

Figure 3-3 Typical BOD Curve for Domestic Wastewater Showing Carbonaceous and Nitrogenous Oxygen Demands.

## SECTION I

### CHAPTER ONE: INTRODUCTION AND DEFINITIONS

#### 1.1 Importance of chemical process industries

Products of the chemical process industries are used in all areas of everyday life.

- Raising of food plants and animals requires chemical fertilizers, insecticides, food supplements and disinfectants
- Building materials have been chemically processed, eg metals, concrete, roofing materials, paints and plastics
- Clothing utilizes many synthetic fibres and dyes.
- Transportation depends upon gasoline and other fuels
- Written communication utilizes paper and printing ink
- The nation's health is maintained by drugs and pharmaceuticals, soaps and detergents, insecticides and disinfectants - all products of the chemical process industry.

#### 1.2 What is the chemical process industry?

Most processes in the chemical industry involve a chemical change. The term "chemical change" is usually interpreted as chemical reaction. It should also be interpreted to include physico-chemical changes such as the separation and purification of the components of a mixture.

Mechanical changes are not considered to be part of the chemical process unless they are essential to latter chemical changes. E.g. manufacture of plastic polyethene from ethylene, produced from petroleum or natural gas involves a chemical process. However, moulding and fabrication of the plastic resin into final shapes is not part of the chemical process.

#### 1.3 Origin and development of the chemical process industry

The chemical industry dates back to prehistoric times when man first attempted to control and modify his environment. Its development is divided into two periods

### 1. Pre-Scientific Chemical Industry:

Probably the oldest chemical process industry is fermentation, although in its earliest times it was more a folk craft than an industry. Vineager (dilute acetic acid) was the earliest known acid since it was formed on the oxidation of fermented liquor. Nitric acid was made from salt peter ( $\text{KNO}_3$ ) and ferrous sulphate by heating the mixture and condensing the distilled nitric acid. The first application of nitric acid was in the separation of gold from silver. HCl was the cheapest and widely used mineral acid.  $\text{H}_2\text{SO}_4$  was used to produce chlorine for bleaching cloth.

### 2. Scientific Chemical Industry

Progress and growth of the early chemical industry were slow because there was little understanding of the scientific principles underlying the various processes. The increased understanding of chemical science led to improvement and new developments in chemical processing. The principal chemical industries in the 19<sup>th</sup> century manufactured alkalis, acids and metals.

#### 1.4 a Disciplinary Definition of Chemical Engineering

Chemical Engineering is the profession in which knowledge of mathematics, physics, chemistry and biology, gained by study, experience, and practice, is applied with judgment to develop economic and safe ways of using materials to benefit mankind.

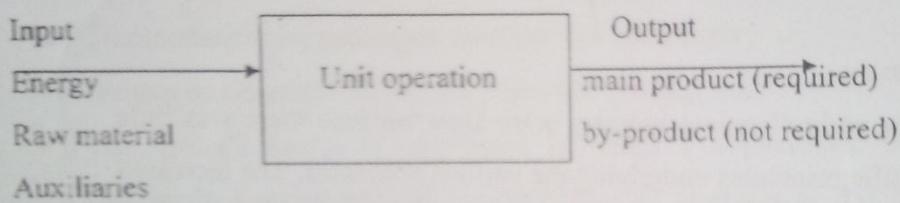
#### 1.4 b Occupational Definition of Chemical Engineering

Chemical Engineering is a broad discipline dealing with processes (industrial and natural) involving the transformation (chemical, biological, or physical) of matter or energy into forms useful for mankind, economically and without compromising environment, safety, or finite resources.

### 1.5 Chemical Processing

In chemical processing, raw materials are converted into useful and profitable products. These products are used both as consumer goods and as intermediates for further chemical and physical modifications into consumer products.

