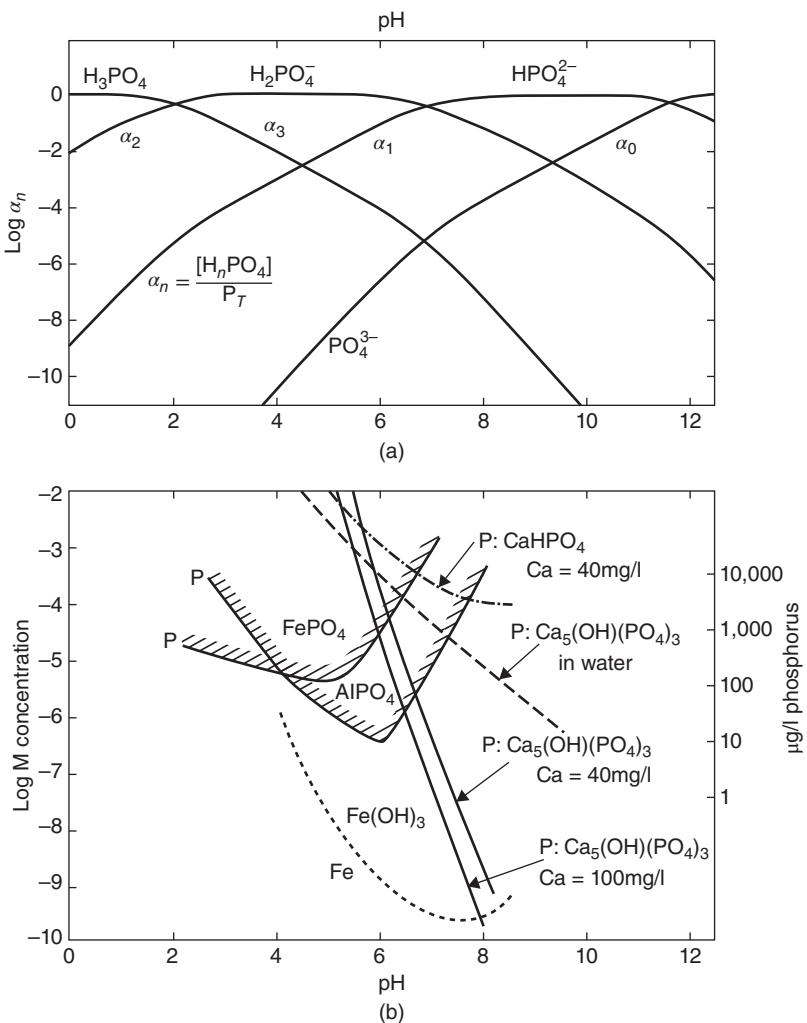
### 16.3 Chemical Phosphorus Removal

Chemical phosphorus removal is precipitation with a divalent cation. The phosphates are insoluble in varying degrees depending upon the cation used. The most common compounds used for phosphorus precipitation include lime, limestone, magnesium, iron salts, aluminum, and alum salts. Of these, alum, ferric chloride, and lime are the most common. Ferric chloride is the most popular because it is the most effective for the price. Alum creates a lighter floc, which settles more slowly, and lime has the disadvantage of raising the pH and possibly interfering with other process applications, generating a higher volume of sludge, and potentially creating pH control problems with the effluent (Figure 16.6).

Common dosages are stoichiometric, and the advantage of chemical additions is that, aside from tankage, pumps, and mixing required for the chemical application (very small capital cost when compared with the initial investment for the treatment plant cost or upgrades for enhancements to the biological processes), the removal of phosphorus can be stepped to achieve almost any desired effluent level.

According to various studies and estimates, domestic sewage contains between 2 and 14 mg l<sup>-1</sup> of total phosphorus, averaging about 6.34 mg l<sup>-1</sup>. Of that, about 3 mg l<sup>-1</sup> is soluble ortho-phosphorus.<sup>8</sup> A normal wastewater treatment plant will remove about 61% of the total phosphorus load and will provide an effluent of about 2–2.5 mg l<sup>-1</sup> under normal circumstances.

The cost of implementing chemical precipitation is approximately half of the cost of implementing phosphorus removal by biological means. However, as the phosphorus limit decreases, the cost differential between various methods decreases because of the need to add additional process equipment



**Figure 16.6** Various phosphate forms and precipitation with metals.

(filtration) to remove fine particulate solids containing phosphorus. It is also not uncommon for a wastewater treatment plant to be adding chemicals (ferric chloride, alum, polymer, or any combination of these) to the value of several hundred dollars per day to the plant effluent for removal of phosphorus.<sup>9</sup>

One of the definitive works on the subject, *Process Design Manual for Phosphorous Removal*, was prepared by Black and Veatch Engineers for the USEPA, in 1971. This publication is still available from the NTIS. The publication is a bit outdated but still contains useful data for design parameters.

**Table 16.1** Precipitation reactions for various phosphate forms (solubility of phosphates and condensed phosphates).

Reactions	$\log_{10}$ equilibrium constant
$\text{Ca}_5\text{OH}(\text{PO}_4)_3 = 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$	-55.6
$\text{Ca}_5\text{OH}(\text{PO}_4)_3 + 3\text{H}_2\text{O} = 2(\text{Ca}_2\text{HPO}_4(\text{OH})_2) + \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-8.5
$\text{Ca}_2\text{HPO}_4(\text{OH})_2 = 2\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{OH}^{2-}$	-27
$\text{CaHPO}_4 = \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-7
$\text{FePO}_4 = \text{Fe}^{3+} + \text{PO}_4^{3-}$	-23
$\text{AlPO}_4 = \text{Al}^{3+} + \text{PO}_4^{3-}$	-21
$\text{Ca}_2\text{P}_2\text{O}_7 = \text{Ca}^{2+} + \text{CaP}_2\text{O}_7^{2-}$	-7.9

The precipitation reactions given in Table 16.1 are important.<sup>10</sup> Most if not all the data were generated in a laboratory in pure water under laboratory conditions. The conditions in a clarifier full of biologically treated wastewater are substantially different from those encountered in the laboratory. The chemical addition for phosphate removal appears to be independent of the location where the precipitants are added. In some cases, it may be just as easy to remove phosphate in the primary clarifier where the increase in sludge volume may not be as significant as it may be in the final clarifier.

The principal concern is the cost of the materials. Waste pickling acid has been used as a source of ferric chloride, as have a number of other products. It is possible to introduce the metal ions directly into the wastewater by using direct current and by generating the ions using sacrificial cathodes.

A recent design by the Trane Company is utilizing sacrificial iron electrodes with very close spacings to introduce ferrous iron into wastewater to react with phosphorus and sulfur compounds, to encourage their precipitation and removal. The removal of phosphorus should also help reduce or eliminate struvite formation in digestion processes.

*A final note:* Handle the chemicals carefully. Each has its own strong and weak points with respect to its use and your treatment options. Consider chemical staining, chemical handling, chemical toxicity, and other things that you would normally look at when you handle chemicals. If lime or hydrated lime is used for precipitation, you may also want to recarbonate the wastewater to add back alkalinity and lower the pH to normal treatment ranges.

A good source for chemical information is [www.siri.org/msds](http://www.siri.org/msds), or one could search for Material Safety Data Sheets (MSDSs). Remember that MSDSs are designed to provide only the basic information and not to answer questions you may have about the chemical properties.

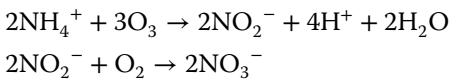
## 16.4 Nitrogen Removal

### 16.4.1 Nitrogen Chemistry and Forms

The principal forms of nitrogen are ammonia, nitrite, and nitrate. Occasionally, one encounters  $\text{N}_2\text{O}$ , but that is infrequent. Organic nitrogen is often found in wastewater, but it is most often found in biosolids and is removed through precipitation or sedimentation.

The first bit of information necessary is an understanding of how the nitrogen cycle works and how the various types of nitrogen are related (see Figure 7.8).

The principal reactions associated with the ammonia to nitrate pathway are the following:

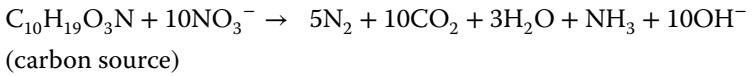


The first reaction takes place with *Nitrosomonas*. The second reaction takes place with *Nitrobacter*. However, the rate of reaction of *Nitrobacter* is about three times the reaction rate of *Nitrosomonas*; nitrite does not accumulate.

The complete reaction for oxidation of ammonia to nitrate requires about  $4.6 \text{ mg l}^{-1}$  of oxygen to oxidize  $1 \text{ mg l}^{-1}$  of ammonia completely.

Denitrification is accomplished by a number of bacteria: *Pseudomonas*, *Micrococcus*, *Achromobacter*, and *Bacillus*.

The principal reactions for denitrification are as follows:



and



where methanol is the principal carbon source for the reaction, but not necessarily the only carbon source to make the reaction proceed. We will come back to this later.

### 16.4.2 Ammonia

The chemistry of ammonia is relatively simple and straightforward, especially in aquatic systems. Ammonia exists in two forms, the ammonium ion ( $\text{NH}_4^+$ ) and un-ionized ammonia ( $\text{NH}_3$ ). Organic nitrogen may contain ammonia as well, but it is generally tied up in the organic molecule and not available as a radical.

Un-ionized ammonia is highly toxic to some forms of aquatic life, while the ammonium ion is significantly less toxic. The distribution of ammonia between those two forms in water is controlled by pH, temperature, and ionic strength. In freshwater sediments at pH 8.0 and 27°C, about 3% of the total ammonia is present in the un-ionized form, while in saline water of the same temperature and pH, about 4% of the total ammonia is in un-ionized form.

The USEPA's chronic water quality criterion for un-ionized ammonia in marine waters is  $0.035\text{ mg l}^{-1}\text{ NH}_3$ , based on the sensitivity of various types of shrimp and fish. The comparable saltwater final acute value for ammonia is  $0.465\text{ mg l}^{-1}\text{ NH}_3$ . For freshwater, the USEPA has established an un-ionized ammonia four-day average chronic standard of about  $0.02\text{ mg l}^{-1}\text{ NH}_3$ . When the pH decreases and the temperature decreases, the standard value falls to approximately  $0.01\text{ mg l}^{-1}\text{ NH}_3$ . Acute:chronic toxicity ratios range from 3–43  $\text{mg l}^{-1}\text{ NH}_3$ .

96-hour LC<sub>50</sub> values were reported as low as  $0.08\text{ mg l}^{-1}\text{ NH}_3$ .<sup>11</sup>

The results vary widely depending upon the species used to run the test, and salmonids are among the most sensitive to ammonia. In short, ammonia, especially un-ionized ammonia (anything over pH about 8.3), is toxic to many forms of aquatic life.

Ammonia complexes with other metals can also increase toxicity, especially some of the heavier metals such as nickel and cadmium. Many biological treatment plants, except those that operate with an extremely long sludge retention time, such as extended aeration, cannot successfully meet the ammonia standard in the effluent, and ammonia toxicity has become a problem in a number of municipal and industrial wastewater treatment plants.

#### 16.4.3 Nitrate

The prime concern with nitrate is water quality, and specifically drinking water quality. Many bacteria and algae have the ability to fix nitrogen from the air. Depending upon the overall ability of a stream or watershed to treat various types of pollution and the categorical usage of the stream (recreation, sport fishing, swimming, and so on), one may find a total nitrogen load (along with a phosphorus load) and/or an ammonia limit on the water quality of the stream. However, nitrate is generally nondeleterious and provides oxygen in times of biological stress on the river.

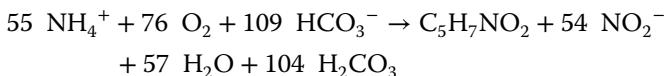
#### 16.4.4 Nitrification

Ammonia is often a byproduct of incomplete treatment such as in activated sludge and contact stabilization.

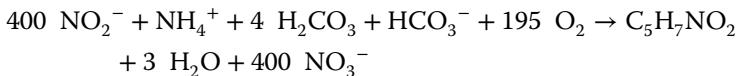
Ammonia can be oxidized to nitrate by one of two principal routes. The reactions given in the Section 16.4.1 above are in brief. In reality, both *Nitrobacter* and *Nitrosomonas* reactions are somewhat more complex because the bacteria also produce solids in the form of new cells, and also respire. Both these processes consume energy.

The overall reactions shown below yield 0.15 mg/cells per mg of  $\text{NH}_4^+ - \text{N}$  converted, and 0.02 mg/cells per mg of  $\text{NO}_2^-$ . It is also important to note from the following equation that nitrification also destroys a lot of alkalinity in the water.

The overall combined reactions are shown in the following equations:



*Nitrosomonas*



*Nitrobacter*

The overall reaction is:

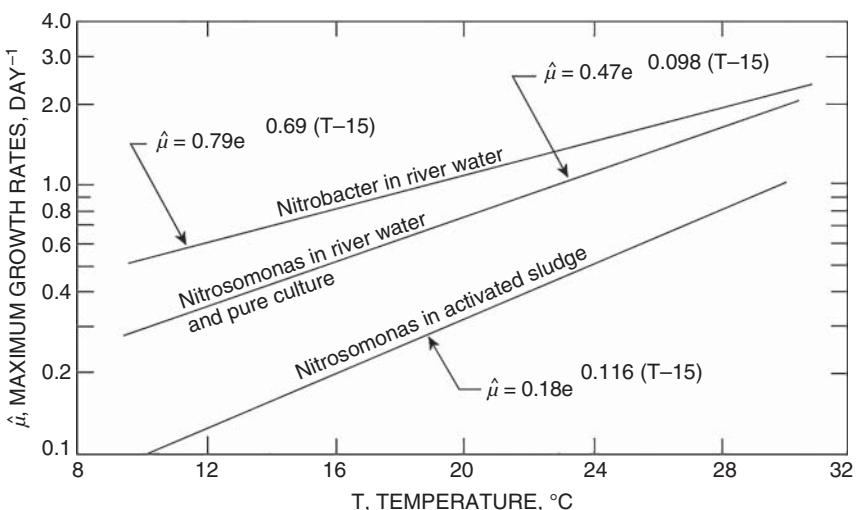
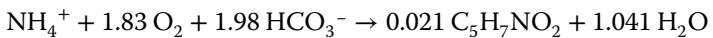


Figure 16.7 Temperature effects on the maximum growth rates of nitrifiers.

The theoretical value is that 7.1 mg alkalinity is destroyed for every mg of  $\text{NH}_4^+$  oxidized. In practice, the actual measured values are between 6.3 and 7.4 mg alkalinity destroyed per mole of  $\text{NH}_4^+$  oxidized. During the process of nitrification, the pH of the liquid may be affected because of the destruction of alkalinity.

$$\text{pH} = \text{p}K_1 - \log(\text{H}_2\text{CO}_3)/(\text{HCO}_3)$$

For example, in a system where there is  $20 \text{ mg l}^{-1}$  of  $\text{NH}_3$  nitrified, it will destroy about  $143 \text{ mg l}^{-1}$  of alkalinity, if there is sufficient alkalinity, or it just might depress the pH and stop the reactions. The kinetic constants for growth of the nitrifying bacteria are as follows:

$$K_N = 10^{(0.51T - 1.158)}$$

where  $T$  is the temperature ( $^\circ\text{C}$ ). This is the half-saturation constant for oxidation of ammonia nitrogen.

Temperature also has an effect on *Nitrosomonas* and *Nitrobacter*, as shown in Figures 16.7 and 16.8. The temperature affects both the half-saturation constant and the overall growth rate.

There is some indication that the completeness of the nitrification reaction is also dependent upon maintaining a minimum oxygen level of  $2 \text{ mg l}^{-1}$  in the aeration basin, and preferably  $4 \text{ mg l}^{-1}$  because the oxidation is more complete. This can be related to the biological half-reaction rates, but it is easier just to keep the dissolved oxygen (DO) at between 2 and  $4 \text{ mg l}^{-1}$ .

