

## Public health priorities

- i) infectious disease (cholera, typhoid, dysentary, etc.)
- ii) toxic materials
- iii) carcinogens

Environmental engineering focused on (i) for most of 20<sup>th</sup> century. Today (~2000) most developed nations have focused a great deal of attention to (ii) & (iii).

ii) & iii) come under the category of "hazardous materials" which are defined below & regulatory documents

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) - already contaminated (Superfund)

RCRA (Resource Conservation & Recovery Act) - new sources of hazardous materials

## Hazardous materials

- listed (on a list)

- characteristic:

ignitable (Flash point  $60^{\circ}\text{C}$  or less)

corrosive ( $\text{pH} < 2$ ;  $> 12.5$ ; corrode metal)

reactive (produce heat, explosion, poisonous fume, vapor, gas)

toxic (fatal if ingested; fail TCLP)

<div></div> <div></div>	<div></div>	<b>Final Rules Effective Through 10/12/2001</b>	<div></div>
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# 40 Code of Federal Regulations

## Protection of Environment

### § 302.4 Designation of hazardous substances.

(a) Listed hazardous substances. The elements and compounds and hazardous wastes appearing in Table 302.4 are designated as hazardous substances under section 102(a) of the Act.

(b) Unlisted hazardous substances. A solid waste, as defined in 40 CFR 261.2, which is not excluded from regulation as a hazardous waste under 40 CFR 261.4(b), is a hazardous substance under section 101(14) of the Act if it exhibits any of the characteristics identified in 40 CFR 261.20 through 261.24.

Table 302.4 -- List of Hazardous Substances and Reportable Quantities

Note: The numbers under the column headed "CASRN" are the Chemical Abstracts Service Registry Numbers for each hazardous substance. Other names by which each hazardous substance is identified in other statutes and their implementing regulations are provided in the "Regulatory Synonyms" column. The "Statutory RQ" column lists the RQs for hazardous substances established by section 102 of CERCLA. The "Statutory Code" column indicates the statutory source for designating each substance as a CERCLA hazardous substance: "1" indicates that the statutory source is section 311(b) (4) of the Clean Water Act, "2" indicates that the source is section 307(a) of the Clean Water Act, "3" indicates that the source is section 112 of the Clean Air Act, and "4" indicates that the source is RCRA section 3001. The "RCRA Waste Number" column provides the waste identification numbers assigned to various substances by RCRA regulations. The column headed "Category" lists the code letters "X," "A," "B," "C," and "D," which are associated with reportable quantities of 1, 10, 100, 1000, and 5000 pounds, respectively. The "Pounds (kg)" column provides the reportable quantity adjustment for each hazardous substance in pounds and kilograms.

Table 302.4 -- List of Hazardous Substances and Reportable Quantities

Hazardous substance	CASRN	Regulatory synonyms	RQ	Code
Acenaphthene.....	83329	.....	1*	2
Acenaphthylene.....	208968	.....	1*	2

Acetaldehyde.....	75070	Ethanal.....	1000	1,3,4
Acetaldehyde, chloro-.....	107200	Chloroacetaldehyde.....	1*	4
Acetaldehyde, trichloro-.....	75876	Chloral.....	1*	4
Acetamide.....	60355	.....	1*	3
Acetamide, N-(aminothioxomethyl)-.....	591082	1-Acetyl-2-thiourea.....	1*	4
Acetamide, N-(4-ethoxyphenyl)-.....	62442	Phenacetin.....	1*	4
Acetamide, 2-fluoro-.....	640197	Fluoroacetamide.....	1*	4
Acetamide, N-9H-fluoren-2-yl-.....	53963	2-Acetylaminofluorene.....	1*	3,4
Acetic acid.....	64197	.....	1000	1
Acetic acid (2,4-dichlorophenoxy)-, salts & esters.	94757	2,4-D Acid,.....	100	1,3,4
		2,4-D, salts and esters....		
Acetic acid, Lead(2+) salt.....	301042	Lead acetate.....	5000	1,4
Acetic acid, thallium (1+) salt.....	563688	Thallium(I) acetate.....	1*	4
Acetic acid, (2,4,5-trichlorophenoxy).	93765	2,4,5-T.....	100	1,4
		2,4,5-T acid.....		
Acetic acid, ethyl ester.....	141786	Ethyl acetate.....	1*	4
Acetic acid, fluoro-, sodium salt.....	62748	Fluoroacetic acid, sodium salt.	1*	4
Acetic anhydride.....	108247	.....	1000	1
Acetone.....	67641	2-Propanone.....	1*	4
Acetone cyanohydrin.....	75865	Propanenitrile, 2-hydroxy-2-methyl-2-Methylactonitrile.	10	1,4
Acetonitrile.....	75058	.....	1*	3,4
Acetophenone.....	98862	Ethanone, 1-phenyl-.....	1*	3,4
2-Acetylaminofluorene.....	53963	Acetamide, N-9H-fluoren-2-yl-.	1*	3,4

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**TABLE 6.8** Environmental Laws Controlling Hazardous Substances