1. **Process:** Any collection of steps involving changes in chemical composition, or physical changes in material being prepared, processed, separated or purified.
2. **Unit operations:** they characterize the physical operations necessary for manufacturing chemicals. E.g. heat transfer, fluid flow, distillation, filtration, crystallization, mixing etc.
3. **Unit processes:** generally classifies chemical operations. E.g. nitrification, sulfonation, chlorination, oxidation, esterification, fermentation etc.



### 1.6 Factors that affect a process

#### Category A:

- Material
- Machines
- Energy
- Environment
- Essential information

#### Category B:

- Methods
- Requirements
- Data
- Facts
- Analysis

## CHAPTER TWO: INDUSTRIAL PRODUCTION, BASIC CONCEPTS AND PROCESSES OF CHEMICAL TECHNOLOGY

### Basic concepts

2.1 Production Systems: production systems do not work in isolation. It involves people, processes and products.

#### 1. People's Chain:

- Relationship linkage
  - Supplier - customer

#### 2. Process Chain: a sequence of processes linked together

- Transformation linkage

3. Product Chain: the steps that need to be taken in order to transform raw material into goods that can be used by consumers. (eg. Apple to apple pie)

- Production linkage

### 2.2 Three key questions during a process

1. How is it going to be carried out: whether the change required will be chemical or physical
2. How far is it going to be carried out: thermodynamics determines ultimate limit of conversion
3. How fast is it going to be carried out: reaction kinetics determines the time required for the completion of the reaction.

### 2.3 Basic Concepts

1. **Equilibrium:** for all combination of phases, there exists a condition of zero net interchange of properties (mass or energy), known as equilibrium position.
2. **Driving force:** when two substances or phases not in equilibrium are brought into contact, there is a tendency for a change to take place, which will result in an approach towards the equilibrium condition. The difference between the existing

condition and the equilibrium condition is the driving force causing the change.

### 3. Yield versus Conversion

**Yield:** it is that fraction of raw material recovered as the main (or desired) product.

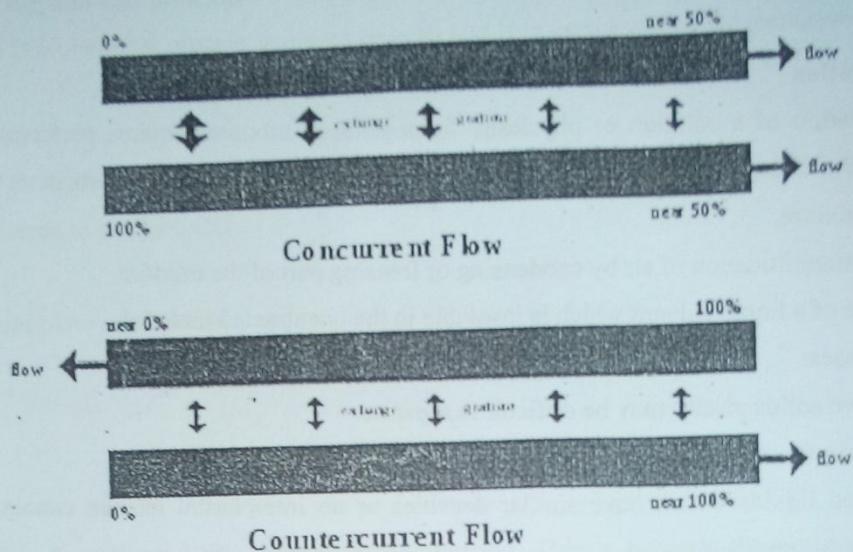
**Conversion:** it is that fraction changed to something else- by-product as well as product.

Conversion is also loosely used to indicate the amount changed by a single pass through an apparatus when multiple passes are used.

E.g. in the synthesis of ammonia, the yield is frequently above 98%, whereas the conversion is limited by equilibrium to about 14% (per pass, which means that 86% of the charge does not react and must be recirculated. The goal of the chemical engineer, always concerned with cost, is to have the conversion equal the yield. Because of low conversion, methanol and ammonia synthesis plants are 4to5 times as large as would be expected if conversion equals yield. By changing the operating conditions, the equilibrium can be shifted and the conversion enhanced. Raising operating pressure improves ammonia and methanol yields, but operating and equipment costs are increased. Increased reaction time allows closer approach to equilibrium ( but requires larger, more expensive equipment); improved catalyst can shorten reaction time but equilibrium remains unaffected.