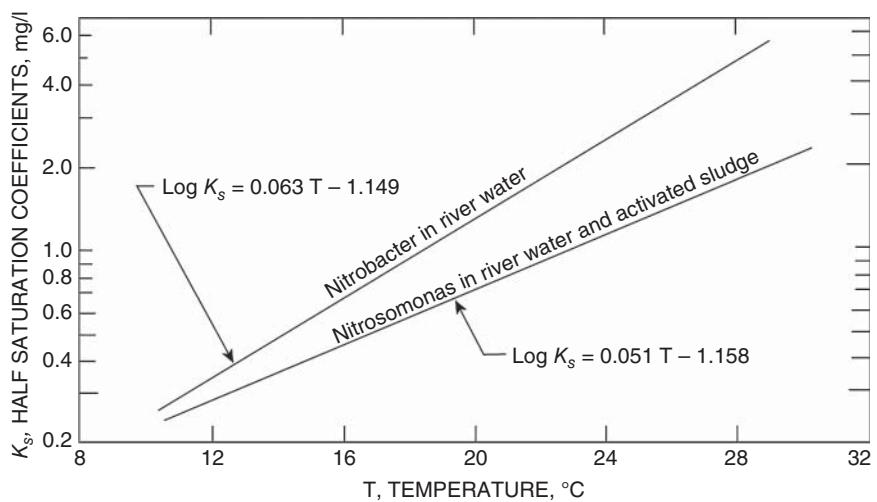
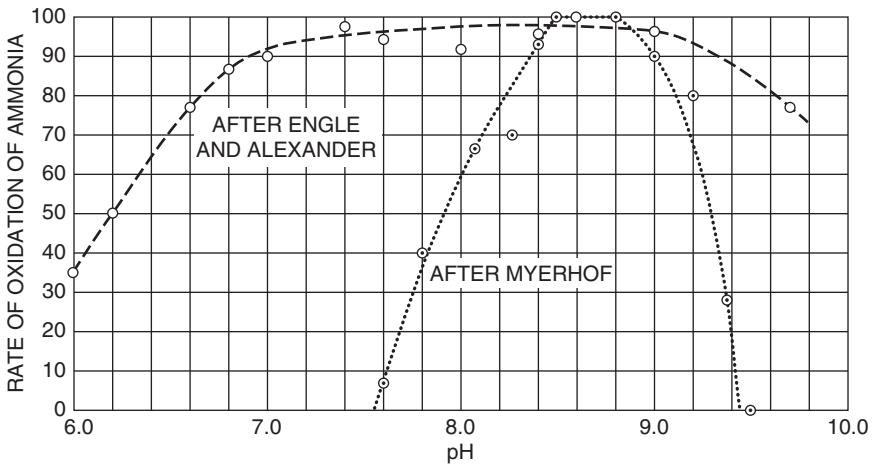
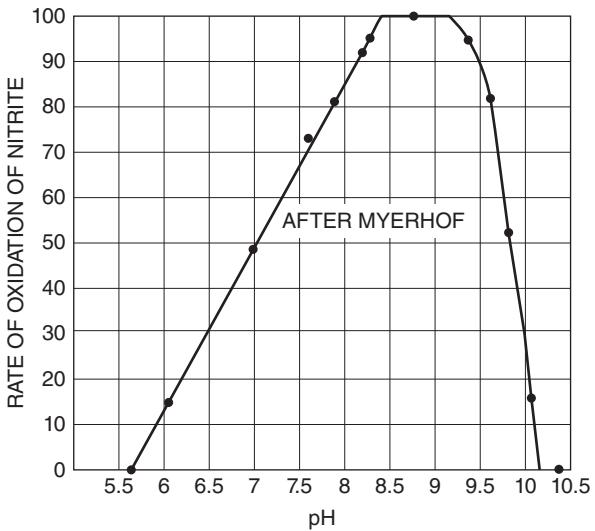


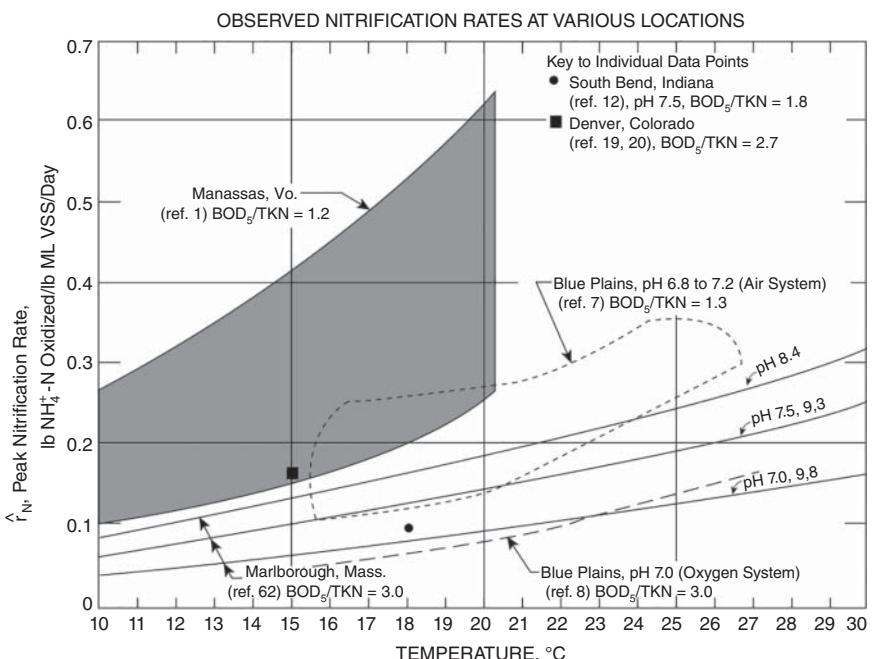
Figure 16.8 Temperature dependence of the half-saturation constants for nitrifiers.



**Figure 16.9** Effect of pH on ammonia oxidation by *Nitrosomonas*. Source: *Nitrification and Denitrification Facilities for Wastewater Treatment* EPA-625/4-004a Revised.



**Figure 16.10** Oxidation of nitrate by *Nitrobacter*. Source: *Nitrification and Denitrification Facilities for Wastewater Treatment* EPA-625/4-004a Revised.



**Figure 16.11** EPA Data for nitrification rates at select locations. Source: *Process Design Manual for Nitrogen Control* (1975), USEPA. Available from: <https://nepis.epa.gov/Exe/tiff2png.cgi/9100PUPQ.PNG?-r+75+-g+7+D%3A%5CZYFILES%5CINDEX%20DATA%5C70THRU75%5CTIFF%5C00002059%5C9100PUPQ.TIF>.

The data in Figures 16.9 and 16.10 are taken from a USEPA manual on *Process Design for Nitrogen Control* and the 1974 *Nitrification and Denitrification Facilities* publication in their Technology Transfer Series. Both documents are available at no cost through the EPA website.

The apparent optimum temperature for nitrification is approximately 30°C. The curve for rate of nitrification is approximated by a parabola starting at 17% at 5°C to a peak rate of 100% at 30°C, and then decreasing to 20% at 58°C (Figures 16.11 and 16.12). Figure 16.11 contains EPA Data on nitrification rates based upon work at the Blue Plains and other treatment plants.

The *Nitrogen Control Manual* is old but still useful.<sup>12</sup> It contains a complete discussion on design parameters, and is recommended for further examination. Good nitrification and low ammonia effluent values, plus a high sludge age (biological solids retention time in the aeration basin) is preferred. That suggests that the MLSS in the aeration chamber should be as high as practical and/or that the system should be designed around extended aeration. Sludge ages beyond 10 days and up to 30 days give good conversion of ammonia. Sludge ages over 30 days are considered excessive for other reasons.

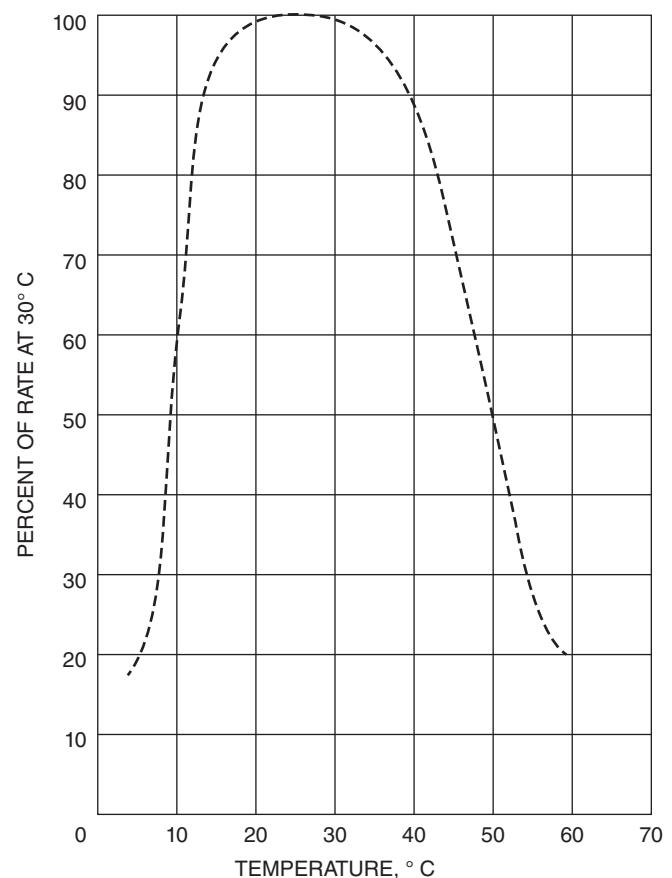


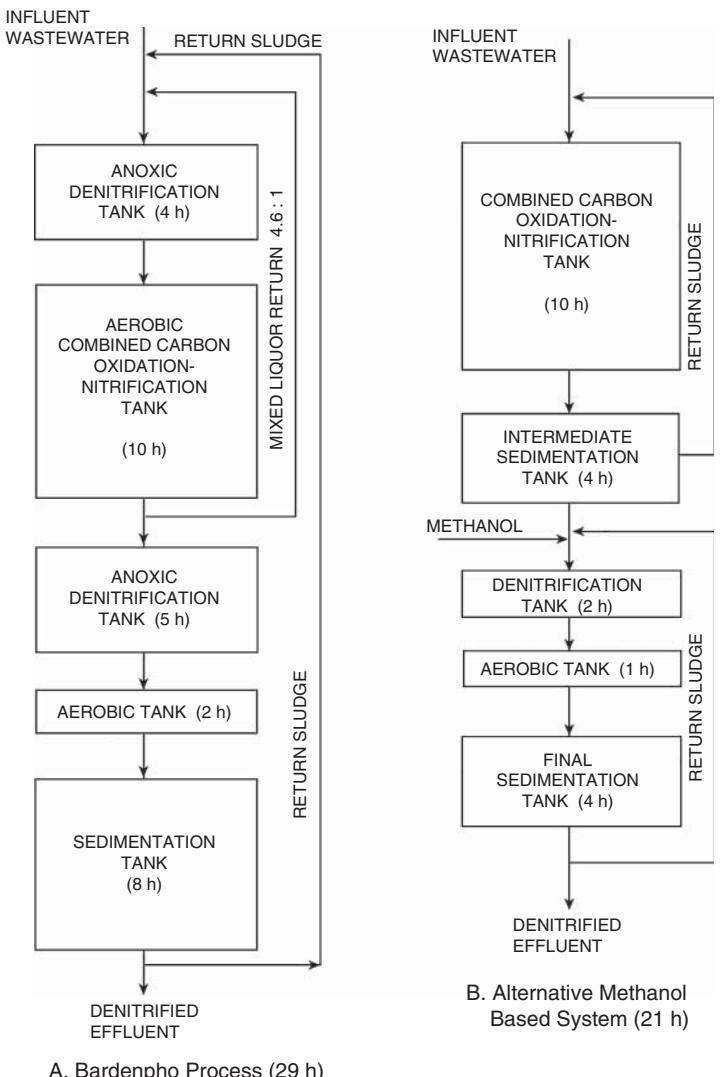
Figure 16.12 Effect of temperature on nitrification.

Excess ammonia in the influent to a wastewater treatment plant causes excessive oxygen demand, as well as the need to re-balance the carbon: nitrogen: phosphorus ratio in the wastewater, for optimum biological growth. One way of solving this problem led to a system of treatment in which *Nitrosomonas* and *Nitrobacter* remove the ammonia first before other treatment. This avoids the need for a supplemental carbon source added after the main aeration chamber.<sup>13</sup>

In the presence of a carbon source such as raw wastes, and the correct supply of other nutrients in the wastewater, the bacteria will continue to respire. Without adding oxygen, the DO levels rapidly drop to zero at which point the wastewater is anoxic. The bacteria turn to nitrate as an oxygen source and reduce the nitrate to nitrite, then ammonia, and finally to gaseous nitrogen. The reactions are quite complex, involving the ADP and ATP chains and a number

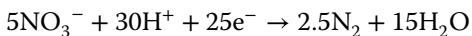
		Substrate Level Denitrification	Endogenous Level Denitrification	Mixed Nitrification/Denitrification	Fixed Film	Chemical (methanol) Addition	Internal Recycle
1. Wuhrman					X		
2. Ludzak-Ettinger		X					
3. MLE		X				X X	
4. Bardenpho		X X				X X	
5. Trickling Filter Filter				X	X X		
6. Activated Sludge Fluidized Bed			X	X X			
7. SBR			X				
8. Oxidation Ditch			X				
9. Biodenitro			X				
10. Biolac			X				
11. Counter Current Aeration			X				
12. Step Feed Denitrification		X X					

Figure 16.13 Some of the many biological nitrogen removal systems.



**Figure 16.14** Schematics of BardenPho and conventional nitrogen removal systems for comparison.

of bacteria. The bacteria that can reduce nitrate to nitrogen include *Achromobacter*, *Bacillus*, *Aerobacter*, *Micrococcus*, *Alcaligenes*, *Flavobacteria*, and *Proteus*. They are all facultative and fit into the general category of chemoorganotrophs.<sup>14</sup> The general stoichiometric equation for denitrification is:



When COD is used as a carbon source, the production of biomass from anoxic synthesis is lower than when methanol is used as a carbon source. The respective values for methanol and COD are 0.55 g cells produced per gram methanol consumed and 0.30–0.25 g cells per gram COD consumed.

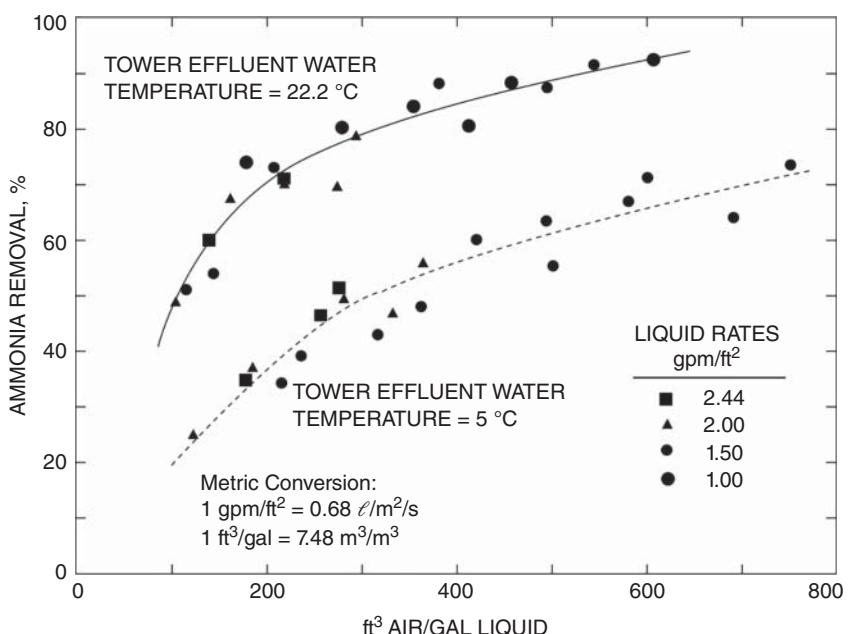
Several systems were developed to reduce the nitrogen in the system before it got into the aeration tank. The most common manner of removal was to turn off the oxygen supply to the head end of the wastewater treatment plant where the return sludge (rich in “hungry” bacteria from the clarifier) was mixed with the incoming waste feed. This effectively turns one end of the aeration system (some designs use separate tanks) into an anoxic zone, and the bacteria in the system would be starved for oxygen and would turn to the nitrogen compounds to reduce nitrate and ammonia to gaseous nitrogen.

There are a number of processes for nitrogen removal shown in the following figures. One of the most popular designs is the BardenPho process, which we will use and compare with other nitrification/denitrification systems (Figures 16.13 and 16.14).

**Table 16.2** Some of the compounds which are toxic to nitrifiers, and which would make biological nitrogen removal difficult or impossible.

Organics	Inorganics
Thiourea	Zn
Allyl-thiourea	OCN <sup>-</sup>
8-hydroxyquinoline	CIO <sub>4</sub> <sup>-</sup>
Salicyladoxine	Cu
Histidine	Hg
Amino acids	Cr
Mercaptobenzthiazole	Ni
Perchloroethylene	Ag
Thichloroethylene	
Abietec acid	

Source: Painter, H.A. (1970). “Review of literature on inorganic nitrogen metabolism.” *Water Research* 4 (6), 393–450.



**Figure 16.15** Ammonia removal data from Blue Plains (Washington, DC) publicly owned treatment works. Source: EPA.

The BardenPho system is very economical when compared with the cost of operation. One pays a penalty for tank sizing and equipment, but that is amortized relatively quickly when the cost of methanol is considered for a carbon source. Methanol is an expensive source for carbon in the process, and research has shown that other sources of carbon such as sugars can be substituted at little or no penalty, and a substantial savings in cost (Table 16.2).

#### 16.4.4.1 Ammonia Stripping

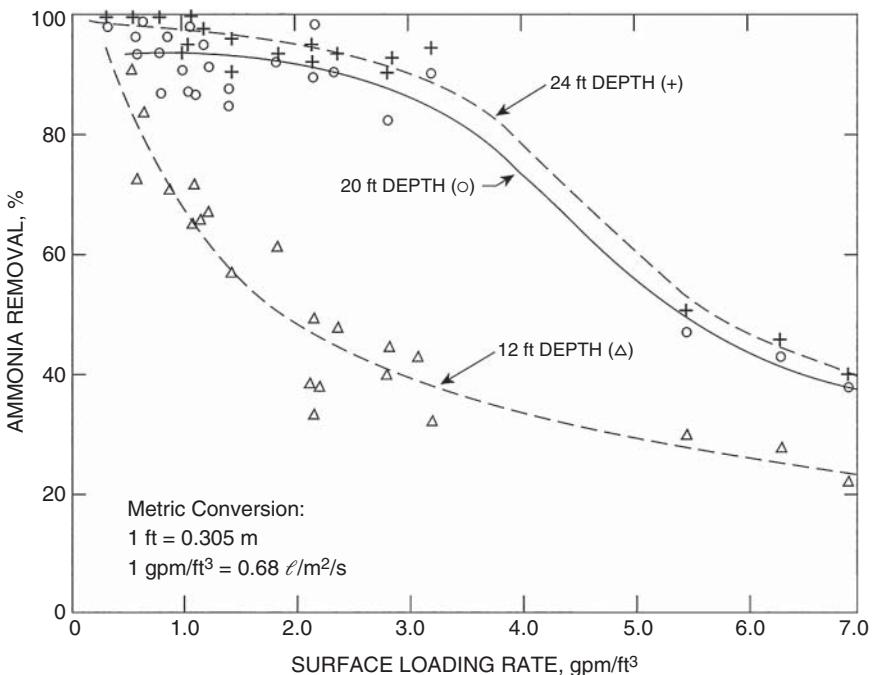
Ammonia ionization is pH- and temperature-dependent (see Figure 7.9). As the ionized form ( $\text{NH}_4^+$ ), it cannot be removed by stripping. To remove ammonia completely, raise the pH to 11.5 and blow air through the wastewater. The effectiveness of the tests has been confirmed at the Blue Plains Treatment Plant in Washington, DC (see Figures 16.15 and 16.16). The chart in Figure 16.15 illustrates the effect of temperature, and hydraulic loading rate on ammonia removal. The system utilized a stripping tower. A cooling tower, suitably de-rated could also be utilized to remove ammonia.

The problem with this solution is that all wastewater treatment plants have a discharge pH limit between 6.0 and 9.0, and the fact that the high pH is inhibitory to the biological activity in the plant, so the wastewater must be neutralized back to a lower pH where biological life is encouraged.

As with any separation process, the significant process variables include the efficiency of the specific tower packing types, depth of packing, and liquid flow rate (see Figure 16.16).

Stripping tower packing size and shape does make a substantial difference.<sup>15</sup> Scale from the aeration of highly alkaline wastewater has frequently caused plugging and packing failures due to carbonate buildup. This can be avoided by paying some attention to design and water chemistry.