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<i>Atomic Energy Act</i> (Nuclear Regulatory Commission)—Regulates nuclear energy production and nuclear waste disposal.
<i>Clean Air Act</i> (EPA)—Regulates the emission of hazardous air pollutants.
<i>Clean Water Act</i> (EPA)—Regulates the discharge of hazardous pollutants into the nation's surface water.
<i>Comprehensive Environmental Response, Compensation, and Liability Act (Superfund)</i> (EPA)—Provides for the cleanup of inactive and abandoned hazardous waste sites.
<i>Emergency Planning and Community Right-to-Know Act</i> (EPA)—Requires written emergency response plans for chemical releases and establishes the Toxic Release Inventory.
<i>Federal Insecticide, Fungicide, and Rodenticide Act</i> (EPA)—Regulates the manufacture, distribution, and use of pesticides and the conduct of research into their health and environmental effects.
<i>Hazardous Materials Transportation Act</i> (Department of Transportation)—Regulates the transportation of hazardous materials.
<i>Marine Protection, Research, and Sanctuaries Act</i> (EPA)—Regulates waste disposal at sea.
<i>Occupational Safety and Health Act</i> (Occupational Safety and Health Administration)—Regulates hazards in the workplace, including worker exposure to hazardous substances.
<i>Pollution Prevention Act</i> (EPA)—Establishes priority of prevention, recycling, treatment, and waste minimization, before disposal in landfills.
<i>Resource Conservation and Recovery Act</i> (EPA)—Regulates hazardous waste generation, storage, transportation, treatment, and disposal.
<i>Safe Drinking Water Act</i> (EPA)—Regulates contaminant levels in drinking water and the disposal of wastes into injection wells.
<i>Surface Mining Control and Reclamation Act</i> (Department of the Interior)—Regulates the environmental aspects of mining (particularly coal) and reclamation.
<i>Toxic Substances Control Act</i> (EPA)—Regulates the manufacture, use, and disposal of specific chemicals.

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## listed wastes

source-specific — { related to industry }  
 generic  
 commercial chemical products

## Relevant laws

TSCA - toxic

CERCLA - past practices

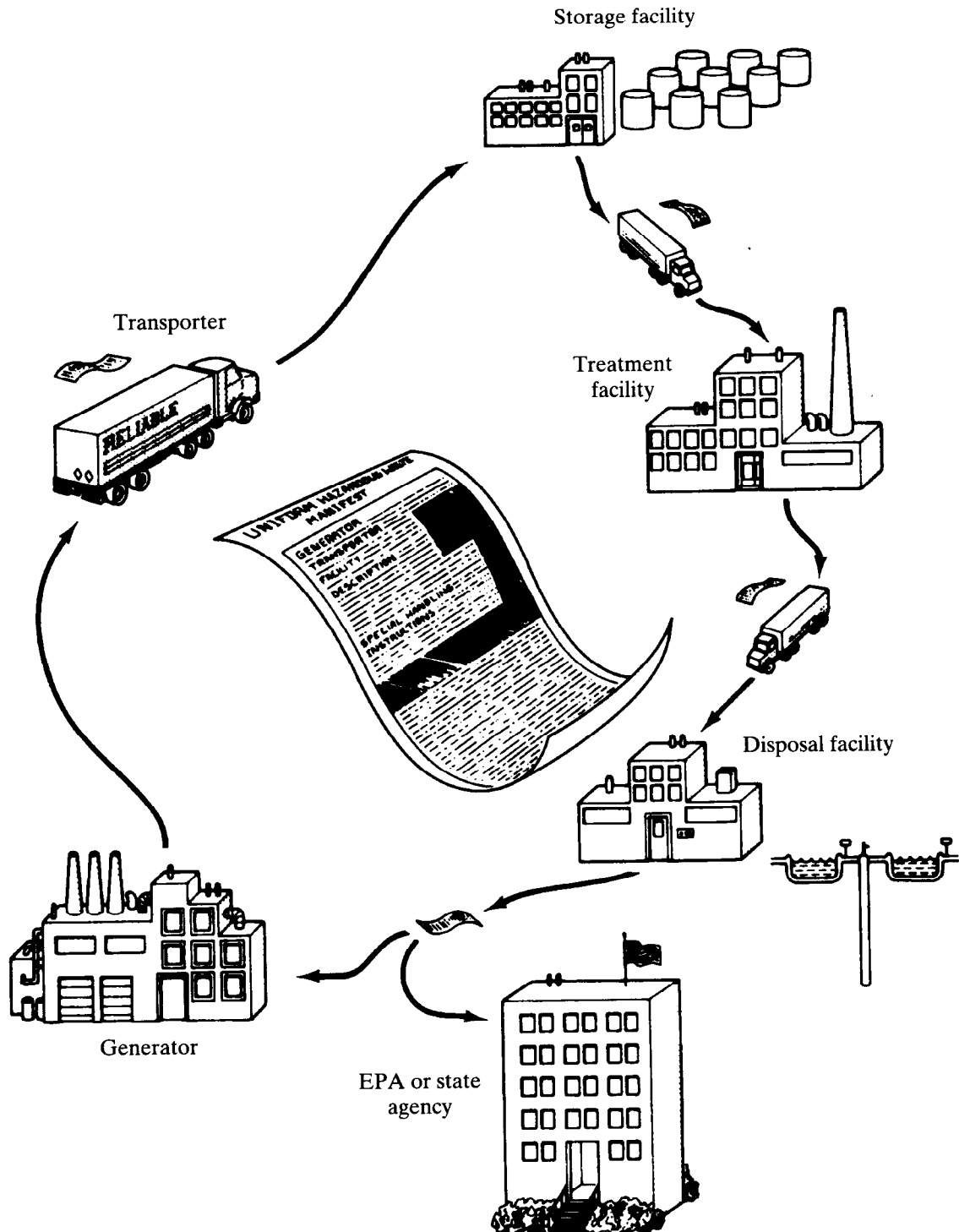
RCRA - current practices

## RCRA

- manifest document; records properties of materials, source & destination
- permits
- disposal rules — ideal is "complete destruction"
- NOS (not otherwise specified)