### 2.4 Flow Patterns

1. **Concurrent Flow:** transfer of say energy with both streams flowing in the same direction
2. **Countercurrent Flow:** transfer of energy between two streams where the streams are made to flow in opposite directions.



## 2.5 Batch vrs. Continuous

**Batch:** Early chemical processing was usually done in batches, and much continues to be done in that way. Batches can be measured most concisely, but temperature control can be troublesome. In small scale operations, where extremely corrosive conditions force frequent repairs and in others for various specific reasons, batch operations are used. When small quantities of material are to be processed, it is often more convenient to change the entire quantity of material to the equipment, process it in place and remove the product. Here, time is a factor. It is also not a steady state. It is a transient state.

**Continuous:** In the majority of chemical processing operations, it is more economical to maintain continuous and steady operation of equipment, with a minimum of disturbances and shut downs. Because of greater productivity of continuously operating equipment, and the resultant lower unit cost, it is usually advantageous to operate continuously. Here time is not a variable in the analysis of such a process. Performance does not change with time. Continuous processes require more concise control of flows and conditions and would be impossible without quality instrumentation. Computer control has been most

valuable.

## 2.6 Separation

The separation of a solution or physically homogeneous mixture requires preferential transfer of a constituent to a second phase which may be physically separated from the residual mixture.

E.g.1. Dehumidification of air by condensing or freezing part of the mixture

2. Use of a liquid solvent which is insoluble in the unextracted material

General cases:

- Two solids phases may be difficult to separate
- A liquid and solid or gas is easily separated
- Two liquids which have similar densities or no interphasial tension cannot be easily separated.

The more homogeneous a mixture is, the more difficult it is to separate.

## 2.7 Waste

Waste is any substance or object which the holder discards or intends to discard or is required to discard by provision of national law. (Basil Convention of 1997).

Parameters of waste:

- Generation rate
- Density
- Moisture content
- Composition ( constituent of the waste)

The generation of waste has to do with the area, the living standard, and the available natural resources.

## 2.8 Greenhouse Gases

They are those gaseous constituents of the atmosphere both natural and anthropogenic that absorb and reemit infra-red radiation leading to increased warming of the earth's atmosphere and consequently cause climate change. These gases include CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O, CFC.

### **2.9 Composting and Combustion**

Combustion is a chemical process that uses oxygen and it is accompanied by evolution of heat.

Composting is another biological process apart from respiration where oxygen is used in an aerobic process to produce CO<sub>2</sub>.

Products of complete combustion

- CO<sub>2</sub>
- H<sub>2</sub>O
- NO<sub>2</sub>
- SO<sub>2</sub>

It is impossible to achieve 100% (complete) combustion. This is because the optimal reduction of the material cannot be achieved.

**2.10 Incineration:** it is the process of combusting materials under controlled and approximate stoichiometric conditions to reduce its weight and volume, and often to produce energy. This is done in the presence of air or oxygen.

**2.11 Pyrolysis:** it is the chemical decomposition of a substance by heat in the absence of oxygen. In the case of organic materials and other hydrocarbons, it leads to the formation of methane (combustible gas).

Advantages of pyrolysis

1. The residual char can be utilized
2. No flue gas cleaning

### **2.12 Introduction-Processes of Chemical Technology**

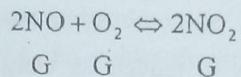
The processing of raw materials into chemical products should be carried out under economically advantageous (optimum) conditions, i.e. under condition which result in low consumption of raw materials, an inexpensive and high quality product and high process rate.

Without knowledge of the laws which govern chemical processes it is impossible to control a modern process and to manufacture chemical products economically. When a new plant is being designed such knowledge aids in selecting a rational flowsheet, i.e. in determining the sequence of production stages, in selecting the design of the equipment to be used and calculating its basic dimensions, in establishing the operating conditions and methods of control, etc.