The challenges with stripping are, as always, slime controls, temperature, and power and salts buildup in the stripping tower. Wintertime operations can inhibit removal of ammonia due to lower temperatures. Use of a tower for removal of ammonia will also dramatically cool the water and could affect the remaining biological activity in the rest of the treatment plant. In environments with cold winter temperatures, the waste stream or the tower may require heat



**Figure 16.16** Efficiency of ammonia stripping at several loading rates under different tower packing depths. Note: For air flows of around  $1000 \text{ ft}^3 \text{ gal}^{-1}$ , in a 24 ft. tower, a comparison of 1.5"-2" redwood slats was made comparing the slats to 4" x 4" plastic truss bars at South Lake Tahoe WWTP. The redwood slats showed virtually 100% ammonia removal versus 75% for the truss bars. The truss bars never did reach the same level of effectiveness that the slats attained, even for air flows up to  $4000 \text{ ft}^3 \text{ gal}^{-1}$ , and the ammonia removal was only 90%. The reasons are somewhat obvious, surface area being a significant factor. Source: See Slechta, C. and Culp, G.L. (1967) Water Reclamation Studies at the South Tahoe Public Utility District. *Journal of Water Pollution Control Federation* 39 (5), 787–814.

to prevent tower plugging from ice. Any tower that is stripping ammonia will also require an air permit for discharge of ammonia.

#### 16.4.4.2 Ion Exchange

A number of naturally occurring “weak ion exchange media” (zeolites) have been used to remove ammonia. One of the most common is clinoptilolite, which is described as follows:

##### Clinoptilolite

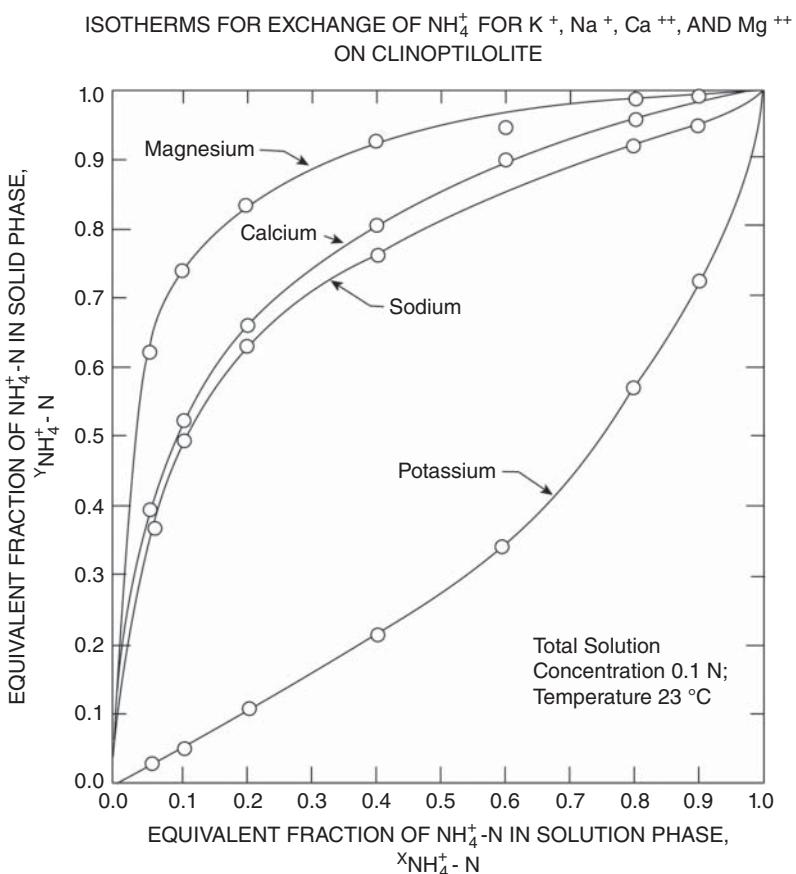
A hydrated alkali aluminosilicate that is one of the most abundant minerals in the zeolite family. Its structure consists of an outer framework of silica and alumina tetrahedra, within which water molecules and exchangeable cations (e.g. calcium, potassium, sodium) migrate freely. Although clinoptilolite's chemical formula varies with composition, a typical representation is given by  $(\text{Na}_2\text{K}_2\text{Ca})_3\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ .

Clinoptilolite's structure closely resembles that of heulandite, another zeolite mineral, but contains a higher proportion of silica and alkalis. Clinoptilolite is somewhat soft and forms platy, nearly transparent crystals of monoclinic symmetry. It is typically colorless in thin sections, but other colors (e.g. brown, pink, red) may occur owing to the presence of impurities such as iron oxide. The dehydrated mineral has the properties of a molecular sieve that selectively extracts nitrogen from a stream of air, leaving the effluent enriched in oxygen. As an ion exchanger, clinoptilolite has been used to remove cesium and strontium from radioactive wastes produced in reprocessing nuclear fuels and to remove ammonia from sewage streams. The mineral is also used as a filler and bulking agent in the manufacture of paper.

Clinoptilolite can be found in many zeolitic sedimentary rocks; in the compacted deposits of volcanic ash commonly called tuffs; as a byproduct of the weathering of basalt; and in some shale deposits. Its sites of occurrence include Oregon, South Dakota, and Wyoming, US; New Zealand; New South Wales, Australia; the Faroe Islands; and Bombay, India.

Source: Encyclopedia Britannica.

Other exchange media are available, but are significantly more expensive than the natural rock materials. The difference in the cost of the exchange media can be substantial. The problems commonly encountered with the backwash of the zeolites includes the possibility that the volume of backwash can be 10% or more of the flow through the exchange bed, and there is a potential for disposal problems associated with a relatively concentrated liquid containing ammonia. It can be helpful to think of ion exchange of zeolites as a concentration operation, where you are taking the wastes from a larger stream and concentrating



**Figure 16.17** Isotherms for ammonia absorption in mixed solutions.

them into a much smaller stream for treatment or disposal. Many facilities dealing with ammonia backwash use a 2%  $\text{NaCl}$  and  $\text{CaCl}_2$  solution to backwash the zeolites at a neutral pH. The ammonia can then be stripped or recovered by other processes.<sup>16</sup> The problem with backwashing an ion exchange process is the following (Figure 16.17):

Assume that you have an ion exchange process where you are removing ammonia. For a typical process, you might have a concentration factor on the basis of between 10:1 and 40:1 for backwashing the volume throughput. When you have the regenerated solution, it will be a 2% brine contaminated with high levels of ammonia and all the other ions you have removed. If you can reuse the liquid, you may be able to strip the ammonia and reuse the liquid, so you will not incur disposal costs. If not, you may have to oxidize the ammonia into nitrate chemically, and send it to the local treatment plant.

If you can find crops that are salt tolerant, it might be possible to use land disposal, at agronomic rates. The other alternative might be to use reverse osmosis to concentrate the ammonia and salts in the rejection stream from the RO process. That process would further concentrate the salts and the ammonia by a factor of up to 20 times.

## 16.5 Conclusions

Nitrogen removal is somewhat of a pay-me-now or pay-me-later choice. If one uses extended aeration systems and manipulates them in ways to generate a highly nitrified effluent, additional stirred tankage (anoxic versus anaerobic) with activated sludge will provide nitrate removal. The key lies in the correct establishment of the reaction rate kinetics. For industrial wastes, that will be waste-specific. The reaction kinetics must be well understood and preferably tested before the plant is built.

Ammonia removal is also the same type of choice, a balancing act between addition of a carbon source for nitrogen removal, or investment of additional capital for new tankage and operation of the system to maximize nitrogen removal.

There is some indication from research that the use of methanol may be beneficial if the removal rates for nitrogen are to be higher. There may be a limiting rate for the process without a readily attainable carbon source.

## Notes

- 1 One of the original purposes of phosphate addition was to make white clothes look whiter due to the fact that phosphate fluoresces under ultraviolet light, and the UV in sunlight would make the “white” more blue-white which is perceived by the human eye as a brighter white color.
- 2 See the USEPA Effluent Guidelines. The actual regulations start at page 7265 of the Federal Register, Vol. 68, No. 29, and generally require “no discharge of process wastes water pollutants into US waters,” with the exception of large precipitation events (24-hour duration and longer, and 25-year return and greater.) The document can be accessed at: <https://www.regulations.gov/document?D=EPA-HQ-OW-2002-0025-0058>
- 3 Litke, D.W. *Review of Phosphorus Control Measures in the United States and their Effect on Water Quality*. USGS Water-Resources Investigation Report 99-4007. Available in pdf format at: <http://water.usgs.gov/nawqa/nutrients/pubs/wri99-4007>.
- 4 Typical laundry formulations for non-phosphate detergents include up to 25% zeolite (sodium aluminum silicate), 15–20% sodium carbonate, 13–15% surfactants, 13–18% sodium perborate, 2–5% sodium sulfate, and about 1% enzymes. Source: CEEP.

- 5 CEEP is a working group within the Central European Chemical Industry Council, located in Brussels, Belgium. Their publications have analyzed the character and performance of phosphate detergents and found that phosphates are not as harmful to the environment as was first thought, and that they are a very effective detergent builder, outperforming their substitutes. The other findings include the fact that phosphate detergents account for about 25% of the total P in the influent of the wastewater treatment plant (the balance is from human sources), and the overall volume of wastewater sludge generated when phosphates are used is significantly lower than when other forms of detergent substitutes are utilized. Some information on phosphates is provided by the parent organization (<http://Cfic.org>), who has adopted the "Responsible Care" initiative similar to that in the US chemical industry.
- 6 USEPA Nutrient Control Design Manual State of Technology Review Report, EPA/600/R-09/012, January 2009.
- 7 Jiang, F., Beck, M.B., Cummings, R.G., Rowles, K., and Russell, D. (2005). *Estimation of Costs of Phosphorous Removal in Wastewater Treatment Facilities: Adaptation of Existing Facilities*. Water Policy Working Paper #2005–011. Available at [http://h2opolicycenter.org/pdf\\_documents/W2005011.pdf](http://h2opolicycenter.org/pdf_documents/W2005011.pdf).
- 8 EU Cost 624 Study, available at <http://www.ensic.u-nancy.fr/COSTWWTP>; and Jiang et al. (2005) in the last endnote.
- 9 A study indicated that municipal wastewater treatment plants on the Etowah River (north of Atlanta, GA) were adding between 110 and 160 gal/day of commercial grade ferric chloride ( $\text{FeCl}_3$ ) or about 4–5 mg/l, to obtain an effluent quality of approximately 0.3 mg/l total P. Internal notes and study for University of Georgia – Warnell School of Forestry, 2005.
- 10 Stumm, M. (1996). *Aquatic Chemistry*. Wiley.
- 11 Miller, D.C., Poucher, S., Cardin, J.A., and Hansen, D.J. (1990). The acute toxicity of ammonia to marine fish and a mysid. *Archives of Environmental Contamination and Toxicology* 19(1): 40–48.
- 12 Scheible, O., et al. (1993). *Process Design Manual: Nitrogen Control*. EPA/625/R-93/010 (NTIS PB94159142).
- 13 Almost any carbon source can be utilized, including simple sugars, methanol, starches, and so on.
- 14 Orhon, D. and Artan, N. (1994). *Modeling of Activated Sludge Systems*. Technomic Publishers, p. 398. The book is now available from John Wiley Online.
- 15 USEPA Nutrient Control Design Manual State of Technology Review Report, EPA/600/R-09/012, January 2009.
- 16 Mercer, B.W., et al. (1970). "Ammonia Removal from Secondary Effluents by Ion Exchange". *Journal of Water Pollution Control Federation* 42 (2): R95–R107.

## 17

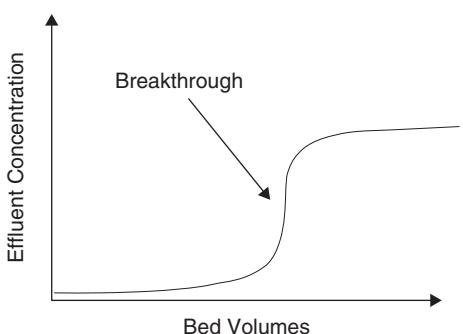
# Carbon Adsorption

## 17.1 Introduction

Adsorption is a surface phenomenon. One of the most commonly used adsorbents is activated carbon. Activated carbon is often made from wood, bamboo, or other materials which have been slowly roasted or burned to provide a very open pore structure in the solid. The roasting process creates a large surface area with respect to the volume of the material.

One of the most common uses is to separate fluid substances, whether they be in air or liquid. The adsorbent is most often prepared in fine particles, and laid up in a bed in a tank. The adsorbent has a finite area for attaching the sorbed material on to its surface.<sup>1</sup> As the surfaces of the adsorbent fill up, it becomes less efficient with respect to the removal of the sorbent. At some point, arbitrarily defined by testing, the adsorbent surface area becomes saturated with respect to the sorbed material, and the amount of material passing the adsorbent increases sharply: this is known as the breakthrough point. The efficiency of adsorption drops rapidly after that, until the entire carbon bed is saturated with the sorbent material and it is exhausted. The process is often plotted and measured in terms of the volume of contaminated materials passing through the carbon bed (bed volumes). The breakthrough curve is established when the gradual concentration of unadsorbed materials increases sharply with respect to the bed volumes. This is shown in Figure 17.1 as a breakthrough curve.

Because of process or regulatory limits where a permit quantity or concentration is involved, the carbon bed is usually changed out (substituted) once the bed reaches the breakthrough point. Carbon is often regenerated by additional application of heat in a dry state. The heat refreshes the carbon by volatilizing the adsorbed chemicals, but is often known to reduce the efficiency and life of the carbon by 10% or more.



**Figure 17.1** Breakthrough curve for carbon adsorption.

The factors affecting adsorption include:

1. Particle diameter (inversely with absorbent particle size [inverse of surface area]).
2. Adsorbate concentration (directly varies).
3. Temperature (direct variation).
4. Molecular weight (generally an inverse variation depending upon the compound weight and configuration of pore diffusion controls).
5. pH (inverse with pH due to surface charge).
6. Individual properties of solute and carbon.
7. Iodine number.

## 17.2 The Freundlich and Langmuir Equations

The basic equations for adsorption are the Freundlich and the Langmuir equations.  $c$  is a concentration at equilibrium between the compound and the adsorbent, usually expressed as milligrams per liter. Depending upon the application, one can use either equation.

Langmuir equation:  $y/m = Kc/(1 + K_1 c)$ , where  $K$  and  $K_1$  are determined constants, and  $y/m$  is the amount of material adsorbed per unit weight of sorbent.

Freundlich equation:  $y/m = Kc^{1/n}$ , where  $K$  and  $c$  are experimentally determined constants.

The most common is the Freundlich equation when it is expressed as:

$$\log(y/m) = \log K + (1/n) \log(c)$$

which plots as a linear form on log paper and makes the determination of the constants relatively easy. The Langmuir equation, when expressed in a convenient form, looks like the following:

$$c/(y/m) = 1/K + K_1/Kc$$

and the variation between  $c/(y/m)$  and  $c$  is linear. Under certain conditions, the Langmuir equation may create a better fit for the data than the Freundlich equation.

Although the manufacturer's curves are fine for initial design, one should use experimentally determined constants on a specific wastewater because of interferences and variables in the wastewater.

### 17.3 Carbon Adsorption Physical Coefficients and Economics

An excellent source for information on adsorption isotherms for toxic organics was prepared by the EPA and is still available from the NTIS: *Carbon Adsorption Isotherms for Toxic Organics*, EPA 600/8-800-023, April 1980. Summary data from that source are presented later in this chapter. The values were determined in an "artificial wastewater" containing approximately  $200 \text{ mg l}^{-1}$  of alkalinity, sodium, calcium, and other ions commonly found in wastewater.

### 17.4 Other Considerations

#### 17.4.1 Carbon Regeneration

The carbon can be regenerated, mainly by thermal or steam oxidation, and re-used. However, the cost of carbon is significant. The following generally applies to situations in the United States.

Virgin carbon can be \$2–\$2.40/lb (\$4.4–\$5.30/kg). Regeneration is about 80% of the cost of new carbon.

If certain compounds are removed from the waste, the carbon could be classified as a hazardous waste, requiring special treatment. Hazardous waste disposal costs can be  $\$1200 \text{ ton}^{-1}$ , plus \$5/mile for shipment to a hazardous waste disposal facility. If the wastes are chlorinated, there will likely be an additional charge based on chlorine. The additional costs incurred may be to insure that there are no liquids in the shipment. In all likelihood, it is quite probable that, in the US, the waste would be sent to an incinerator.

#### 17.4.2 The PACT™ Process

PACT™ was originally developed by DuPont, but is now owned by Zimpro (Zimpro is now owned by Siemens, and the web link for a technology and product description is: <https://www.oilandgasonline.com/doc/zimpro-wet-oxidation-0001>). The process adds powdered activated carbon to the wastewater treatment tank. It is used where there are biologically resistant organics or

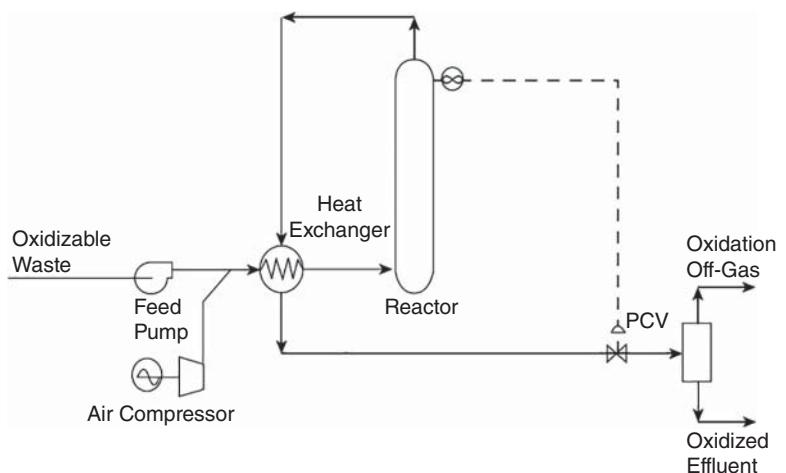
toxics in the wastewater, and it provides a combination of carbon pretreatment and increased retention time that enables the bacterial population to acclimatize and degrade the organics. It is also useful in reducing some metal concentrations. Carbon dosages vary considerably with the organics, and the activated carbon adds solids to the clarifier and can add substantially greater quantities of abrasives to the clarifier underflow. Generally, the concentration maintained in the aeration basin is under several hundred milligrams per liter. In recent years, Siemens has begun marketing the system (now called “wet air oxidation”) to the oil and gas industry.

Wet oxidation is the oxidation of soluble or suspended oxidizable components in an aqueous environment using oxygen (air) as the oxidizing agent. The oxidation reactions occur at elevated temperatures and pressures.

#### 17.4.3 Wet Air Regeneration for PACT Systems

Wet air regeneration is a liquid phase reaction in water using dissolved oxygen to oxidize absorbed contaminants and biosolids in a spent carbon slurry, while simultaneously regenerating the powdered activated carbon.