## waste reduction (priorities)

- (i) eliminate generation
- (ii) reduce generation
- (iii) reuse/recover (includes energy recovery)
- (iv) treat
- (v) disposal (includes destruction)



**FIGURE 6.14** A one-page manifest must accompany every waste shipment. The resulting paper trail documents the waste's progress through treatment, storage, and disposal, providing a mechanism for alerting the generator and the EPA if irregularities occur. (U.S. EPA, 1986)

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CERCLA/SARA

priorities

- (i) human & environmental health (imminent threat)
- (ii) remediation

comparable risk

new legal concepts

-retroactive, strict, joint-and-several liability

↑ if no single suspect; then all are liable

↑ diligence is not a defense; if acceptable in past, still liable in future.

↑ acts prior to legislation are not exempt. (violates U.S. Constitution, but has withstood repeated court challenges;)

repeated court challenges have failed to strike the "new legal concepts" and CERCLA stands — ∴ Engineers must accept provisions and design to prevent/meet CERCLA requirements.

Brownfield restorations.

To declare war, grant letters of marque and reprisal, and make rules concerning captures on land and water;

To raise and support armies, but no appropriation of money to that use shall be for a longer term than two years;

To provide and maintain a navy;

To make rules for the government and regulation of the land and naval forces;

To provide for calling forth the militia to execute the laws of the union, suppress insurrections and repel invasions;

To provide for organizing, arming, and disciplining, the militia, and for governing such part of them as may be employed in the service of the United States, reserving to the states respectively, the appointment of the officers, and the authority of training the militia according to the discipline prescribed by Congress;

To exercise exclusive legislation in all cases whatsoever, over such District (not exceeding ten miles square) as may, by cession of particular states, and the acceptance of Congress, become the seat of the government of the United States, and to exercise like authority over all places purchased by the consent of the legislature of the state in which the same shall be, for the erection of forts, magazines, arsenals, dockyards, and other needful buildings;--And

To make all laws which shall be necessary and proper for carrying into execution the foregoing powers, and all other powers vested by this Constitution in the government of the United States, or in any department or officer thereof.

Section 9. The migration or importation of such persons as any of the states now existing shall think proper to admit, shall not be prohibited by the Congress prior to the year one thousand eight hundred and eight, but a tax or duty may be imposed on such importation, not exceeding ten dollars for each person.

The privilege of the writ of habeas corpus shall not be suspended, unless when in cases of rebellion or invasion the public safety may require it.

⊗ No bill of attainder or ex post facto Law shall be passed.

No capitation, or other direct, tax shall be laid, unless in proportion to the census or enumeration herein before directed to be taken.

No tax or duty shall be laid on articles exported from any state.

No preference shall be given by any regulation of commerce or revenue to the ports of one state over those of another: nor shall vessels bound to, or from, one state, be obliged to enter, clear or pay duties in another.

No money shall be drawn from the treasury, but in consequence of appropriations made by law; and a



## Hazardous waste treatment

- chemical destruction
- biological destruction
- thermal destruction
- phase change/stabilization
- encapsulation

## Physical methods

- Sedimentation (similar to solids removal in wastewater treatment)
- air stripping (phase change)
- filtration, osmosis, ion exchange (phase change)

## Chemical methods

- neutralization (adjust pH)
- precipitation; (similar to sedimentation)
- oxidation/reduction
- UV oxidation

## Biological methods

- use existing WW treatment technology

## Incineration

- Thermal destruction

Portland cement, or vitrifying it to create a glassy substance. Solidification is most often used on inorganic sludges.

Choosing an appropriate technology to use in any given situation is obviously beyond the scope of this text. Not only are there many different kinds of hazardous wastes, in terms of their chemical makeup, but the treatability of the wastes depends on their form. A technology suitable for treating PCBs in sludges, for example, may not be appropriate for treating the same contaminant in dry soil. Table 6.9 gives a partial listing of available treatment technologies appropriate for a variety of types of hazardous

**TABLE 6.9** A partial list of treatment technologies for various hazardous waste streams.

Treatment process	Hazardous waste streams												Form of waste		
	Corrosives	Cyanides	Halogenated solvents	Nonhalogenated organics	Chlorinated organics	Other organics	Oily wastes	PCBs	Aqueous with metals	Aqueous with organics	Reactives	Contaminated soils	Liquids	Solids/Sludges	Gases
Separation/filtration		×	×	×	×	×			×	×			×		
Carbon adsorption									×	×	×		×		
Air and steam stripping			×	×	×	×				×			×		×
Electrolytic recovery									×				×		
Ion exchange	×								×	×			×		
Membranes									×	×			×		
Chemical precipitation	×								×				×		
Chemical oxidation/reduction		×								×			×		
Ozonation		×		×		×					×		×		×
Evaporation			×	×	×	×							×	×	
Solidification	×	×										×	×	×	
Liquid injection incineration			×	×	×	×	×						×		×
Rotary kilns			×	×	×	×	×	×				×	×	×	×
Fluidized bed incineration			×	×	×	×	×	×				×	×	×	×
Pyrolysis			×	×	×	×						×	×	×	
Molten glass			×	×	×	×	×			×			×	×	×

Source: Based on Freeman (1989)

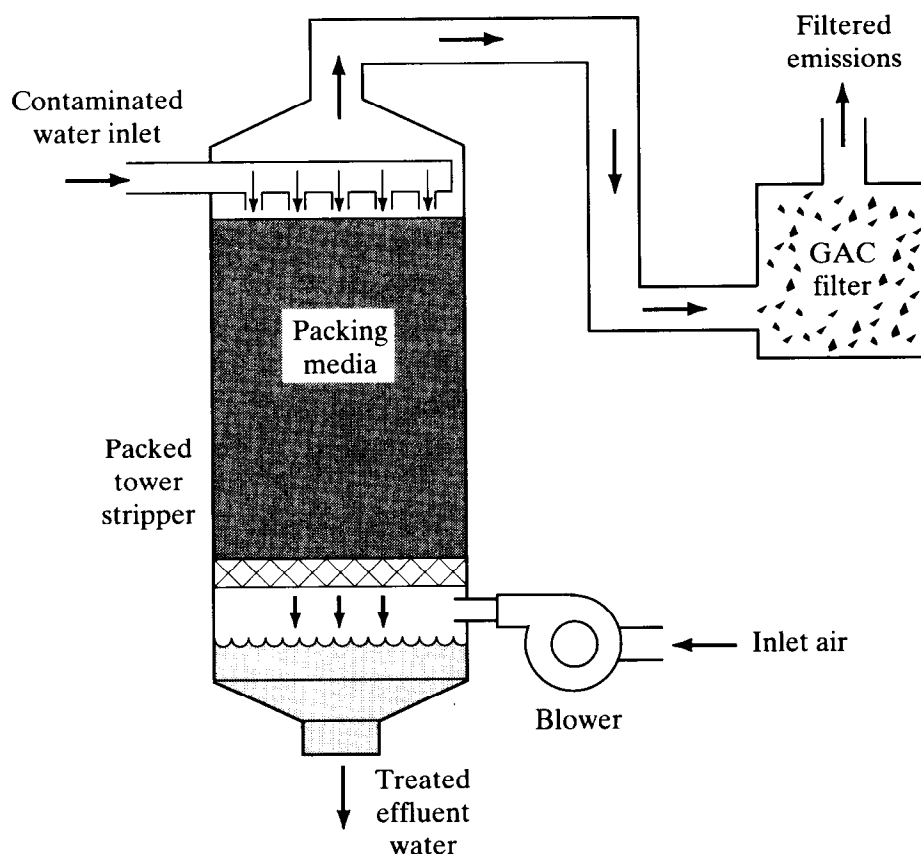


FIGURE 6.18 An air-stripping tower followed by a granular activated carbon filter provides effective removal of VOCs. To remove nonvolatiles, the treated water coming out of the tower may be pumped through other carbon adsorbers.

and cations in solution. In the past, electrodialysis was most often used for purifying brackish water, but it is now finding a role in hazardous waste treatment. Metal salts from plating rinses are sometimes removed in this way.

### Chemical Treatment

Chemically treating hazardous waste has the potential advantage of not only converting it to less hazardous forms, but can also produce useful byproducts in some circumstances. By encouraging resource recovery, the treatment cost can sometimes be partially offset by the value of the end products produced.

**Neutralization.** There are many chemical processes that can be used to treat hazardous wastes, and the process decision depends primarily on the characteristic of the waste. For example, recall that one of RCRA's categories of hazardous waste is anything corrosive—that is, having a pH of less than 2 or more than 12.5. Such wastes can be chemically *neutralized*. Acidic wastewaters are usually neutralized with slaked lime [ $\text{Ca}(\text{OH})_2$ ] in a continuously stirred chemical reactor. The rate of addition of lime is controlled with a feedback control system that monitors pH and adjusts the feed rate accordingly.

Alkaline wastewaters may be neutralized by adding acid directly or by bubbling in gaseous  $\text{CO}_2$ , forming carbonic acid ( $\text{H}_2\text{CO}_3$ ). The advantage of  $\text{CO}_2$  is that it is