Regeneration is conducted at moderate temperatures of 400–500 °F (205–260 °C) and at pressures from 700 to 1000 psig (50–70 bar). The process converts organic contaminants to CO<sub>2</sub>, water, and biodegradable short-chain organic acids; sorbed inorganic constituents such as heavy metals are converted to stable, nonleaching forms that can be separated from the regenerated carbon, if necessary.



**Figure 17.2** Schematic diagram of Zimpro wet oxidation process for treating and regenerating powdered activated carbon (PACT process).

**Table 17.1** Summary of carbon adsorption capacities, from EPA data.

Compound	Adsorption <sup>a)</sup> capacity, mg g <sup>-1</sup>	Compound	Adsorption <sup>a)</sup> capacity, mg g <sup>-1</sup>
bis(2-ethylhexyl)phthalate	11 300	Guanine*	120
Butylbenzyl phthalate	1520	Styrene	120
Heptachlor	1220	1,3-dichlorobenzene	118
Heptachlor epoxide	1038	Acenaphthylene	115
Endosulfan sulfate	686	4-chlorophenyl phenyl ether	111
Endrin	666	Diethyl phthalate	110
Fluoranthene	664	2-nitrophenol	99
Aldrin	651	Dimethyl phthalate	97
PCB-1232	630	Hexachloroethane	97
b-endosulfan	615	Chlorobenzene	91
Dieldrin	606	p-xylene	85
Hexachlorobenzene	450	2,4-dimethylphenol	78
Anthracene	376	4-nitrophenol	76
4-nitrobiphenyl	370	Acetophenone	74
Fluorene	330	1,2,3,4-tetrahydro-naphthalene	74
DOT	322	Adenine*	71
2-acetylaminofluorene	318	Dibenzo( <i>a,h</i> )anthracene	69
a-BHC	303	Nitrobenzene	68
Anethole*	300	3,4-benzofluoranthene	57
3,3-dichlorobenzidiene	300	1,2-dibromo-3-chloro-propane	53
2-chloronaphthalene	280	Ethylbenzene	53
Phenylmercuric acetate	270	2-chlorophenol	51
Hexachlorobutadiene	258	Tetrachloroethene	51
g-BHC (lindane)	256	<i>o</i> -anisidine*	50
<i>p</i> -nonylphenol	250	5-bromouracil	44
4-dimethylaminoazobenzene	249	Benzo( <i>a</i> )pyrene	34
Chlordane	245	2,4-dinitrophenol	33
PCB-1221	242	Isophorone	32
DDE	232	Trichloroethene	28
Acridine yellow*	230	Thymine*	27
Benzidine dihydrochloride	220	Toluene	26

(continued)

Table 17.1 (Continued)

Compound	Adsorption <sup>a)</sup> capacity, mg g <sup>-1</sup>	Compound	Adsorption <sup>a)</sup> capacity, mg g <sup>-1</sup>
b-BHC	220	5-chlorouracil*	25
<i>N</i> -butylphthalate	220	<i>N</i> -nitrosodi- <i>n</i> -propylamine	24
<i>N</i> -nitrosodiphenylamine	220	bis(2-chloroisopropyl) ether	24
Phenanthrene	215	Phenol	21
Dimethylphenylcarbinol*	210	Bromoform	20
4-anhinobiphenyl	200	Carbon tetrachloride bis-(2-chloroethoxy) methane	11
b-naphthol*	200	Uracil*	11
a-endosulfan	194	Benzo( <i>ghi</i> )perylene	11
Acenaphthene	190	1,1,2,2-tetrachloroethane	11
4,4-methylene-bis-(2-chloroaniline)	190	1,2-dichloropropene	8.20
Benzo( <i>k</i> )fluoranthene	181	Dichlorobromomethane	7.90
Acridine orange*	180	Cyclohexanone*	6.20
a-naphthol	180	1,2-dichloropropane	5.90
4,6-dinitro- <i>o</i> -cresol	169	1,1,2-trichloroethane	5.80
a-naphthylamine	160	Trichlorofluoromethane	5.60
2,4-oichlorophenol	157	1,1-dichloroethylenedi chloroethylene	4.90
1,2,4-trichlorobenzene	157	Dibromochloromethane	4.80
2,4,6-trichlorophenol	155	2-chloroethyl chloroethyl vinylether	3.90
b-naphthylamine	150	5-fluorouracil*	3.90
Pentachloropheno1	150	1,2-dichloroethane	3.60
2,4-dinitrotoluene	146	1,2- <i>trans</i> -dichloroethene	3.10
2,6-dinitrotoluene	145	Chloroform	2.60
4-bromophenyl phenyl ether	144	1,1,1-trichloroethane	2.50
<i>p</i> -nitroaniline*	140	1,1-dichloroethane	1.80
1,1-diphenylhydrazine	135	Acrylonitrile	1.40
Naphthalene	132	Methylene chloride	1.30
1-chloro-2-nitrobenzene	130	Acrolein	1.20
1,2-dichlorobenzene	129	Cytosine*	1.10
<i>p</i> -chlorometacresol	124	Benzene	1.00

(continued)

**Table 17.1** (Continued)

Compound	Adsorption <sup>a)</sup> capacity, $\text{mg g}^{-1}$	Compound	Adsorption <sup>a)</sup> capacity, $\text{mg g}^{-1}$
1,4-dichlorobenzene	121	Ethylene-diamine-D33tetra-acetic acid	0.86
Benzothiazole*	120	Benzoic acid	0.76
Diphenylamine	120	Chloroethane	0.59
		<i>N</i> -dimethylnitrosoaniline	$6.8 \times 10^{-5}$

a) Note: Distilled water used with the following ion addition ( $\text{mg l}^{-1}$ ). Representative test conditions were as follows

Compound	Typical concentration	Compound	Typical concentration
Na	92	$\text{PO}_4$	10
K	12.6	$\text{SO}_4$	100
Ca	100	Cl	177
Mg	25.3	Alkalinity	200

The system is claimed to be more cost-effective and energy-efficient than that of furnace technology for regeneration. Regeneration is done in a slurry without  $\text{NO}_x$ ,  $\text{SO}_x$ , or particulate air emission problems. According to Zimpro, the operating cost for PACT can range between \$0.50 and \$1.00 per 1000 gal treated (\$0.13–\$0.30 per  $\text{m}^3$ ).

A simplified, general wet oxidation flow diagram, and coefficients of carbon adsorption are shown in Figure 17.2 and Table 17.1, respectively.

## Note

- 1 Adsorption is a surface phenomenon that is often highly reversible. Adsorption generally involves an interaction with the sorbent material (e.g., chlorine is absorbed in water). Chlorine can often be removed from water by passing it through a carbon adsorber.

## 18

# Ion Exchange

The ion exchange (IX) process occurs when ions that are held to functional groups on a solid surface by electrostatic forces are exchanged for ions of a like charge in a solution in which the solid is immersed. The solid is called a resin.

IX can be performed either in batch processes or in columns. Batch systems are less complex than the columnar system; however, they are also inefficient. For this reason, most IX processes are performed in a column.

## 18.1 Resins

There are both synthetic and natural resins. Natural “resins” include zeolites, greensands, clinoptilolites, and natrolites. Soils and peat materials also have some smaller amount of ion exchange (IX) capacity. However, with few exceptions, most of the resins used today are synthetic. They are made of a polymer matrix with soluble ionic functional groups attached to the polymer chains. When the resin is used up, a concentrated solution of the charged functional group can be applied to regenerate the resin. Because the resin is expensive, in most cases the regeneration is an economic imperative.

## 18.2 Physical Characteristics

Resins may be in the form of either a gel or a macroporous resin. Macroporous resins may have fewer exchange sites than resins. Resins are more expensive than gels, but they are tougher than gels, and may last longer before replacement. Compare the costs of resins and gels, and consider the environmental conditions in which they will be operating.

## 18.3 Chemical Structure

*Strong acid resins* contain sulfonic acid groups as the exchange sites. They have a regeneration efficiency of 30–50%. Regeneration is usually done using strong acids such as  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ .

*Weak acid resins* contain carboxylic acid groups as the functional species. They are extremely stable thermally and can be regenerated with any acid that is stronger than the functional group. Regeneration is nearly 100%. However, they must only be used in water with a pH greater than 7.

*Strong base resins* usually contain quaternary amine groups as the functional species. Regeneration is usually done with  $\text{NaOH}$  and has an efficiency of 30–50%.

*Weak base resins* can contain tertiary ( $-\text{NR}_2$ ), secondary ( $-\text{NHR}$ ), or primary ( $-\text{NH}_2$ ) amino groups, or a mixture of them as the functional species. The water must have a pH less than 7. They can be regenerated by  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{NH}_4\text{OH}$  at nearly 100% efficiency.

*Chelating resins* are developed to be more selective towards certain ions compared with others. They can be regenerated under acidic conditions because these are weakly acidic. Many of these resins are imidodiacetic acid groups attached to some crosslinked polystyrene. Some ion exchangers containing specific groups that are selective for particular ions are shown in Table 18.1.

### 18.3.1 Selectivity

Selectivity is a property of an ion exchange medium; it represents the preferential activity the medium has for different ions. This is also often related to valence. It shows that compounds of higher valence, either positive or negative, will be preferentially exchanged.

At low concentrations and room temperature, polyvalent ions get preference over monovalent ions.

Generally, ion exchangers prefer counter ions, which (i) have a higher valence; (ii) are smaller in equivalent volume; (iii) have greater polarizability; (iv) interact more strongly with the fixed ionic group of the matrix; and (v) participate least in combining into complex formulations with the co-ions.

**Table 18.1** Selective chelating resins in ion exchange.

Type of ion	Specific compound
Nickel, mercury, other select heavy metals	Thiol (Azko Chemicals)
Copper	Amidoxime (Duolite)

### 18.3.2 Selectivity Coefficient

Ion exchange reactions are stoichiometric and reversible. They are of the following type:



where R is the resin,  $A^+$  is the functional ion, and  $B^+$  is the ion originally found in the solution. The degree to which the exchange occurs depends upon the selectivity of the resin for the exchanged ion.

The selectivity coefficient  $K$  is defined as the relative distribution of ions when a charged resin is made to contact with different, but similarly charged, ions.

$$K = \frac{[B^+] \text{ in resin}}{[A^+] \text{ in resin}} \times \frac{[A^+] \text{ in solution}}{[B^+] \text{ in solution}}$$

The magnitude of  $K$  represents the relative preference to absorb  $[B^+]$  as compared with  $[A^+]$ ; the greater the magnitude of  $K$ , the greater the preference for

**Table 18.2** Ion preference and affinity for selected compounds.

Strong acid cation exchanger	Strong base anion exchanger	Weak acid cation exchanger	Weak base anion exchanger	Weak acid dictate & dumper
Barium (2+)	Iodide (1-)	Hydrogen (1+)	Hydroxide (1-)	Copper (2+)
Lead (2+)	Nitrate (1-)	Copper (2+)	Sulfate (2-)	Iron (2+)
Mercury (2+)	Bisulfite (1-)	Cobalt (2+)	Chromate (2-)	Nickel (2+)
Copper (1+)	Chloride (1-)	Nickel (2+)	Phosphate (2-)	Lead (2+)
Calcium (2+)	Cyanide (1-)	Calcium (2+)	Chloride (1-)	Manganese (2+)
Nickel (2+)	Bicarbonate (1-)	Magnesium (2+)		Calcium (2+)
Cadmium (2+)	Hydroxide (1-)	Sodium (1+)		Magnesium (2+)
Copper (2+)	Fluoride (1-)			Sodium (1+)
Cobalt (2+)	Sulfate (2-)			
Zinc (2+)				
Cesium (1+)				
Iron (2+)				
Magnesium (2+)				
Potassium (1+)				
Manganese (2+)				
Ammonia (1+)				
Sodium (1+)				
Hydrogen (1+)				
Lithium (1+)				

the ion by the exchanger. Table 18.2 shows selectivities of IX resins in order of decreasing preference.

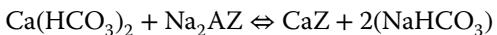
When there is a high affinity for the ion to be exchanged, there is a sharp breakthrough curve, a shorter IX column, and a greater flow rate. However, a higher regenerant concentration is required.

## 18.4 Design Considerations

### 18.4.1 Pretreatment

Pretreatment for solids removal is often required. What is needed here is common sense. Anything that can attack the resin, including acids, organics, and even some solids, should be avoided. Resins also do not like strong acids or bases. Many use salt for regeneration. Iron and calcium can blind the resins, as can certain types of silicates.

Note that when an exchange takes place, it does not necessarily affect other ions in the system. Thus,



so calcium bicarbonate hardness is exchanged for sodium bicarbonate. Note that nothing happens to the bicarbonate.

It is possible to exchange in a mixed bed ion exchange unit. That allows both cations and anions to be exchanged at the same time. If demineralized water is desired, then hydrogen and hydroxide ion exchange resins should be utilized.

On the basis of old water treatment measurements of hardness, being measured as grains/gallon (US), many resins have exchange capacities expressed in grains/ft<sup>3</sup>.

$$1 \text{ grain} = 1/7000 \text{ lb}$$

$$1 \text{ grain/ft}^3 = 2.884 \text{ g m}^{-3}$$

$$1 \text{ grain/gal} = 17.118 \text{ mg l}^{-1}$$

Ion exchange capacity is often expressed in terms of milliequivalents of CaCO<sub>3</sub>. The milliequivalents are calculated on the basis of an assumed molecular weight of 100.00 rather than 100.08.

Backwash volume is often 8–12% of throughput volume. The backwash will contain the regenerant plus the material removed and may be a hazardous waste.

An example here might help illustrate the point. Recently we were asked to provide an deionization system to remove hardness from water for a boiler application. The flow was 200 gal min<sup>-1</sup> (757 l min<sup>-1</sup>). The removal was for cations and anions in the raw water. The regeneration flow was approximately 6% of the throughput. The backwash stream thus concentrates the quantity of removed ions approximately 1/0.06 = 16.67 times.

Additionally, ion exchange backwash systems often require the addition of hydroxide for the regeneration of the anion exchange, and acid for the regeneration of the cation exchange resin. Depending upon the raw water constituent and the local discharge and sewer standards, you may not be able to discharge the backwash to either the sewer or directly to a watercourse. Either way, you might require a discharge permit, and possibly pretreatment before discharge.

Demineralized water is often aggressive water. The selection of materials is important, and plastic or glass pipes may be required for certain types of backwash and tank linings.

During backwash, the bed can be handled as either upflow or downflow. Bed suspension is not always necessary but it is recommended on larger units.

For more help and information on sizing ion exchange resins, go to the Rohm and Haas websites listed below. They have a sizing calculator, which is very handy. The Osmonics website is equally informative.

<http://www.osmonics.com/products/page838.htm>

[http://www.rohmhaas.com/ionexchange/fr\\_resins.htm](http://www.rohmhaas.com/ionexchange/fr_resins.htm)

[http://www.rohmhaas.com/ionexchange/fr\\_special.htm](http://www.rohmhaas.com/ionexchange/fr_special.htm)

## 19

# Dissolved Air Flotation and Techniques

## 19.1 Design Basics for DAF

Dissolved air flotation (DAF) and flotation in general is mostly dependent upon the solubility of nitrogen and oxygen in water. The normal saturation value for oxygen in water is about 11 ppm at common environmental conditions. Nitrogen is approximately 6 ppm under similar conditions.

Flotation is removal of suspended solids by the process of reverse Stokes settling and coagulation. Some flotation units use induced air at low pressures, while others use compressed air. The mining industry uses aerators to beat the air into the water (much like a kitchen mixer) for separation of the ores in a process called beneficiation. The beneficiation process usually handles large quantities of solids, which have a greater density than those generally handled by most environmental flotation processing plants. Many environmental flotation facilities are used for removing grease, oils, fats, and low-density solids from the wastewaters. Some commercial bakeries, dairies, fish processing, and poultry plants use DAF to remove everything from fats to blood from the wastewater.

In “conventional” DAF, a part of the flow is pressurized between 40 and 100 psig (2.72–6.8 atm). At those pressures, nitrogen and oxygen are substantially more soluble in water than at atmospheric pressure.

For example, the release of nitrogen from decompression at 40 psi is about  $211 \text{ cm}^3 \text{ l}^{-1}$ , and that of oxygen is about half of that value. So overall, from the release of pressure at 40 psig, we can generate about 320 ml of gas per liter of water pressurized.

Most organic environmental solids have a density less than  $2 \text{ g cm}^{-3}$ . Silica has a density of  $2.65 \text{ g cm}^{-3}$ . In an earlier chapter we discussed reduction in apparent specific gravity by particle agglomeration. If air ( $\text{density } 1.28 \times 10^3 \text{ gm cm}^{-3}$ ) can be made to adhere to a sand or silt particle, it does not take many bubbles to make even sand “float”<sup>1</sup>.

The inverse of the Henry's law constant, multiplied by the partial pressure of the gas above the solution, is the molar solubility of the gas.

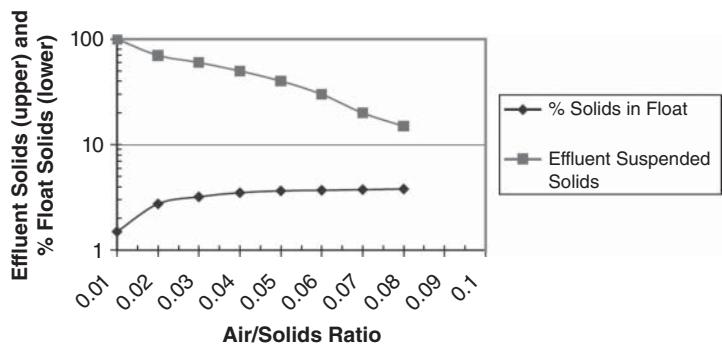


Figure 19.1 Performance of typical dissolved air flotation systems. Source: Eckenfelder, T. (1974). *New Concepts in Wastewater Treatment*. New York: Jenkins Press.

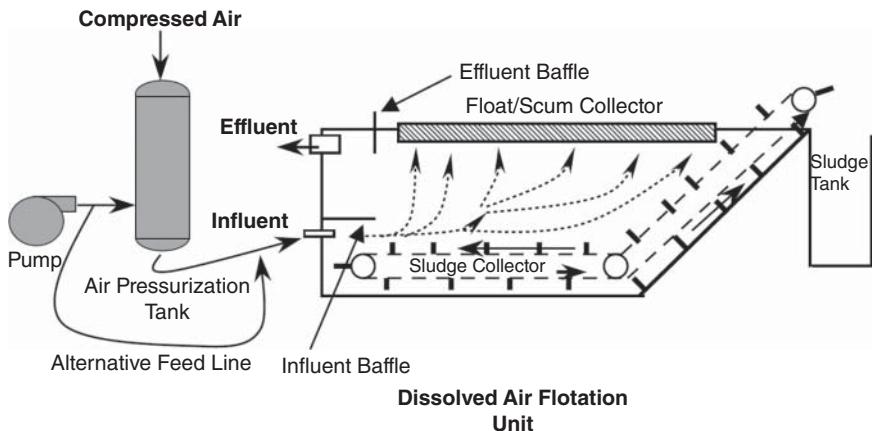


Figure 19.2 Configuration of a dissolved air flotation system.