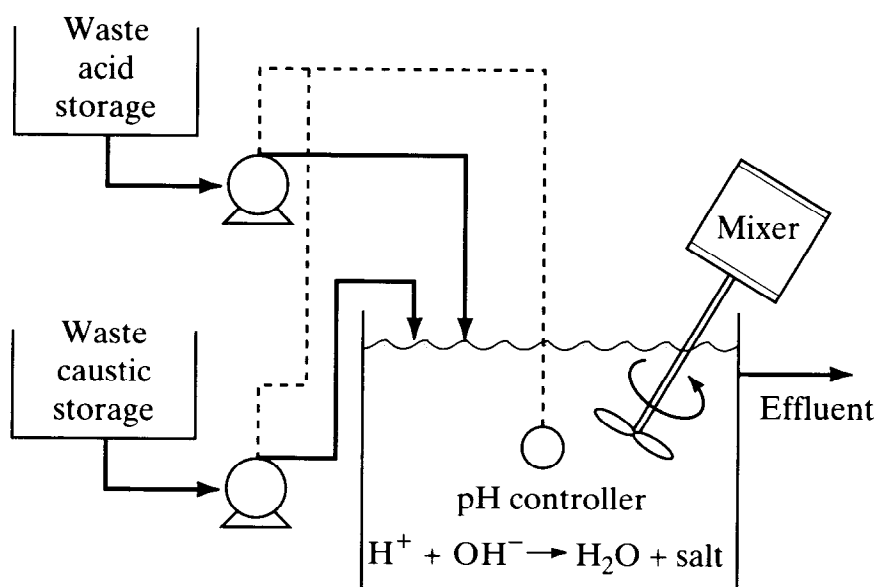
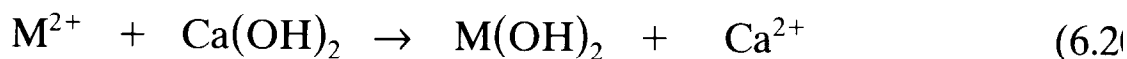


FIGURE 6.19 Simultaneous neutralization of acid and caustic waste. (U.S. EPA, 1987a)

often readily available in the exhaust gas from any combustion process at the treatment site. Simultaneous neutralization of acid and caustic waste can be accomplished in the same vessel, as is suggested by Figure 6.19.

**Chemical Precipitation.** The ability to adjust pH is important not only for waste neutralization, but also because it facilitates other chemical processes that actually remove undesirable substances from the waste stream. For example, a common method for removing heavy metals from a liquid waste is via *chemical precipitation*, which is pH dependent. By properly adjusting pH, the solubility of toxic metals can be decreased, leading to formation of a precipitate that can be removed by settling and filtration.

Frequently, the precipitation involves the use of lime,  $\text{Ca}(\text{OH})_2$ , or caustic ( $\text{NaOH}$ ) to form metal hydroxides. For example, the following reaction suggests the use of lime to form the hydroxide of a divalent metal ( $\text{M}^{2+}$ ):



Metal hydroxides are relatively insoluble in basic solutions, and, as shown in Figure 6.2 they are *amphoteric*—that is, they have some pH at which their solubility is a minimum. Since each metal has its own optimum pH, it is tricky to control precipitation of a mixture of different metals in the same waste. For a waste containing several metals, it may be necessary to use more than one stage of precipitation to allow different values of pH to control the removal of different metals.

While hydroxide precipitation using lime is the most common metal removal process, even lower concentrations of metals in the effluent can be obtained by precipitating the metals as sulfides. As can be seen in Figure 6.20, metal sulfides are considered

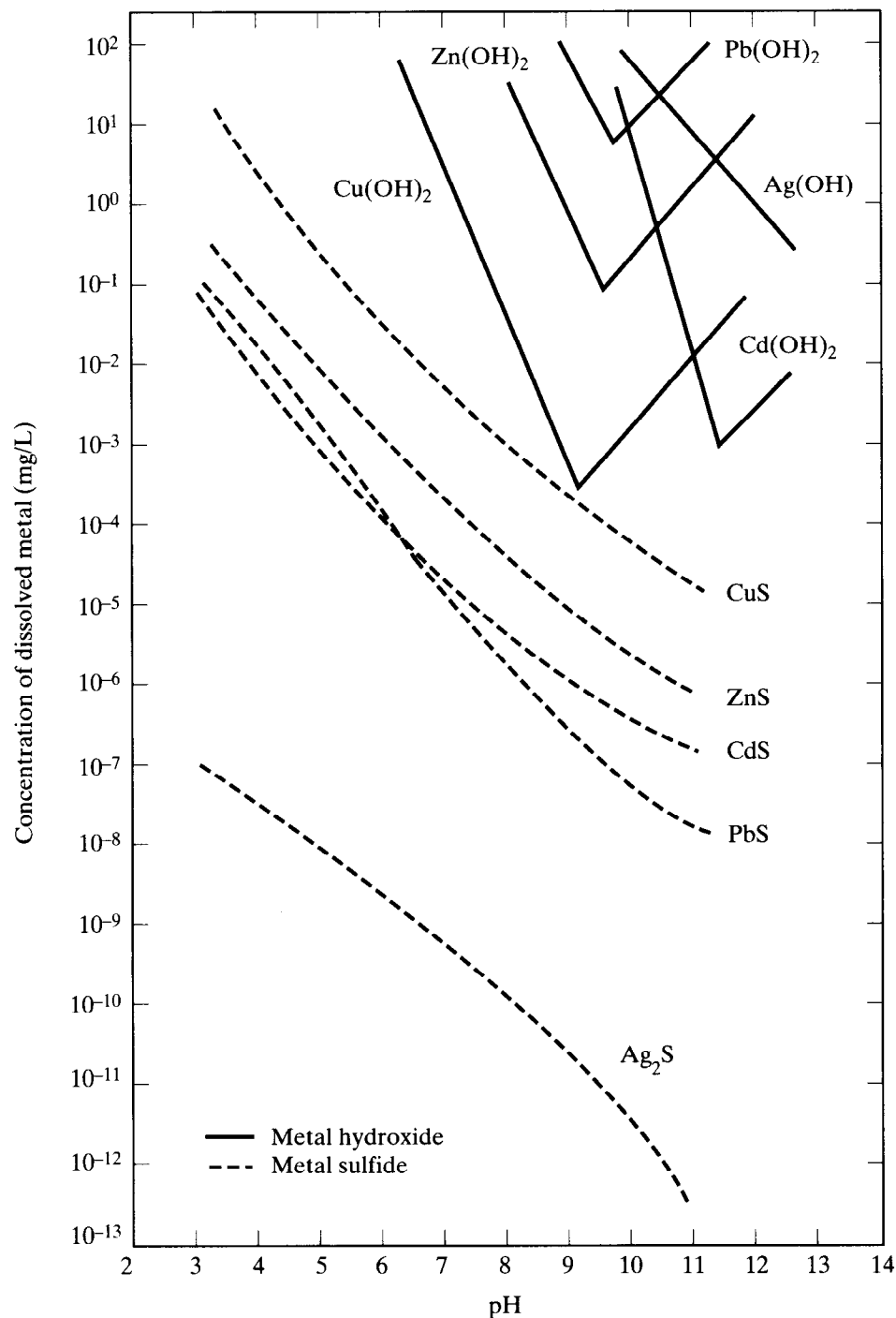
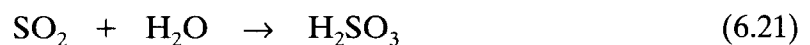