Thus oxygen at 1 atm would have a molar solubility of  $(1/756.7) \text{ mol dm}^{-3}$  or  $1.32 \text{ mmol dm}^{-3}$ . The key to measurement is the air/solids ratio. Typical curves are shown in Figure 19.1

The design of a DAF unit is relatively straightforward. A typical design configuration is shown in Figure 19.2.

## 19.2 Operating Parameters

The surface overflow rate is somewhat higher than that of a clarifier:  $0.7\text{--}2.71 (\text{m}^2/\text{s})^{-1}$  ( $2\text{--}5 \text{ gal (min/ft}^2)^{-1}$ ) (this is a vertical velocity or overflow rate on a par with filtration rates). Air/solids ratios from 0.01 to 0.2 have been

used in design, but as a practical matter, 0.03–0.05 air/solids ratios will give the best suspended solids removals. Laboratory and pilot tests must be used to determine the best values. Detention times in the system can vary from about 15 min to over 1 h.

Side water depths of the tanks are between 1.3 and 3 m (5–10 ft). The recycle ratio for water ranges from 10% to 100%, with general values from 20% to 60% depending upon the solids concentration and chemical addition.

With proper coagulant dosage and emulsion breakers as required, the solids removals can easily approach 95–99% of the suspended solids, and depending upon the chemistry, 50% or more of the total dissolved solids.

When de-emulsifying oily wastewaters, DAF units have been known to produce an effluent with less than 5 mg l<sup>-1</sup> total oil, but 15 mg l<sup>-1</sup> is much more reliable and attainable, even with influent concentrations of 1000–16 000 mg l<sup>-1</sup> oil.

### 19.3 Theory and Design

One theory of removal by DAF depends upon the collision theory and the work of Tambo and Wantanabe (1968).<sup>2</sup> They developed a theory indicating that the population of particles with air bubbles attached depends upon kinetic factors, the concentration of the particles, the concentration of the air bubbles, and the collision between the two. The result is an equation involving a first-order differential equation and a rather messy integration of the form of:

$$\frac{dN}{dt} = -kN(a_m N_{bo} - a_{m-1} N_{bo-1})$$

where  $N$  is the number of air bubbles;  $N_{bo}$  is the concentration of particles without air bubbles;  $k$  is a kinetic coefficient; and  $a$  is an attachment factor. The important thing that came up with this work was the realization that the kinetic coefficient is equal to the velocity gradient times the cube of the sum of the bubble and floc diameters. The bubbles have a fixed size from 40 to 100 µm, and the collision rate increases with floc size. It is far easier to use a model that is analogous to a filter contact model.

This model is the “whitewater” model, because it describes the condition of the water in the saturation zone where the air is released into the water. The basic assumption in the model is that:

$$h_t = h_d + h_i + h_s$$

where  $h_t$  is the total collisions;  $h_d$  is Brownian diffusion;  $h_i$  is the interception; and  $h_s$  is the differential settling (particles relative to bubbles).

Furthermore, there is an attachment ratio, or “a,” which is further applied to represent the missed particles. Rather than going through and giving the entire theory, we will break down the significant equations:

### (1) Bubble mass

$$C_b = (C_r - C_n)r/(1 + r)$$

where  $C_b$  is the mass concentration of air released;  $C_r$  is the mass concentration of air in the recycle flow ( $\text{mg l}^{-1}$ );  $C_n$  is the mass concentration of air in the floc tank effluent ( $\text{mg l}^{-1}$ ); and  $r$  is the recycle ratio (decimal).

### (2) Particle bubble rise

$$\text{By Stokes law : } V_{pb} = g(\rho_p - \rho_{pb})d_{pb} \times 2/18 \mu$$

where  $V_{pb}$  is the rise velocity of the particle + bubble ( $\text{m h}^{-1}$ );  $g$  = gravity;  $\mu$  = viscosity;  $d$  is the diameter of the bubble or particle; and  $\rho$  is the density of the particle or the particle plus the bubble, respectively.

### (3) Bubble volume concentration

$$\phi_b = C_b = \rho_{air}$$

where  $C_b$  is given in (1), and  $\rho_{air}$  is the density of air saturated with water vapor.

### (4) Bubble number concentration

$$Nb = 6\phi_b/(\pi d_b^3)$$

where  $\phi_b$  is from (3), and  $d_b$  is the mean bubble diameter in microns.

## 19.4 Ranges of Data

Particles per milliliter range from 1000 to 10 000 for drinking water applications, and on the basis of TSS loadings alone, for many industrial applications the values for industrial wastes could be 100 000–300 000 per milliliter.

Bubble diameters depend upon saturator pressure and recycle rates. For recycle rates between 6% and 15%, the general estimate of bubble diameters is about 40  $\mu\text{m}$  median size, and the number of bubbles for low solids content water is between  $10^5$  and  $2 \times 10^5$  bubbles per milliliter. The estimated bubble to particle ratio is approximately 200 : 1.

For various types of waste streams, the amount of air is often independent of the suspended solids in the system, unless the TSS is more than 1000  $\text{mg l}^{-1}$ . For surface waters low in solids, the approximate range of air to solids is about 380 ml of air per gram of solids. For sludge thickening applications, the air requirement is between 15 and 30  $\text{ml g}^{-1}$ .<sup>3</sup>

## 19.5 Electroflotation

Electroflotation is a much-overlooked technology. It is accomplished by disassociation of water by electricity either in an atmospheric tank or in a pressure tank. The atmospheric tank is the most common application. The equipment is still used in the oil industry, especially in locations where the conductivity of the oily water is above 1000 micro-mohs.

The basic reactions are the ones for the disassociation of water:



For every 4 C of electrical charge one gets 2 mol of hydrogen and 1 mol of oxygen released into the water. If there are salts such as chlorides, they will also disassociate into chlorine, at some reduced efficiency, but at no electrical penalty.

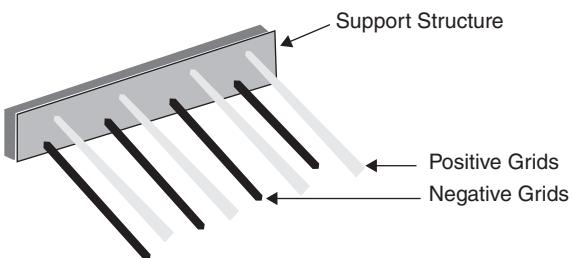
The use of this system generates a cloud of microbubbles that are far more gentle on flocs than those generated by many of the existing systems, which utilize pressurized air/water systems. Also, the flotation is continuous while the power is turned on. Regulation can be by control of the power supplied to the unit, and one can obtain greater or smaller amounts of flotation by adjusting the "gas/solids" ratio as opposed to an air/solids ratio. In this case, the gas/solids ratio is appropriate because the system does not use air, but the principal mechanism of flotation is excess hydrogen and oxygen generated at the level of the electrode and also allowed to bubble to the surface.

The power generation requirements are modest and can compete successfully with other types of flotation, especially where high recycle rates are employed. The applied voltage is dependent upon the conductivity of the water, but seldom above 12 V. The amperage is significant and can be several hundred amperes. One system used a maximum voltage of 12 V, and about 300 A, or about 3.6 KW to treat up to 100 gal per min in a flotation system basin of approximately 6.2 m<sup>2</sup>, or 64 ft<sup>2</sup>. The bubbles are small (between 10 and 20 µm, and many smaller), but there are many more of them and they have a lower density than that of air.

One of the few disadvantages of the electroflotation system is the fact that some of the byproducts of the flotation are hydrogen and oxygen, which are trapped in the foam, and perhaps some free chlorine if chlorides are present in the water. If the foam generated is viscous, it can trap and retain the hydrogen and oxygen together, creating the potential for a small hydrogen explosion, which is limited because of the limited amount of foam and the presence of water in the foam.

When ignited, it can sound like a firecracker going off, but, at the same time, one can see how this would upset people and cause safety concerns. Given a well-ventilated room, and/or a vacuum system to collect and collapse the foam, the hazard is minimal.

One type of electrode configuration is shown in Figure 19.3.



**Figure 19.3** Typical electroflotation system grid configuration.

These systems have been used, in the mid- and late 1970s, to perform oil removal, predominantly in the meat packing industry. The US Air Force rediscovered the technology through a technology exchange program with Russia in the early 1990s and tried to commercialize it for treating oily wastewaters from machine shops. Some of the systems are still in use in the oil industry, working principally on brines for oil separation. However, most of the systems are of a marginal design, which limits their effectiveness and performance.

The significant problems with this type of system were found to be the electrode materials of construction. Those problems can be solved by selection of materials including high-silicon iron, carbon, stainless steel, and titanium. There are other uses of the technology, such as electrocoagulation.

### 19.5.1 Electroflotation Theory and Design

The theory discusses the depth, length, and other parameters involved in sizing the electrodes and determining the electrical losses in the system. The power consumption in passing an electric current between two long bars or rods can be found to be a function of the current passed through the circuit, the diameter of the rods, the length of the rods, the temperature of the solution, the depth of immersion of the electrodes, the resistivities of the electrode materials, the gap between the rods, and the molality of the electrolyte.

The power requirement for the system is the product of the current and the total circuit voltage, where the total circuit voltage will be the sum of the decomposition voltage of the electrolyte, the anode overvoltage, the cathode overvoltage, the ohmic drop through the electrolyte, and the ohmic drop through the electrodes and buss works.

$$\text{Power} = I \times E_{\text{total}}$$

$$E_{\text{total}} = E_{\text{decomposition}} + h_a + h_c + h_W + h_{hw}$$

$$E_{\text{decomposition}} = E_{\text{rev},T,P} = 1 + (RT/nF) \ln[a_{H_2}(a_{O_2})^{1/2}/a_{H_2O}]$$

The temperature ranges from 298 to 523 K, and the pressures are expressed in atmospheres.

$$E_{\text{rev},T,P} = 1.5184 - 1.5423 \times 10^{-3}T + 9.524 \times 10^{-5}T \ln T$$

$$E_{\text{decomposition}} = E_{\text{rev},T,P} = 1 + 4.309 \times 10^{-5} T \ln \frac{(P - P_{\text{H}_2\text{O}})^{1.5} P_{\text{H}_2\text{O}}^0}{P_{\text{H}_2\text{O}}} \\ \ln P_{\text{H}_2\text{O}}^0 = 37.043 - \frac{6275.7}{T} - 3.4159 \ln T \\ \ln P_{\text{H}_2\text{O}} = 0.016214 - 0.13802m + 0.19330m^{1/2} + 1.0239 \ln P_{\text{H}_2\text{O}}^0$$

where  $m$  is the molality of electrolyte in moles per kilogram of solvent.

$$P = P_{\text{atm}} + \frac{\text{sg}_{\text{solution}}(\text{depth})}{33.9}$$

(sg denotes the specific gravity; and the depth is in feet)

$$\text{Voltage drop : } \eta_{\text{hw}} = \left( \frac{I}{3} \frac{L\rho}{A} \right)_{\text{anode}} + \left( \frac{I}{3} \frac{L\rho}{A} \right)_{\text{cathode}}$$

where  $L$  is the length of the electrode,  $A$  is the cross-sectional area,  $\pi D^2/4$ , and  $\rho$  is the resistivity of the electrode material.

$$\eta_c = 2.303 \frac{RT}{F\alpha} \log \frac{i}{i_o}$$

where  $R/F = 4.309 \times 10^{-5}$ ,  $\alpha$  is 0.5, and  $-\log i_o$  is  $\sim 6$  for an iron cathode, and  $i$  is current density in  $\text{A cm}^{-2}$ .

$$\eta_a = 0.37 \log \frac{i}{1.7 \times 10^{-5}}$$

The equation is for an iron anode; for both anode and cathode overvoltages, the electrode material has the largest influence.

$$\eta_\Omega = i L_{\text{gap}} \rho$$

where  $i$  is the current density in  $\text{A cm}^{-2}$ ,  $L_{\text{gap}}$  is the distance between electrodes in cm, and  $\rho$  is the resistivity of the electrolyte.

Note: current density is given by current divided by the active surface area of electrode.<sup>4</sup>

## 19.6 Electrocoagulation

The difference between electrocoagulation and electroflootation is only in the design of the electrode. In electroflootation, one uses high-silica iron or other materials, which are essentially resistant to erosion by impressed current. In electrocoagulation, the electrode is designed to be sacrificial.

The principles are the same for both, but as the electrode is eroded, the voltages will have to be higher to compensate for the increased spaces between the

electrodes. This technology is the equivalent of adding iron or alum directly to the water without the anion half of the compound. The ions are placed in water as hydroxides rather than as a sulfate, chloride, or other ion. In some instances, this technology has been coupled with flotation for enhanced removals.

These systems were being manufactured by Kwire, a Japanese company, which apparently is no longer in business (<http://www.kwire.com/watertr.htm>). A report from EPA covers the subject of electrocoagulation.<sup>5</sup> The application of electroflotation has been researched since the mid 1970s, but not intensively researched. The Russians were, at one time, promoting electroflotation for separation of petroleum-based oil and grease from wastewaters generated by aircraft and naval operations, but the US was not interested in the process. Other researchers have demonstrated the successful use of electroflotation for removal of various metals from ore processing.<sup>6</sup> Other researchers have also investigated electroflotation and electrocoagulation for treatment of feedlot wastewaters.<sup>7</sup>

At one time some research activities the author was associated with attempted to commercialize the removal of oil, grease, and blood from the kill floors of slaughterhouses in Chicago and Philadelphia. The wastes contained grease and oil in excess of 5000 mg/l, and by the application of chemicals and electroflotation the effluent was less than 15 mg/l as fats, oils and grease (FOG). The process was sold to a competitor, and the research was discontinued for business reasons.

Other tests on flocced wastes containing electroplating waste streams showed removals in excess of 95% on a weight basis. The electroflotation had a significant advantage over conventional DAF because it did not have high shear associated with the release of pressure from the air chamber in the DAF.

## Notes

- 1 This was calculated from the Henry's law constants we used in Chapter 1.
- 2 Tambo, N. and Wantanabe, Y. (1968). *A Kinetic Study of Dissolved Air Flotation*. World Congress of Chemical Engineering, Tokyo, pp. 200–203.
- 3 See Chapter 7 in *Water Quality and Treatment* by the American Water Works Association, 5th ed. New York: McGraw Hill.
- 4 *Comprehensive Treatise of Electrochemistry*, Vol. 2, 6 (1981), Plenum Press; *Electrochemical Cell Design* (1984), Plenum Press.
- 5 EPA (1998). *Cure Electrocoagulation Technology Innovative Technology Evaluation Report*, EPA/540/R-96/502. Available at <http://www.epa.gov/ORD/SITE/reports/540r96502.pdf>, <http://www.powellwater.com/electrocoagulations-vs-chemical-coagulation>, and [https://www.ampc.com.au/uploads/cgblog/id172/ENV\\_2003\\_Electrocoagulation\\_process\\_for\\_wastewater\\_treatment.pdf](https://www.ampc.com.au/uploads/cgblog/id172/ENV_2003_Electrocoagulation_process_for_wastewater_treatment.pdf).

- 6 Oliveira da Mota, I., Castro, J.A., Casquiera, R.G., and Oliveira, A.G. Jr. (2015). Study of electroflotation method for treatment of wastewater from washing soil contaminated by heavy metals. *Journal of Materials Research and Technology* 4(2), 109–113. <https://doi.org/10.1016/j.jmrt.2014.11.004>
- 7 [http://www.deswater.com/DWT\\_references/vol\\_101\\_references/101\\_2018\\_77.html](http://www.deswater.com/DWT_references/vol_101_references/101_2018_77.html).

## 20

# Coagulation, Flocculation and Chemical Treatment

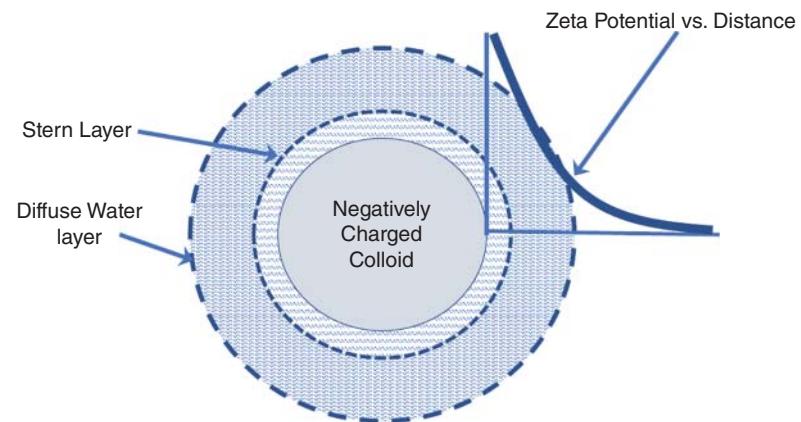
## 20.1 Introduction

Coagulation is all about bringing things together. It is joined with flocculation and chemical treatment because all the processes are necessary for chemical treatment and precipitation.

Coagulation is defined as destabilization by particle charge neutralization and initial aggregation of colloids. Flocculation is agglomeration of coagulated colloidal and finely divided suspended material either by physical mixing or by chemical coagulant aids. Chemical treatment is what we do to make coagulation and flocculation happen by adjusting the chemical charges on contaminants through the process of adding chemicals.

The most effective coagulant aids are divalent and trivalent metallic ions, usually iron and aluminum, but can include calcium, magnesium, and manganese. The other things that can be used as coagulant aids are polymers and sols.

The metric for the effectiveness of a coagulant process is Zeta potential. Zeta potential is a measure of the electrochemical charge of a particle and the layer of surrounding ions of opposite charge. Water is a polar molecule and it has positive and negative ends. Because water has two H<sup>+</sup> atoms attached to it with an approximately 105° angle between them, and because the oxygen molecule has a strong attraction, the oxygen end of a water molecule carries a slight negative charge, and the hydrogen end of the molecule carries a slight positive charge. Because most particles and colloids in nature have a net negative surface charge, the positive end of water molecules will line up on the surface of the colloid and be attracted to it. Subsequently, the now-surrounded colloid will have a second layer of water molecules attracted to it because the “new” surface is negatively charged as well, and so on and so on until the surface charges are too weak to attract new water molecules (Figure 20.1). This first layer of water molecules attached to the colloid is the Stern Layer. The Stern Layer is roughly the boundary at which the layer of charged fluid becomes more diverse and less cohesive, and easier to shed when the colloids approach each other. However, it is the surrounding layer of charged fluid outside the Stern Layer that keeps the colloid in



**Figure 20.1** Zeta potential of a colloid (ionic charges and double layer around particles).

suspension, because the thickness of this layer prevents coulombic forces from bringing two particles together.

For example, if a particle has a negative charge, it will be surrounded with a layer of positively charged  $H^+$  ions surrounding the particle. It is this layer of particles that helps make a colloid stable. Another definition of Zeta potential is that it is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

The Zeta potential is measured by the mobility of colloidal particles across a cell. For many stable colloids in wastewater, the measured Zeta potential is between  $-16$  and  $-22$  mV, but can range from  $-3$  to  $-40$  mV. Coagulation generally occurs when the Zeta potential is lowered to less than  $-0.5$  mV.

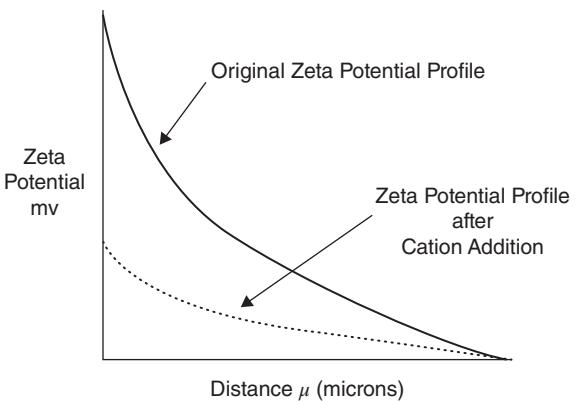
Another way of describing coagulation is that it occurs when the surface charge is lowered enough to permit van der Waal's attractive forces to make particles adhere when they collide or interact. Different valences of ions have varying effects in reducing the Zeta potential. The charge on the ion and the size of the ion also have an effect on the same.

By comparison, for a specific coagulation effect,  $KCl$  takes  $103\text{ mg l}^{-1}$ ,  $K_2SO_4$  requires  $0.219\text{ mg l}^{-1}$ , and  $K_3(FeCN)_6$  takes  $0.096\text{ mg l}^{-1}$  to achieve coagulation. Similar effects take place with cations (Figure 20.2). This is almost entirely attributed to the stronger charges in the divalent molecules.

Commercial Zeta potential units measure the net charge on ions, and the Zeta potential is often plotted on one axis with the turbidity of the sample on a parallel axis against the coagulant dose. The minimum turbidity is selected as the optimum point for precipitation and chemical dose.

Although good Zeta potential is used for measuring the charge for coagulation, it should never be the sole measure of determining coagulant dosage.

**Figure 20.2** Effect of cations on Zeta potential of a colloid.



That job is left to the jar test, and in fact, the Zeta potential is more of a confirmation of the observations of jar testing. The Zeta potential allows for optimization of dose, but then so does a jar test, without the expensive analyzer.

High weight and high molecular charge polymers are also used as coagulant aids. These are predominantly valuable because the equivalent charge is many hundred times that of even trivalent ions, and the effect of polymers can be substantial in reducing ion consumption. One milligram per liter of polymer added to a solution can replace as much as 30–50 mg l<sup>-1</sup> of other salts.

Polymer sales is a bit like snake oil sales, only one doesn't drink it and they make no health claims. The typical polymer salesperson will approach your wastewater with a host of beakers and several chemical polymers (non-ionic, cationic, and anionic). The chemicals have high molecular weights and are mixed up on-site. The wastewater is placed in beakers, and aliquots of the polymers are added to individual jars to see which one comes up with the best visual appearance for floc size and settleability. It is a trial-and-error procedure, but one that is fascinating to watch.<sup>1</sup>

## 20.2 Sols

Before the invention of polymers and their application to wastewater, sols were used as an early form of coagulant aid. Silica sols are semi-stable emulsions generally made from sodium silicate. The sodium silicate solution is highly alkaline, and it is diluted with water to a strength of several grams per liter, and then the solution is back-titrated to a near-neutral pH with a combination of acid and cations or other anions including chlorine. Sols serve as a nucleating and weighting agent and can make a fragile floc substantially stronger and heavier. Sols are an inexpensive alternative to polymers. A brochure on the preparation

of silica sols can be obtained from the Technical Service Division of Philadelphia Quartz Company.

## 20.3 Flocculation and Mixing

Flocculation is also known as mixing. It is a slow, thorough, and low shear mixing. Thomas Camp, investigating the phenomenon back in the 1940s, found that the average gradient  $G$  is significant in mixing.

$$G = (P/V\mu)^{0.5}$$

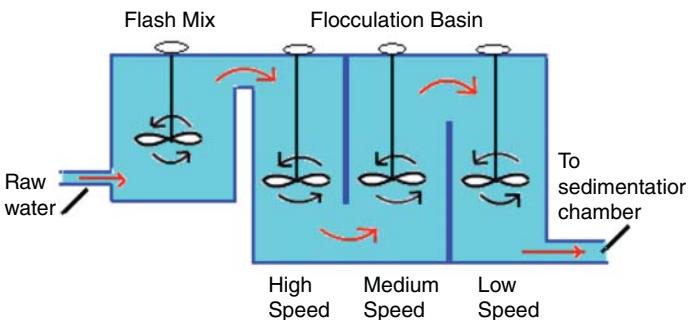
where  $G$  is in  $s^{-1}$ ;  $P$  is the power input in ft-lb/s (1 ft pound-force/second = 1.3558179 joule/second);  $V$  is the mixing chamber volume in  $ft^3$  (1 cubic foot = 28.316846712 cubic decimeter); and  $\mu$  is the absolute viscosity of the fluid in  $lbf\cdot s/ft^2$  (1 pound-force second/square foot = 47 880.259 cP).

Fragile flocs such as biological flocs use  $G = 10\text{--}30$ ; medium strength (turbidity) flocs use  $G = 20\text{--}50$ ; and chemical precipitation flocs use  $G = 40\text{--}100$ . For hydraulic mixing chambers use:

$$P = Qwh$$

where  $Q$  is the flow rate in  $ft^3/s$ ;  $w$  is the weight of fluid in  $lb/ft^3$ ; and  $h$  is the friction head loss.

Flocculators have slow mixing. Tanks with slowly rotating paddles, or other mixing devices including baffles and even air bubbles are adequate for the purpose (see Figure 20.3). The most common type is a center shaft with opposing paddles set transverse to the length of the flow. A good discussion on the issue can be found in the *Water Environment Federation Manual of Practice*



**Figure 20.3** Schematic of mixer and flocculator used in treating drinking water and wastewaters. Source: Courtesy: <https://chemistry.tutorvista.com/physical-chemistry/flocculation.html>.

Number 8 (WEF MOP#8). Several older water treatment books also contain good drawings of flocculators.

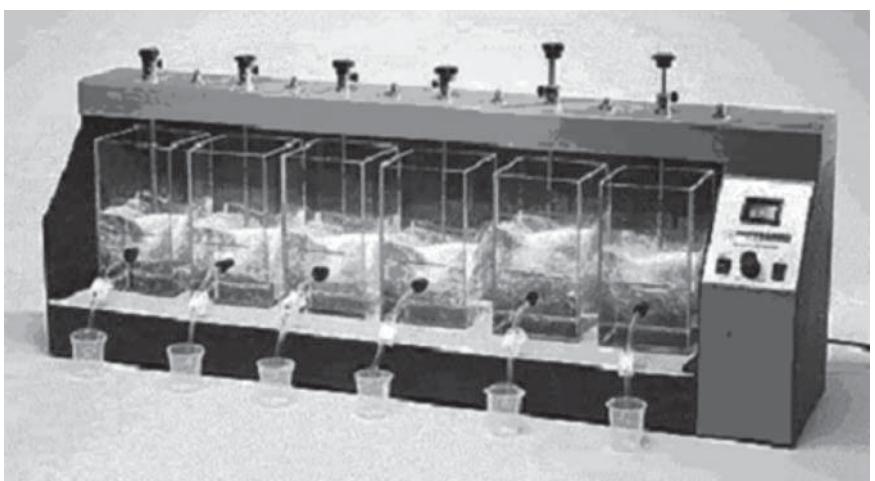
## 20.4 Practice

The key to good flocculation is the jar test apparatus. It is a multigang paddle stirrer. It is best used with medium- to large-sized beakers of 600–1000 ml.

After varying dosages of chemical addition, the paddle speed is turned up to give a flash mix and then turned way down to a very few revolutions per minute to promote floc growth. The best gauge is the visual formulation of the appearance of the floc and the clarity of the water. At the end of the flocculation, the paddle stirrer is removed and then the ability of the floc to settle and coalesce is examined.

Aliquots of the wastes are examined and further processed as may be necessary. One note of caution on settling tests: edge effects of the container can shape the performance of the material and provide false indications of the ability of a particular floc to behave in the desired manner. A minimum of 1 l should be used for this type of experiment, and large diameter vessels are better than small ones.

The jar testing apparatus shown in Figure 20.4 costs approximately \$3500.00 but it can be rented or leased if required. Otherwise, use clean glass stirring rods dedicated to each jar test and don't mix them.



**Figure 20.4** Photo of a Stuart Flocculation Jar Tester – 6 place. The model shown is manufactured by Cole Parmer: <https://www.coleparmer.com/i/stuart-flocculation-jar-tester-6-place-230-v/9955105>.

## 20.5 Modeling

There are at least three or four different theoretical models available for modeling coagulation. The models involve determining the particle sizes, the shear rate, dynamic viscosity of the fluid, and collisions per unit time. Unfortunately, most of these models require much more work to predict the results of a simple jar test than the running of the jar test, and the models are useful primarily as research tools.

A recent work by a PhD student at the University of Ghent and a conference on Population Balance Modeling indicate the status of the work in the field and how much knowledge there is, and how much is still to be gained.<sup>2</sup> Computational fluid dynamics is being applied to flocculation theory, but it is still difficult to predict the size and distribution of sizes of various types of flocs, let alone the number of collisions, and when Zeta potential is introduced into the equations, the effort rapidly becomes a substantial research problem.

## Notes

- 1 I had the opportunity to watch several polymer trials with representatives of various polymer sales companies. The most fascinating one was when I was in Katowice, Poland, and it was identical to the ones I had observed in the US, except the language was Polish. The procedures were identical, which speaks to the quality of the training of the Nalco representatives who conducted the testing.
- 2 Govorneau, Ruxandra. Activated Sludge Flocculation Dynamics: Online Measurement Methodology and Modeling [PhD Thesis], 2003–2004. Available at the Biomath Web site for the University of Ghent and Proceedings of the 2nd International Conference on Population Balance Modeling, Valencia, Spain, May 5–7, 2004.

## 21

# Heat Transfer Processes: Boilers, Heat Exchangers and Cooling Towers

All boilers and heat exchangers rely upon conduction and the development of a thin film of liquid to transfer heat. Cooling towers rely upon evaporative cooling to perform their assigned tasks. In this chapter we will look at heat exchangers and boilers more closely because their water quality limits tend to be much more restrictive than cooling towers.

## 21.1 Boilers

Boilers come in several types and configurations. The designations are for the US, and other countries may use different designations and pressure definitions for boilers. Low-pressure steam boilers generally have a working pressure of less than 15 psig (1 bar); they are used primarily for heating buildings such as schools, apartments, warehouses, and factories, and for heating domestic water. These boilers can be of fire tube, water tube, or cast iron sectional type. Boiler size will vary based on the quantity of steam required.

High-pressure steam boilers are used in generating electricity and in processing operations in industry; refineries and chemical plants use steam for petroleum distillation, stripping, dryers, and other processes. Steam is also used in water desalination. A high-pressure steam boiler operates at pressures above 15 psi and over 6 *boiler horsepower*. A “boiler horsepower” is defined as the evaporation of 34.5 lb (15.65 kg) of water per hour at a feed water temperature of 212 °F (100 °C).

A general comment on preferences of fire tube vs. water tube boilers: the energy stored in a fire tube boiler tends to be significantly more than in a water tube boiler. If the boiler is not maintained properly and fails, the mass of high pressure water and steam available from a fire tube boiler can cause a catastrophic explosion because the entire boiler contents are under pressure.

## 21.2 Boiler Classifications

### 21.2.1 Fire Tube Boilers

In this type of boiler, hot gases flow inside tubes that are submerged in water within a shell. Design operating pressures are about 150 psig (10.1 bar), producing up to 29 000 lbs (13 155 kg) of steam per hour, from 10 hp to 850 hp. Fire tube steam boilers may be either high- or low-pressure boilers. Three types of fire tube steam boilers are the *horizontal return tubular boiler*, the *scotch marine boiler*, and *vertical fire tube boilers*.

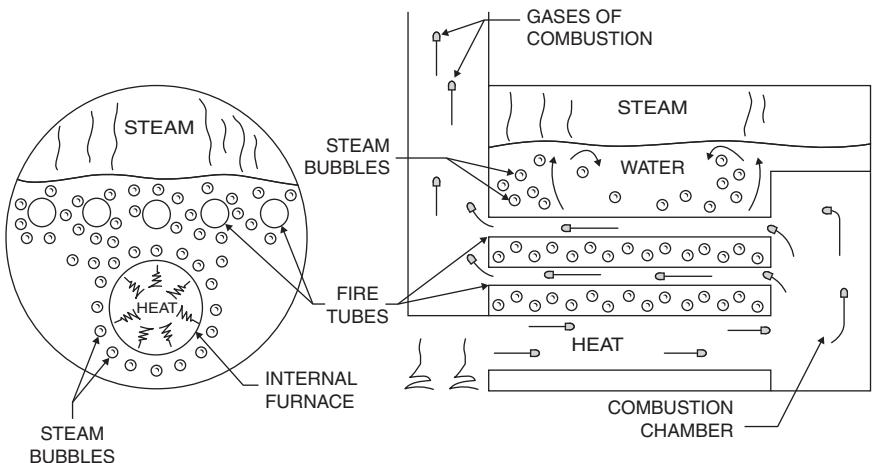
A schematic of a fire tube boiler is shown in Figure 21.1.

### 21.2.2 Water Tube Boilers

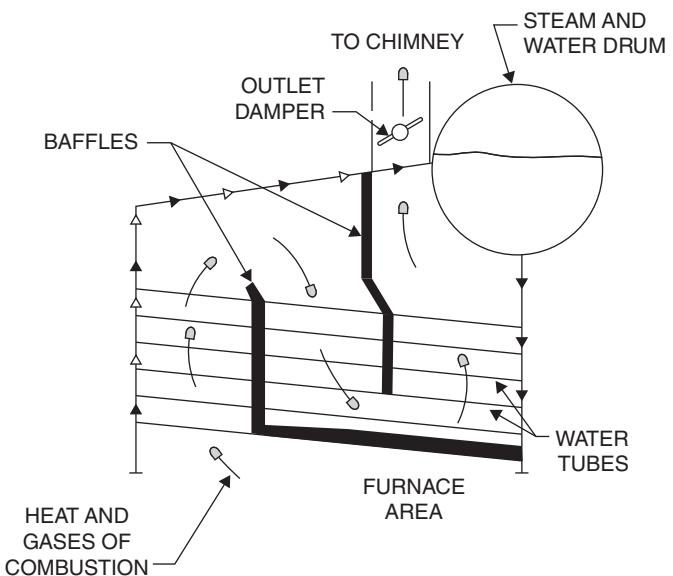
Water flows through tubes that are surrounded by hot combustion gases in a shell. The steam bubbles that form at the heated surfaces rise and finally break through the water surface in the steam and water drum.

Water tube boilers are rated from about  $2000 \text{ lbs h}^{-1}$  ( $900 \text{ kg h}^{-1}$ ) to  $10 000 000 \text{ lbs h}^{-1}$  ( $4.5 \times 10^6 \text{ kg h}^{-1}$ ) steam. They have been designed to operate at pressures as high as 3206 psi (220 bar), also known as the critical pressure of steam – the point at which the density of the water and steam is the same. The arrangement of the tubes and the water drums determines the designations and the type of instrumentation and controls for the boiler. The classifications are A, D, and O. Figure 21.2 shows a typical arrangement for a simple water tube boiler.

The gas is heated in the furnace area and is passed across and around the water tubes to heat the water. One common feature of all water tube boilers is



**Figure 21.1** Schematic of a fire tube boiler.



**Figure 21.2** Water tube boiler schematic.

a mud drum. The mud drum collects sediment and suspended solids to help prevent the solids from building up in the boiler tube. Boiler blowdown generally occurs through the steam drum or the mud drum, and its purpose is to remove the solids buildup arising from the evaporation of water and from use of chemical additives.

### 21.3 Boiler Water Quality Requirements

The water quality requirements for a boiler depend upon the pressure and temperature of the operating conditions and the end use of the steam. The American Society of Mechanical Engineers has published standards for boiler water quality based upon operating pressure.<sup>1</sup> The ASME Water Boiler Water Quality Table (Table 21.1) is supplemented by recommendations for boiler operating water quality from a boiler manufacturer seen in Table 21.2. Other companies may have slightly different requirements for their turbines.

Note: In all cases one must check with the boiler manufacturer as the final determinant of water quality requirements. The information in Table 21.2 is presented for general guideline purposes only.

1. Boiler and turbine manufacturers recommend that the total dissolved solids (TDS) should not exceed 100 mg/l total.

**Table 21.1** ASME guidelines for water quality in continuously operated water and fire tube boilers.

Boiler feed water				Boiler water		
Drum pressure pounds/sq in.	Iron as Fe mg/l	Copper as Cu mg/l	Total hardness as CaCO <sub>3</sub> mg/l	Silica as SiO <sub>2</sub> mg/l	Total alkalinity as CaCO <sub>3</sub> mg/l	Specific conductance in $\mu\text{Mhos}/\text{cm}$ unneutralized
0–300	0.100	0.050	0.300	150	700	7000
301–450	0.050	0.025	0.300	90	600	6000
451–600	0.030	0.020	0.200	40	500	5000
601–750	0.0025	0.020	0.200	30	400	4000
751–900	0.020	0.015	0.100	20	300	3000
901–1000	0.020	0.015	0.050	8	200	2000

**Table 21.2** The recommended guidelines for steam purity limits for both startup and continuous operation of steam turbines.