FIGURE 6.20 Chemical precipitation of metals can be controlled by pH. Metal sulfides are less soluble than metal hydroxides. (U.S. EPA, 1980)

reaction, hence the abbreviation redox. One of the most important redox treatment processes is the reduction of hexavalent chromium (Cr VI) to trivalent chromium (Cr III) in large electroplating operations. Sulfur dioxide is often used as the reducing agent, as shown in the following reactions :



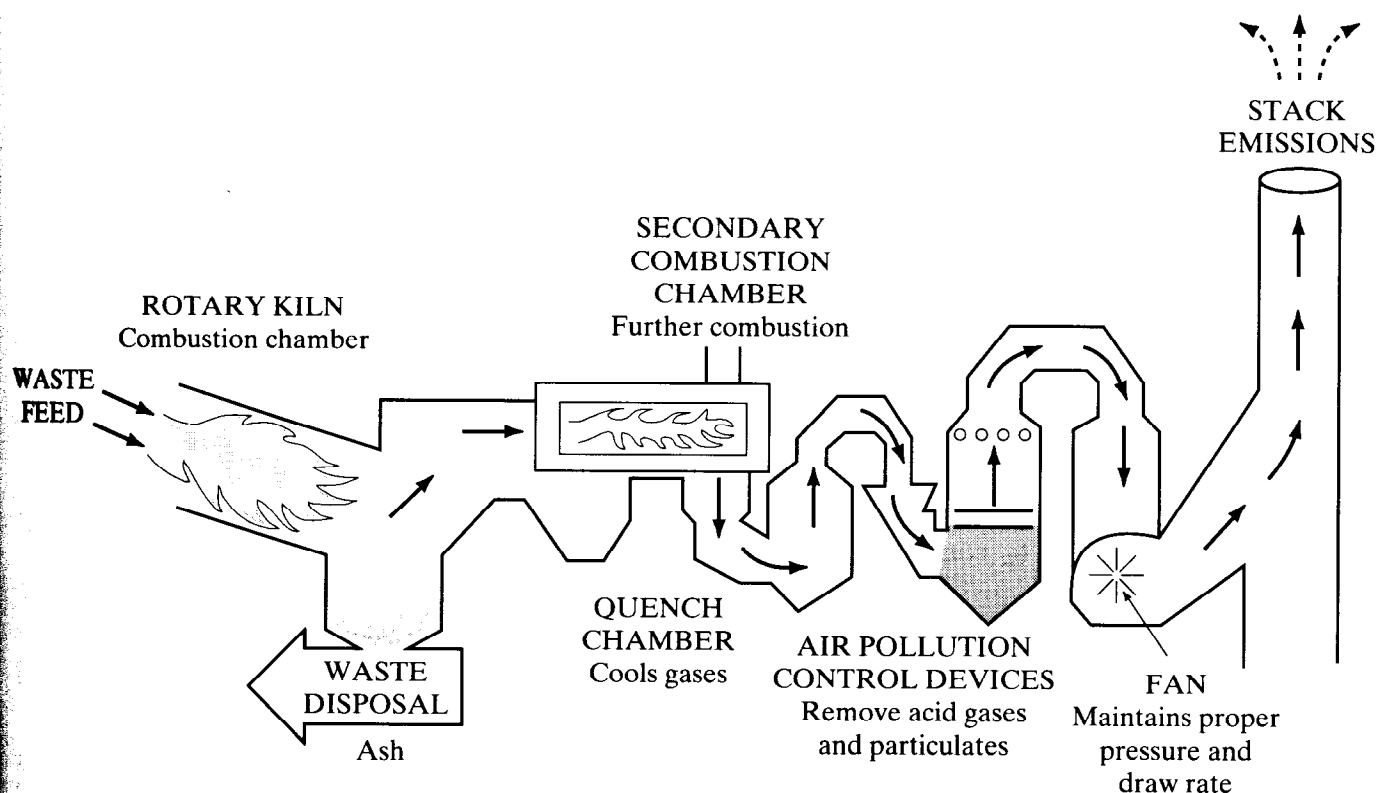


FIGURE 6.23 A rotary kiln hazardous waste incinerator (USEPA, 1988).