	Continuous	Startup
<b>Conductivity</b> (micromohs/cm at 25 °C):		
Drum	0.3	1.0
Once through	0.2	0.5
SiO <sub>2</sub> (ppb, max.)	20	50
Fe (ppb, max.)	20	50
Cu (ppb, max.)	3	10
Na + K (ppb, max.)		
Up to 800 psig (5516 kPag)	20	20
801–1450 psig (5517–9998 kPag)	10	10
1451–2400 psig (9999–16 548 kPag)	5	5
Over 2400 psig (over 16 548 kPag)	3	3
Chlorine (ppb, max.)	10	10–30

Source: Adapted from Table 9.2 of NEMA SM23-1991 with the chlorine limit values added.

2. Consult the turbine and boiler manufacturers for limits on other contaminants.

The point of the previous tables is to indicate that extreme caution must be taken when designing or specifying a treatment system for boiler feed waters. Boiler steam is most often recycled as condensate, and the solids in the system

will accumulate and ultimately deposit solids on the inside of the boiler tubes and the drum, decreasing the heat transfer.

The total solids in the boiler are controlled by blowing down the drum (wasting part of the water in the drum), and replaced with "clean," treated water which helps meet the quality requirements.

Two of the greatest concerns in boilers is the hardness and the silica content. Silica is of a particular concern where there is high-speed rotating equipment such as a turbine. Silica will create deposits on the turbine blades, and in extreme cases could cause the turbine to go out of balance.

Of particular concern in all boilers is the presence of dissolved oxygen. In general, the concentration of dissolved oxygen in the boiler water feed should be less than 7 parts per billion ( $7 \mu\text{g/l}$ ). In order to help achieve this level of dissolved oxygen, many boilers have preheaters on their feed water. The general range of the pH should be between 8.5 and 9.5. Often sodium sulfite is added to the boiler water to scavenge dissolved oxygen, and a polyelectrolyte is also added to help prevent iron deposition.

Monosodium phosphate can consume sodium hydroxide and lower boiler water pH. Trisodium phosphate reacts with water to form a caustic solution that raises boiler water pH. Chelating compounds such as ethylamine diamine tetraacetic acid, EDTA salts, and virtually all biochemicals exhibit the ability to dissolve certain metal cations. Thus, proteins, polysaccharides, and polynucleic acids are excellent polydentate ligands for many metal ions. Organic compounds such as the amino acids glutamic acid and histidine, organic diacids such as malate, and polypeptides such as phytochelatin are also typical chelators.<sup>2</sup>

Caustic embrittlement of boiler tubes can occur at points of greatest stress within the boiler. Caustic embrittlement occurs along the grains of the metal, and has a characteristic pattern that can be observed by microscopic examination. When it occurs, caustic embrittlement can cause rupture of boiler tubes, often with catastrophic consequences.<sup>3</sup> Caustic embrittlement of boiler tubes and steel is a definite challenge. For low-pressure boilers, sodium nitrate is used for embrittlement control. For higher-pressure boilers, a combination of pH and phosphate levels is used for embrittlement control.

Hydrazine and hydroquinone are often used to passivate the iron surfaces on the inside of a boiler. Hydrazine is soluble but volatile and is a potential carcinogen. Hydroquinone is a phenol derivative and may be bioaccumulative in aquatic environments. In both cases, caution should be used when sampling waters containing either compound.

The foregoing indicates that the wastes coming from boiler blowdown will have a variety of salts, silica, iron, amines, and other compounds. Aquatic toxicity of boiler blowdown may be a wastewater permitting problem, and one of the best solutions would be to discharge the wastewaters to a wastewater treatment plant – the successive dilution and biological activity of the plant will

consume the compounds, except nitrate and phosphate, but with additional post-treatment efforts, those compounds can be treated as well.

A source for information on effluents from large-scale power plants is the following EPA website: [https://www.epa.gov/sites/production/files/2015-06/documents/steam-electric\\_detailed\\_study\\_report\\_2009.pdf](https://www.epa.gov/sites/production/files/2015-06/documents/steam-electric_detailed_study_report_2009.pdf).

## 21.4 Cooling Towers

Cooling towers are almost insensitive to water quality. Occasionally, they have been used as aeration systems for wastewater treatment plants. However, in most cooling tower applications, growth of bacterial slimes and bacteria, corrosive oxidation of the tower internals, and the chemical attack of in-plant heat exchangers and piping is a critical water quality requirement.

Factors that principally influence water loss in a cooling tower include: wind drift, relative humidity of the air, temperature difference between the air and the fluid, the amount of heat to be rejected by the cooling tower, the number of cycles of cooling tower water use, and the amount of blowdown and makeup water removed from and added to the tower. Drift losses from a cooling tower generally range from 1–3%, and evaporative losses depend directly upon the heat dissipated. The number of cycles in the tower is calculated by dividing the makeup water flow by the sum of the drift losses plus the blowdown. A second method of calculating cooling tower cycles is measurement of chlorides in the circulating water divided by the chlorides in the makeup water. For many cooling towers, one of the limiting factors in cooling tower operation is the concentration of silica in the tower water. If there is ammonia in the process water, and phosphates and magnesium (common in some groundwaters), then struvite formation ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) is a distinct possibility. Struvite can form hard deposits, reduce the efficiency of the cooling tower, and create deposits in heat exchangers in the associated processes.

Cooling towers are oxygen-rich environments because of the aeration and heat loss of the cooling fluids, and the presence of dirt, pollen, and other air pollutants which the tower pulls from the local air environment. As such they are an ideal location to support bacterial growth and provide a high dissolved oxygen atmosphere, which will help corrode metals and wood in the tower. At one time cooling towers utilized Californian redwood slats because they were rot-resistant. Now, however, many towers are made from aluminum or steel, and the passivation of the metal is extremely important.

Cooling tower waters contain bacterial inhibitors, generally quaternary ammonia compounds and/or heavy metals as passivators. A passivator is added to cooling tower waters to form a protective coating on the metals to prevent corrosion. In most cases the passivator contains compounds that form an oxide coating on the tower internals to resist oxidative corrosion.

At one time, hexavalent chromium was the preferred passivator/inhibitor because it was relatively cheap and effectively passivated the tower metal and the connected heat exchangers and piping, and prevented bacterial growth in the tower. Hexavalent chromium is highly toxic to aquatic life, was banned in comfort (air conditioning) cooling towers, and finally banned in all cooling towers in the US during the 1990s. Europe banned the use of hexavalent chromium in 2003. For a time, antimony compounds became a replacement for Cr(VI). Antimony is also quite toxic, but less so than hexavalent chromium.

Other chemicals used in cooling tower passivation include polyphosphate, organic phosphate, and orthophosphate compounds, zinc, molybdenum, and nitrite. Nitrite is not effective in open tower systems because it promotes bacterial growth and does not form the required protective film. Cooling tower operating pH should be between 6.5 and 8.5, and hardness of the water should be at least  $30 \text{ mg l}^{-1}$  to up to  $400 \text{ mg l}^{-1}$ , depending upon the recommendations of the tower manufacturer.<sup>4</sup> The phosphate levels are generally several hundred  $\text{mg l}^{-1}$ . There has also been some interest in passivation using Cr(III) because it provides only slightly less passivation than Cr(VI), but the potential for oxidation of Cr(III) to Cr(VI) will be pH-dependent.

Treatment of cooling tower wastewaters will have to contend with high levels of phosphate; treatment with iron or aluminum salts is recommended to precipitate the phosphates in the tower blowdown prior to the time it gets to the treatment plant. The discharge of high phosphate to treatment plants should be avoided as it can cause problems downstream. In all cases, it is a good idea to inspect the safety data sheets supplied by the chemical service company.

## Notes

- 1 <https://www.scribd.com/doc/54927629/ASME-Guidelines-for-Water-Quality-in-Modern-Industrial-Water-Tube-Boilers>.
- 2 <https://courses.lumenlearning.com/boundless-chemistry/chapter/reactions-and-applications-of-coordination-compounds>.
- 3 For fire tube boilers, caustic embrittlement is a significant item of concern. The water tube boilers are essentially large pressure vessels, where a failure in the shell would have disastrous consequences because of the quantity of energy released when the shell fails. A tube failure in a water tube boiler has a much lower potential disaster profile.
- 4 <https://www.coolingtowerchemicals.com/Cooling-Tower-Cleaning-s/66.htm77>.

## 22

# Evaluating an Existing Wastewater Treatment Plant Design using Modeling Software

This is a description of how to set up a model of an existing plant or designed plant and determine its capacity using modeling software.

The original of this document was related to the development using wastewater treatment (WEST<sup>®</sup>) software, now produced by the Danish Hydraulic Institute (DHI). I have attempted to adapt it to more generic modeling efforts, and if one follows the principles and steps, you should be able to use almost any commercial software designed for the purpose.

By following the steps outlined below you will be able to set up and run a model and match either existing conditions or proposed conditions.

The steps are:

1. Information gathering
2. Model selection
3. Laboratory and other data organization
4. Flow sheet setup and model organization (getting the flowsheet right)
5. Model compilation and setup
6. Input and output file preparation
7. Initialization of the model parameters and first runs
8. Parameter adjustments

In the following text material, that which is specific to WEST software is in *italics* but may be generally applicable to other wastewater treatment plant modeling software.

## 22.1 Step 1: Information Gathering

Your objective is to make a model that represents a form of reality. That reality may represent either the dynamic behavior of a new facility, or the dynamic behavior of an existing facility. The purposes are predictive, and or historical. In the first case, you may want to find out how the facility will work and whether a specific design is adequate. In the second case you may be looking to duplicate

the performance of a real plant by preparation of a model and matching the data from the model to the data from the real plant. In this latter instance, you can then use the data to predict future performance or investigate plant modifications.

Modeling is a very good but imperfect process. When you are dealing with an existing facility, you will almost never have enough information about the facility to satisfy your model and requirements. You will have to make some intelligent and reasonable guesses at certain things. You also may never know all that you want about a particular facility, but at the same time, you may know more about the facility than you ever dreamed of knowing, because the data are often in the wrong place or of the wrong type. It will be easier to make assumptions about a new facility than to model the behavior of an existing one.

This is not quite an “abandon all hope, ye who enter here” type warning, but rather a practical admission that you will be trying to reconstruct an event or make estimates of what may be happening with a model in an imperfect world.

What you will need:

- An initial idea of which model you might want to use and the requirements of that model.
- Plant drawings and flow sheets.
- Aerator sizes and capacities.
- Physical dimensions of units.
- Maximum flows to each unit. This is particularly important in pumped flow situations where you have a maximum capacity on the size of the pumps. Locations include clarifier underflow, and in nitrification plants, the return rates or recirculation rates for the system.
- Chemical data on the plant:
  - Influent data
  - Effluent data
  - Water quality data and effluent requirements
  - Internal plant operating records and logs
  - Chemicals added and operating set points

If you have read the discussion of biochemical oxygen demand (BOD) and COD relationships, you may begin to realize that the most of the models are based on COD and most of the data you have are BOD. You may have to go back into the laboratory for more information in order to establish the necessary correlations to create the partition for the influent file.

*Some software platforms speak BOD, others only COD, and still others have a BOD to COD transformer. Be advised that the transformers make fractionation decisions on the BOD data and some of the COD data. These are made to transform the data into a form usable for the models. The transformer assumptions*

*about the way in which the BOD and COD are fractionated for the influent file may or may not accurately represent your waste stream. Also, the relationships (parameters and fractions) may change over time and with temperature and other influences. The program does not make those changes.*

If you are working on a new design, you have liberty to make many choices about the type and kind of data you use.

Depending upon the need for accuracy and performance, you may have to go into the laboratory and reproduce oxygen uptake rate (OUR) data, as well as yield and specific growth data, and also data for settling characteristics. If you are not going to be reproducing data from an existing plant, the effort at gathering detailed data may not be worth the trouble or expense.

A major caution should be raised here. If you are seeking to model any type of industrial waste, you should probably perform some minimum characteristics testing, and should include some pilot plant testing as well as testing for settling characteristics, as the issue of toxicity and hindered settling can often be associated with industrial waste treatment systems.

## 22.2 Step 2: Model Selection

Table 22.1 lists the input variables to each of the three principal activated sludge models: ASM1, ASM2d, and ASM3.

Model ASM1 is the oldest and has the most history behind it. It can be used for nitrogen removal in biological nutrient removal plants. ASM2 and ASM2d were formulated later to consider the specific ability of the cell to store food materials. ASM2d is formulated to allow the addition of metal hydroxides for phosphorus precipitation.

The ASM3 model is the newest. It was formulated to address some of the deficiencies and difficulties with ASM1 resulting from assignment of the COD fractions of the influent. (See the discussion on COD and BOD and preparation of the influent file.)

*For most of the data below the concentration units are in mg l<sup>-1</sup>, and in specific concentrations of the elements. For example, flow is in mass units/time, but COD is in mg l<sup>-1</sup> or g m<sup>-3</sup>.*

A comment on the use of the models is in order here. ASM3 is the newest of the models, but many in the modeling community do not like it because of its formulation and have expressed that the lumping of wastewater fractions and overall formulation of the model away from observed cellular behavior is objectionable. Others have described the previous lot as unnecessarily fussy. The difference in model formulation between ASM1 and ASM3 is substantial.

**Table 22.1** Input variables to each of the three principal activated sludge models.

Name of variable	Description
<b>ASMI</b>	
H <sub>2</sub> O	Water
S_I	Inert soluble matter
S_S	Readily biodegradable matter
S_O	Dissolved oxygen
S_NO	Nitrate and nitrite
S_NH	Ionized and un-ionized ammonia
S_ND	Soluble biodegradable organic nitrogen
S_ALK	Alkalinity
X_I	Inert particulate matter
X_S	Slowly biodegradable matter
X_BH	Heterotrophic biomass
X_BA	Autotrophic biomass
X_P	Particulate products resulting from biomass decay
X_ND	Particulate biodegradable organic nitrogen
<b>ASM2d</b>	
H <sub>2</sub> O	Water
S_I	Inert soluble matter
S_O	Dissolved oxygen
S_N <sub>2</sub>	N <sub>2</sub>
S_F	Fermentable, readily biodegradable organic matter
S_A	Fermentation products considered to be acetate
S_NO	NO <sub>2</sub> <sup>-</sup> and NO <sub>3</sub> <sup>-</sup> nitrogen
S_PO	Inorganic soluble phosphorus, primarily ortho-phosphates
S_NH	Ammonium nitrogen, NH <sub>4</sub> -N
S_ALK	Alkalinity of the wastewater
X_I	Inert particulate matter
X_S	Slowly biodegradable matter
X_H	Heterotrophic biomass
X_PAO	Phosphate-accumulating organisms: PAO
X_PP	Poly-phosphate
X_PHA	A cell internal storage product of phosphorus-accumulating organisms
X_AUT	Autotrophic biomass
X_TSS	Total suspended solids, TSS
X_MeOH	Metal hydroxides
X_MeP	Metal phosphate, MePO <sub>4</sub>

(continued)

**Table 22.1** (Continued)

Name of variable	Description
<b>ASM3</b>	
H <sub>2</sub> O	Water
S_I	Inert soluble organic matter
S_S	Readily biodegradable organic substrate
S_O	Dissolved oxygen
S_NH	Ammonia
S_N <sub>2</sub>	Dinitrogen
S_NO	Nitrate
S_ALK	Alkalinity
X_I	Inert particulate organic matter
X_S	Slowly biodegradable substrates
X_H	Heterotrophic organisms
X_STO	Cell internal storage product of heterotrophic organisms
X_A	Nitrifying organisms
X_TS	Total suspended solids

Quoting and paraphrasing from the International Water Association (IWA) description of ASM3 and ASM1 differences:

- ASM1 does not include kinetic expressions that can deal with nitrogen and alkalinity limitations of heterotrophic organisms. The result is that computer code cannot be based on the original form of ASM1 where, under certain circumstances, negative concentrations of ammonia may occur.
- ASM1 includes biodegradable soluble and particulate organic nitrogen as model compounds. These cannot be easily measured.
- ASM1 differentiates inert particulate organic material depending upon its origin, influent or biomass decay, but it is impossible to differentiate these two fractions in reality.
- ASM1 does not directly predict the MLSS concentration.
- In ASM1, hydrolysis has a dominating effect upon prediction of oxygen consumption and denitrification by heterotrophs. In reality, the process contains a number of coupled reactions.

So ASM3 is a different model formulation altogether.

*In WEST, the nomenclature for total suspended solids (TSS) has recently been changed from X\_TS to X\_TSS. This changes the differentiation between modeling using ASM2 and ASM3.*

## 22.3 Step 3: Laboratory and Other Data Organization

The objective is to gather enough data to be able to make an estimate of the magnitude and change in the flow sufficient to characterize the waste stream and its elements.

Depending upon the model you are planning to use, you may have to go into the laboratory and obtain additional information. The number of samples and complexity of the sampling program is up to you and the budget you have available. We have observed everything from 12 to 15 samples run to establish some basic correlations, to a complete sampling campaign using automated equipment which allows the collection and analysis of up to six sampling points and multiple analyses for each sampling location.

It is difficult to provide specific guidance on an unknown waste stream, but it would be nice if the laboratory data one obtained were reproducible to within about 10–20%. The entire discussion of precision and accuracy and the number of samples required therein is outside the scope of this chapter.<sup>1</sup>

Here are some suggestions for running ASM1 and ASM2 and 2d testing from a proposal to a client:<sup>2</sup>

Any modeling or characterization effort requires a substantial amount of data. In this instance, we will probably need access to the plant analytical and operating records, chemical addition and other records for at least 6 months, and perhaps a full year. The scope of the request is somewhat more extensive than the description might indicate, as it includes such routine operating data as the pump characteristics and rate, hours of operation, timing of the operations, aerator horsepower, and hours of operation for each day, etc. The data should also include the quantity and type of chemicals used at various parts of the plant.

Wastewater characteristics are divided into several elements. The principal elements include

- Total and filterable COD
- Total and filterable TKN
- Total ammonia and nitrate
- TSS and VSS
- Total phosphate, filterable phosphate, and orthophosphate
- Alkalinity
- Volatile fatty acids (measured as acetate) (for ASM2 and 2d only)

Analyses should be run in parallel with routine influent and effluent analyses for a period sufficient to determine reliable parameter variation and fractionation with routinely measured variables.

A sampling campaign of between one and two week's duration is suggested for the wastewater characterization study. The study should collect and

analyze daily composite samples on influent and effluent. The study should be conducted in parallel with the routine sampling data being collected at the plant now.

Automatic sampling equipment that collects hourly grab samples of water and wastewater is often as good as can be obtained in a sampling campaign. Daily composite samples can be used, but are often unreliable because the waste stream fluctuates with time and composite data will mask the diurnal and other variations.