In spite of numerous controls, hazardous waste incinerators have the potential to emit amounts of noxious gases that may be unacceptable to neighbors. Emissions may include unburned organic compounds from the original waste, various *products of incomplete combustion* (PIC) formed in the incinerator itself, odors, carbon monoxide, nitrogen and sulfur oxides, hydrogen chloride, and particulates. The unburned ash and sludge from the air pollution control devices are considered hazardous wastes themselves and must be treated as such. If they are transported off site, then not only are there hazardous materials transported into the facility, but there are some leaving as well. The perception of potentially adverse impacts associated with incineration has made the siting of these facilities an extremely difficult task.

Liquid injection incinerators have been built into two ships, the *Vulcanus I* and the *Vulcanus II*, for hazardous waste incineration at sea, but public opposition has prevented their use. Proponents of incineration at sea point out the advantages of incineration, the difficulties associated with land-based siting, and the reductions in human risk that would come with incineration far from any centers of population. Opposition has focused on the chances of hazardous waste spills and the near impossibility of controlling such a spill should it occur. Also, the small amounts of unburned wastes routinely released, as well as those that might be released should the incinerator ever be improperly operated, could have unknown implications for marine life.

An ongoing debate is being conducted between advocates of incineration as a way to avoid land disposal (with its potential for toxic leakage into groundwater) and a

## Disposal (encapsulation)

Landfill - traditional techniques. Proper lining to prevent leakage

Lagoon - similar to oxidation pond; washout a problem

Deep well injection - inject into depressurized reservoir. (Deer Park). Fate of materials is a concern

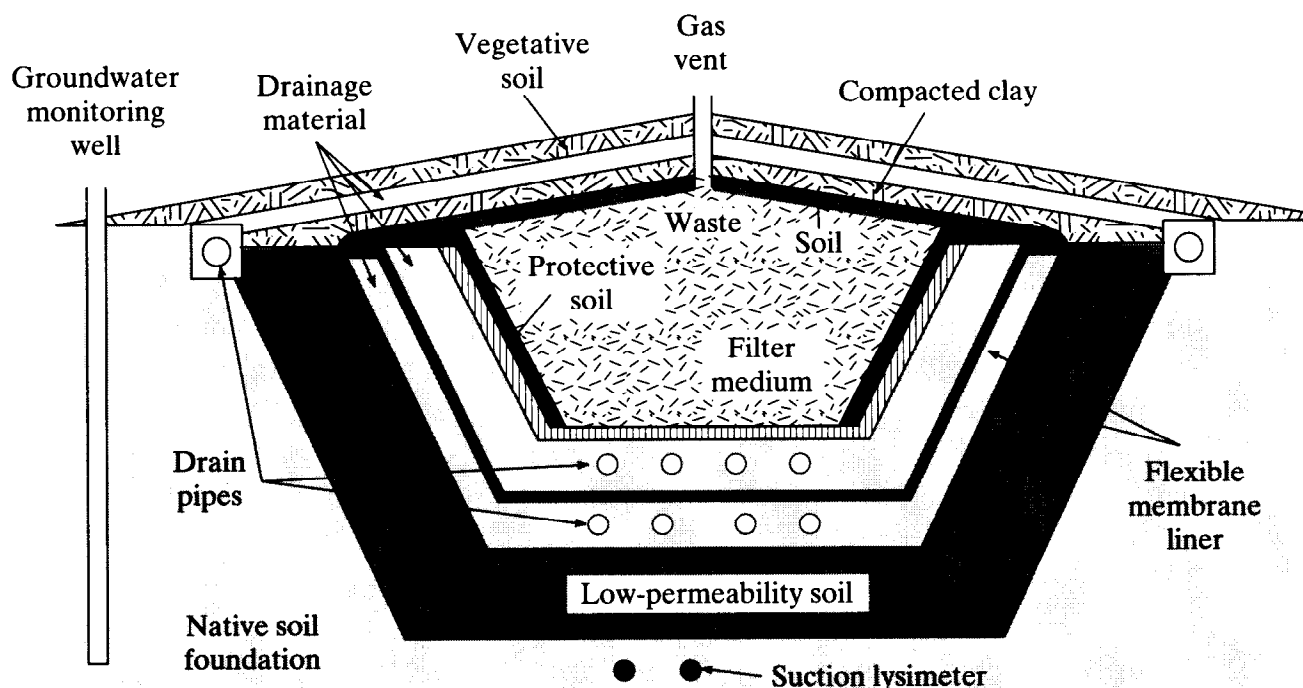


FIGURE 6.24 Schematic of a hazardous waste landfill.

to 1980 only about one-fourth were lined and fewer than 10 percent had monitoring programs (U.S. EPA, 1984). The same survey also found that surface impoundments were usually poorly sited. More than half were located over very thin or very permeable soils that would allow easy transport of leachate to groundwater. Over three-fourths the impoundments were located over very thick and permeable aquifers that would allow relatively rapid dispersion of contaminants should they reach the water table. Moreover, about 98 percent of the surface impoundments were located less than one mile from sources of high-quality drinking water.

As a result of these poor siting, construction, and management problems, surface impoundments are the principal source of contamination in a large number of Superfund sites. Recent EPA regulations require new surface impoundments, expansions to existing impoundments, to have two or more liners, a leachate-collection system, and monitoring programs similar to those required for landfills. However, the legacy of past practices will undoubtedly take billions of dollars and decades of time to remediate.

**Underground Injection.** The most popular way to dispose of liquid hazardous wastes has been to force them underground through deep injection wells (Figure 6.25). To help assure that underground drinking-water supplies will not become contaminated, injection wells used to dispose of hazardous industrial wastes are required to extend below the lowest formation containing underground sources of drinking water. Typical injection depths are more than 700 m below the surface. Since the main concern with underground injection is the potential for contamination of underground drinking water supplies, the regulation of such systems has come under



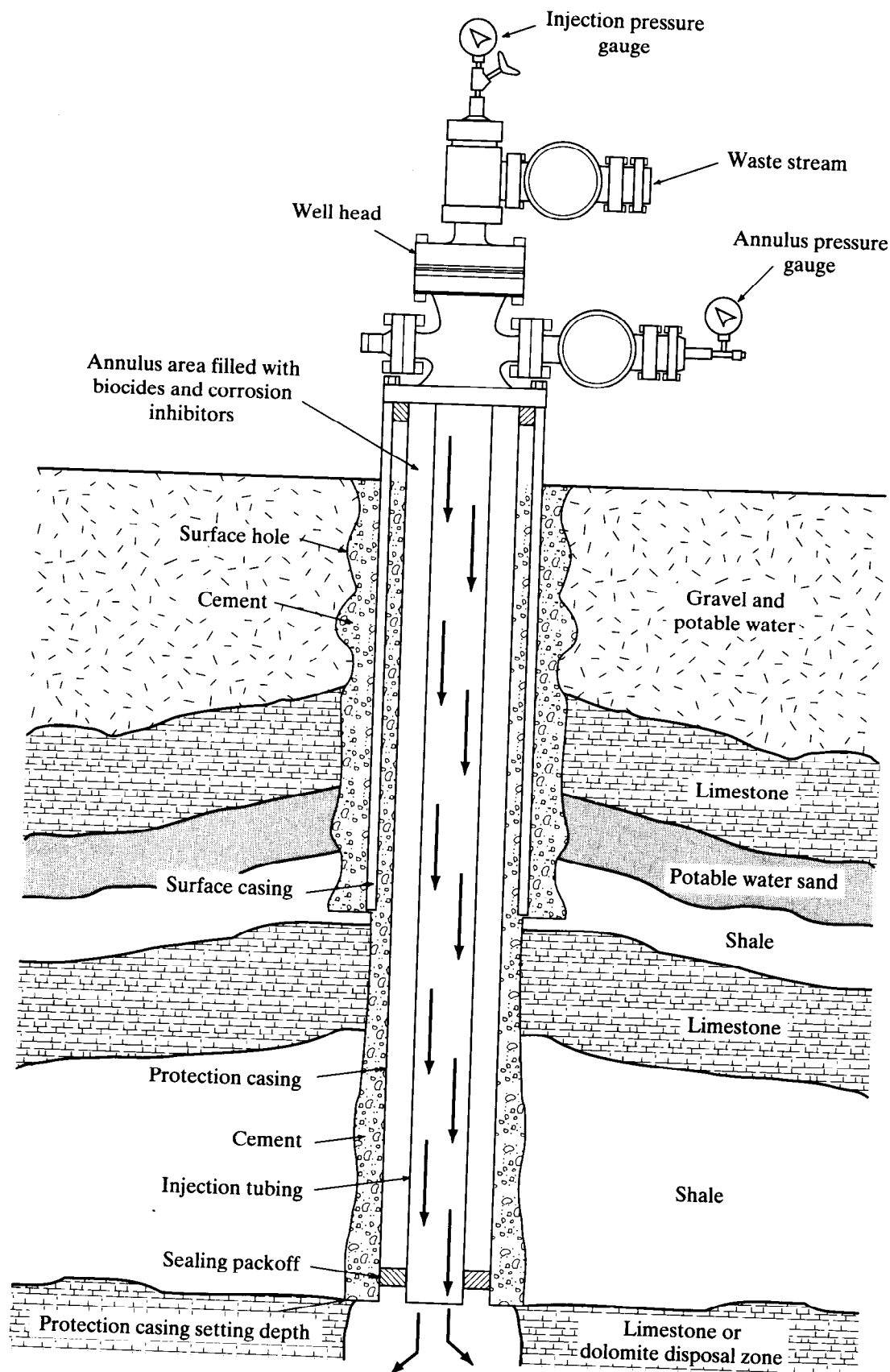


FIGURE 6.25 Cross section of a hazardous waste disposal well. (Source: Wentz, C. A., *Hazardous Waste Management*. Copyright © 1989 by McGraw-Hill, Inc. Used with permission of the publisher.)