Flowmeter readings are often unreliable, even when the flowmeter works. Calibration and inspection is suggested. For Internal calibration, you will need some data relating to TSS and VSS (filtered and unfiltered in various parts of the plant), along with DO measurements, and possibly some respirometry data, recycle rates, sludge levels in the clarifier, sludge wasting data, and just about everything you can imagine that an operator would need to run the plant properly. The trouble is that the data often do not exist, or exist in the wrong form.

An example might be a notation in the plant operating log – “wasted sludge for two hours.” That tells you that the operator wasted sludge for between 1.5 and 2.5 hours, but nothing else unless you have either the valve settings, and the MLSS at the time of the wasting. If you are fortunate, you will find that he took an MLSS sample immediately before or after the wasting. If not, you may have to guess from the pump flow rate and talking to the operator. The key is that the operator almost always has a favorite method of operation which can often be recovered. He or she may know that if they turn the valve wide open, something will happen which will cause them work down the way, and so they leave the valve partially shut so that he or she doesn’t have to clean up the floor of the sludge treatment facility.

The operation of the aeration equipment is often manual as well. It is safe to assume that about the only instrumentation you may find is the flowmeter, and that may not even work.

### 22.3.1 Generating the Flows Without the Data

*In instances where you have only BOD data, or BOD, COD and TSS data, many programs have a BOD transformer and/or a BOD/COD transformer that can be used to fractionate the flow into the necessary components.*

*Sometimes, you may only have only one grab sample of the plant influent per day, plus some TSS and TKN data, you may have to generate the data for the input file using either the sinusoidal waste flow generator or a double sinus flow generator, or even an Excel spreadsheet. (See the other notes on construction of an influent file for instructions. You may have to plot the BOD, COD, TSS, and other data.)*

If you have little data and have to generate dynamic and/or diurnal flow patterns from your source, you may want to use a sinusoidal pattern for generation of the data. All good books on environmental engineering have

some form of generic flow pattern for domestic wastewaters. Rationally speaking, the flows are often highest between 9 a.m. and 4 p.m., and lowest in the early morning hours when most people are asleep. Often there is a secondary peak in flow associated with the dinner and early evening hours when food preparation is the greatest.

You may want to look at your time data at the time it was collected from the influent and try to fit a time curve with each flow and concentration element, to see whether there is any variability in the data and to determine whether you need to have the biosolids and chemical composition run counter or with the hydraulic basis.

The following example may help to explain this point.

Assuming that a process discharges a uniform concentration of material, and the flow varies. Then the concentration of contaminants would vary directly with the flow. If, however, the process discharged at a constant rate and contaminant level, and if we add periodic boiler blowdown and filter backwash to the waste stream, and some kitchen waste water (which peaks from about 1–2 hours either side of mid-shift), then the flows and the concentration may vary inversely with each other or may spike at mid-shift. It may depend upon the quantity of blowdown and backwash.

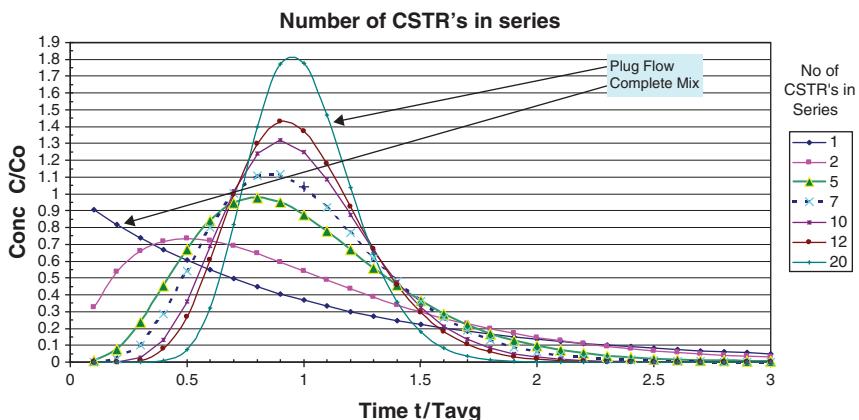
### 22.3.2 Getting the Hydraulics and the Tankage Correct

As part of the overall process, and before you set up the flow sheet, you will need to address the issue of hydraulic similitude for the system. This is really an issue of comparing how well the model you are using matches the hydraulic performance and hydraulic mixing of the system you are modeling.

The best way to determine how well your system is performing is to conduct dye or tracer studies on the tank system. The purpose of the dye testing is to find out whether you are operating in a plug flow regimen, or a complete mix, or some other regimen. The difference between the two regimens is shown in Figure 22.1. Peak concentrations close to average time ( $1.0 \text{ Time } t/T_{\text{avg}}$ ) and higher concentration factors ( $\text{Conc } C/C_o$ ) indicate stronger correlations to plug flow. The difference between plug flow and complete mix is significant, and the characteristics and behavior of the two types of systems are quite different.

If you cannot perform dye testing to determine the mixing requirements, you should examine the system you are modeling carefully. There may be some logical divisions in the system that suggest that it should be modeled using a specific number of tanks. For example, an extended aeration system such as an oxidation ditch may have a number of aerators, and the physical positioning of the aerators may suggest a logical number of tanks to use for modeling the flow.

Each tank or tank division will have its own aeration capacity (Kla) which can be adjusted. Multiple aerators may suggest a configuration that needs more



**Figure 22.1** Labeled flow sheet: number of completely stirred tank reactors (CSTRs) in series. For long narrow tanks that attempt to model plug or linear flow, it is important to utilize more than two CSTR modeling tanks in series. Three or four tanks in series is the optimum that can be modeled; using more than four tanks in series will increase the computational time and slow down the modeling effort.

than one tank, and an interlaced flow diagram to suggest the right type of flow connections. This is a matter to be settled by the judgment of the engineer.

At this point it may be a good idea to rough out the flow sheet for your model. This is also a first draft of the process and instrumentation diagram or P&ID. It may not be detailed but rather simple. You can always fill in controls and details later when you set up the compositional model.

#### 22.3.2.1 When You Cannot Dye-test Your Tanks – a Procedure

In Chapter 7 we discussed the difference between BOD and COD. It is important to remember the difference and how each is determined. If BOD and COD are discussed in the software manual, it is imperative that you understand how these parameters are employed in the model.

A correlation that relates the internal mixing characteristics (number of compartments or stages) to the physical properties (for diffused air systems) was used. The correlation, in SI units, is  $N = 7.4 Q_S ((1 + R) L / WH)$ , where

$N$  = number of compartments;

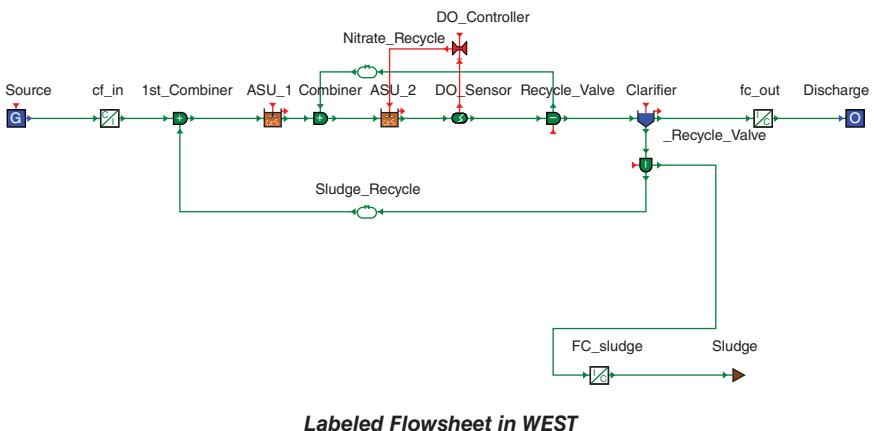
$Q_S$  = flow,  $\text{m}^3 \text{s}^{-1}$ ;

$R$  = RAS ratio;

$L$  = length, m;

$W$  = width, m; and

$H$  = depth, m.



**Figure 22.2** Example of a simple flow sheet. Note that the Combiners are only mathematical methods for combining one or more inputs from other operations. The boxes labeled cf\_in and cf\_out are units to convert concentrations into and out of mass flux used in the model, and have no physical existence.

This formula was first published by Chambers.<sup>3</sup> The values have to be in the overall range of the following:

$$28 < L < 500$$

$$2 < W < 20$$

$$2.4 < H < 6$$

$$0.7 < R < 1.5$$

$$1.3 \text{ hours} < t < 3 \text{ hours}$$

$$\text{where } t = 3600 \times Q \times (1 + R)$$

A simple flow sheet is shown in Figure 22.2.

Note that when you set up the model in the software platform there are a number of ways that you can set up the tanks for various activated sludge model configurations. This was designed with similitude in mind. If you set up individual tanks you can select from pumped flow, variable volume, and constant volume options, and each has its own variations. The pumped flow and constant volume options are somewhat self-explanatory. The variable volume corrects for the presence of an effluent weir, and you will supply the weir formula in the simulator.

Before you proceed to Step 4, it might be a good idea to review the models guide that comes with the software platform. There are a number of different models in your modeling software platform, and the selection of the right model can greatly assist your work and help insure a satisfactory outcome.

Clarifier selection is also an important choice both for the model and the complexity of the models. What follows is largely personal opinion about the process and which models to use for the setup of your experiments.

*For a primary clarifier, you may want to consider the Lessard-Beck model or the OttorpolohFreund, or Primary Point Settler, if they are available.*

*For a simple system where suspended solids in the influent or effluent are not an issue, use a point-settling model for a clarifier. It has no volume, but you can control the amount of solids flowing over the clarifier effluent weir as a decimal fraction of the total suspended solids in the clarifier. Note that if you are investigating a membrane bioreactor, or a DAF unit, or even a centrifuge, where the percentage of solids recovered is known or can be estimated, the point settler can be used with great efficiency and accuracy.*

*For a secondary clarifier, and even multiple clarifiers, you may want to consolidate the area of the clarifier into one large unit with equivalent area and volume and use a Takacs clarifier, but not the Takacs reactive or propagator model clarifiers. The Takacs clarifier subdivides the clarifier into 10 layers and assumes that the waste is in the middle layer. The top layer goes out over the effluent weir, while the bottom layer goes into sludge. The reason not to use the Takacs reactive and propagator clarifier models is that each layer of the model needs to be initialized, and that often needlessly complicates the model and the workload. With the reactive and propagator models, you will have to supply many more parameters (approximately six times more parameters) than for the non-reactive model.*

*The MarsiliLibelli clarifier can be used as a sludge thickener, but before doing so, additional research and reference to the model is suggested.*

## 22.4 Step 4: Flow Sheet Setup and Model Organization

Start with your elemental drawing and put the basic icons in place. Annotate it with the details you need to prepare the drawing of the plant so that it reflects the P&ID as shown above. Then open the compiler and begin your work.

*Preparing a P&ID in your modeling software is essentially a three-pass process; you may want to see the help guide, the User's Guide, and the Quick Tour for assistance in completing these steps. The easy thing to remember is that the right click on the mouse gets you additional tools in model building, and double-clicking on the models gets you to their setup areas.*

1. *The first pass puts the critical elements in place.*
2. *The second pass is to give the models their names and select the models. The selection of specific models is discussed briefly below.*
3. *The third pass is to make the connections between the models. Make sure that your directions and connections are right and properly connected.*

*A word of advice on naming the influent file might be helpful here. If you name the influent file with a long name, you will find that the columns in your data files get extremely crowded, as WEST uses the name of the influent icon in the program to name the file for both the input and the output files in the data headers. Select a simple and short name and you will be much happier.*

*Before starting the build and parsing processes, take a good look at your flow diagram and double-check it to make sure that all the connections are connected, and that wherever you have a loop, you may need a loop breaker.*

*Some models use concentration to flux (C/F) conversion systems. This is an additional area to watch out for. WEST uses C/F and F/C conversion programs to change concentration data into mass flux data for the output files. If you do not have the C/F and F/C converters in place or have not selected the correct type of input or output file to match the converter, you may get an error message that tells you that you have an “incompatible nature.” It is not being insulting or demeaning to you, just telling you to check your input and output files to make sure that they are matched for flux or concentrations.*

## 22.5 Step 5: Model Compilation and Setup

Setting up a model in the simulator is a multi-part process. The parts include:

1. Initial definition of the model critical model parameters
2. Initialization of the variables
3. Setting up the integrator

Start by initializing the model. First start with the parameters. Most of them are biological parameters which you will not have to adjust, and probably should not adjust.

Concern yourself with the physical parameters first. You will want to set things like tank volumes and make initial guesses to determine the oxygen transfer rates (called the K<sub>la</sub> in many models), suspended solids levels in the tanks, and various other parameters. (Often the K<sub>la</sub> will be specified based upon characteristics of particular aeration systems or types of equipment.)

You will also have to go through and make an estimate as to the initial operating conditions for the reactors by going into the variables and filling them out.

One of the other types of errors that can be generated in ASM1 particularly is *negative ammonia*. Negative ammonia is caused by an unbalanced waste in the model. The configuration of ASM1 is such that it does not have a “trap” for negative ammonia, and what the model is really saying is that the feed conditions are such that the ammonia is being consumed at a faster rate than it is being supplied by degradation of the organic material in the waste. Obviously it is an impossible condition, but the model doesn’t know the difference. Sometimes the autotrophs in the waste are too high, and a simple adjustment in the feed will correct that problem.

This is one reason why it is often more convenient to set up and run a steady-state model for the initial run. The steady-state system allows you to balance the model before you begin dynamic modeling.

### 22.5.1 Initial Values versus Derived Values

After the steady-state model is balanced and running properly, and after you have set the various values to the approximate levels you will need for your initial conditions, it is then time to go back and recalibrate the model using your derived state variables. The purpose of this is to bootstrap the model with the values you will be using rather than wait for it to reach equilibrium.

### 22.5.2 Integrator Settings

The settings of the integrator is often a matter of choice. The defaults are often set for RK4 (Runge Kutta fourth order) because it is fast and gives closure over a wide range of models. Set the number of iterations to be a very large number. Set the size of the increments to be about a tenth of the value of your increment available in the influent file. This is a very rough estimate, but it will provide you with a smooth curve and reasonable response to changes. Coarser settings on the integrator will provide a more angular graphical output. Small steps in the integrator, combined with high precision, will cause the model to run slower.

## 22.6 Step 6: Input and Output File Preparation

Often, the modeling platform will discuss the preparation of influent and output files. The influent file is a spreadsheet containing time-stamped concentrations of the model input parameters. Depending upon the amount of information available, the influent file can have many rows, one for each influent parameter. The effluent or output file will contain a complete list of the predicted final concentrations of the components on the input file, plus other important characteristics based upon the model formulations.

For all initial modeling applications, it is strongly suggested that the initial model should be set up with a steady-state case. This will allow the fine-tuning of various variables and parameters before the dynamic data are utilized. The preparation of the steady-state influent file has been discussed.

## 22.7 Step 7: Initialization of the Model Parameters and First Runs

The first run of a model may produce unexpected results. *In some programs, when values are outside expected ranges, warnings are issued.*

The unusual results are not unexpected, and to some extent, that is why one sets up a static model first. When the static model has been evaluated and balanced, it is then necessary to use the final values for variables and modify them to represent starting variables for the first runs.

### 22.7.1 What to Balance or Adjust

There are a limited number of things that can be adjusted in most models. They include:

- Primary clarifier underflow rate (removes solids)
- Oxygen transfer rates ( $K_{la}$  values) for each tank
- Flow proportion in each tank (if flow sheet permits)
- Recycle rate on loops (can take almost infinite adjustment)
- Secondary clarifier underflow (increases sludge return and improves effluent solids)
- Sludge wasting rate (decreases solids in the system)

*Adjustment of the rate coefficients and parameters is not recommended on initial runs!* Adjusting these coefficients prematurely may mess up your results in later runs.

### 22.7.2 What to Key in on During Your Modeling

It is important to examine the same measurements as the plant operator uses for control of the wastewater treatment plant: suspended solids, oxygen levels, sludge wasting rates, hours of operation of certain processes, and flow rates. Look specifically at weekends, because many plants are essentially unmanned on weekends.

These are the operator's only tools. The two or three hardest to measure are frequently the MLSS values in the tanks, the oxygen levels in the tanks when and where it is measured, and any other chemical parameters.

When you have the model balanced for steady-state flows, then start dynamic modeling. If you are fortunate enough to have good quality data on the plant, you may be able to get traces where peaks and valleys in the model results can be compared with the peaks and valleys in the performance data for the plant. It is almost like curve matching, but you are looking to see that any disturbances in the plant (and there will always be some) are matched by disturbances in the model. The results may be very interesting as the peaks may not match in height, but they should be at about the same times and for the same duration as obtained from the plant data.

## 22.8 Step 8: Parameter Adjustments

Adjustment of the parameters is well beyond the scope of this book. It needs to be done only after a detailed analysis of the waste and the characteristics, and after the evaluation of the modeling results compared with a case where there are sufficient data to enable comparison. From the literature, the one

case where parameter adjustment may be necessary is in phosphorus modeling. The sensitivity of the various coefficients and uptake rates can affect the storage of phosphate and the final results. The adjustment of parameters should be undertaken only after careful consideration and experience, and probably substantial laboratory testing and/or a number of model runs to compare results with actual performance.

*Many software companies publish the model parameters and they can be adjusted.* The published parameters are general for wastewater and are those used and developed by the IWQ committees when they developed the ASM models. They can be adjusted at the modeler's discretion, but it should be noted that many of the parameters are interrelated. It should be noted that different models may use different parameters, and while the models indicate that they are the same, those used by other companies are different, sometimes by factors of 5 or more.<sup>4</sup>

## Notes

- 1 For a discussion of the issues involved in sampling and analysis, there is a good article in the October 1980 issue of *Chemical Engineering Magazine*, entitled: "Monitoring and Sampling Liquid Effluents," by David L. Russell, or download it from [www.globalenvironmental.biz](http://www.globalenvironmental.biz).
- 2 For additional guidance you will want to see the descriptions of the models themselves.
- 3 Chambers, B. (1992). "Design methodology for optimization of aeration efficiency in activated sludge plants," in *Proceedings of the 6th Forum on Applied Biotechnology*, 17, 1631–1642. Med. Fac. Ladnbouww., University of Ghent.
- 4 A good comparison between the models is found in *The COST Simulation Benchmark Description and Simulator Manual*. The manual describes an older version of many of the models, but since the essential model formulation has not changed dramatically since that time, much of the publication is still pertinent. The book can be obtained from the Scientific Officer, European Commission, rue de la Loi/Wetstraat 200 (SDME, 9/70) B1049, Brussels, Belgium (e-mail: fulajar@cec.eu.int). The ISBN number is 92-984-1658-0.

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