Of the basic laws of chemistry and physics, which serve as the foundation for chemical engineering, the law of conservation of mass, the periodic law and the law of conservation of energy are among the most important.

### 2.13 Homogeneous (Uniform) and Heterogeneous (Non-Uniform) Processes

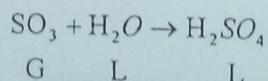
In homogeneous (uniform) systems or processes all the interacting substances are in the same phase: gaseous (G), liquid (L), or solid (S). For instance, the oxidation of NO to NO<sub>2</sub> by the reaction:



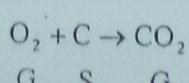
is a homogeneous process in the gas phase. If the reacting substances (reactants) are in solution, the process is homogeneous and in the liquid phase.

Heterogeneous (non uniform) systems consist of two or more phases. Thus, in two-phase systems the reactants may be in the following states: gas-liquid (G-L); liquid-solid (L-S); liquid-liquid (L-L) (immiscible liquids); solid-solid (S-S).

All heterogeneous systems have an interface. For instance, absorption of sulphuric anhydride, SO<sub>3</sub>, by water leading to the formation of sulphuric acid, H<sub>2</sub>SO<sub>4</sub>, proceeds by the reaction (heterogeneous system G-L)



The interaction of oxygen and carbon by the reaction (heterogeneous system G-S)



#### **2.14 Reversible Processes, Chemical Equilibrium, and Irreversible Processes**

In reversible processes the products of interaction between the initial substances react with each other to reform the initial substances. If initial substances A and B react, and the products obtained are C and D, such a reaction will be expressed by



At the beginning of the reversible process, when the concentration of the initial substances A and B is high, the rate of the reaction from left to right—the forward reaction—will be high but as the substances C and D are formed the concentration of A and B will decrease and the rate of the forward reaction will gradually slow down. At the same time the reaction products C and D will interact to form the initial substances A and B, the rate of the reverse reaction (from right to left) increases with increase in the concentration of C and D. Finally a point will be reached where the rates of the forward and reverse reactions become equal, i.e. the number of molecules formed per unit time as a result of interaction between the products C and D will be equal to the number of reacting molecules of the initial substances A and B. Such condition of the reacting system is called **chemical equilibrium**.

In practically irreversible processes at equilibrium there is almost complete conversion of the reactants to the reaction products. Among such reactions are, for instance, the combustion of coal ( $C + O_2 \rightarrow CO_2 + Q$ ), etc.

#### **2.15 Rate of Chemical Processes**

The rate of a chemical process is usually expressed in terms of the amount of the product obtained per unit time. The rate of chemical process is the resultant of the rates of the forward and reverse reactions. The higher the rate of the forward reaction and the lower the rate of the reverse one, the higher will be the rate of the overall process, i.e. the greater the yield of the product per unit time.

The rate of a chemical process depends not only on the concentration of the reactants, but also on a number of other factors, such as the temperature and pressure, the presence of catalysts, the physical and chemical properties of the reactants, the design of the reactor, the rate of flow of the reactants, the efficiency of stirring.

### 2.16 Mixing of Reactants

The degree of mixing of the reactants strongly influences the rate of chemical reactions. In homogeneous (uniform) processes vigorous stirring results in practically uniform concentration of the initial substances throughout the entire volume and thus in accelerating their interaction.

In heterogeneous (non uniform) systems stirring increases the interface area of the reacting phases.

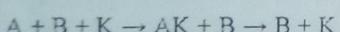
### 2.17 Catalytic Processes

The utilisation of catalyst in almost all new chemical processes has made it possible to use new raw materials and to obtain various complex products from hydrogen, nitrogen, carbon monoxide, methane, ethylene, etc. The catalytic synthesis of ammonia and methanol, reactions of hydrogenation, oxidation, and polymerisation are used extensively in the chemical industry.

One of the features of a catalyst is that after taking part in a reaction it normally is not changed chemically.

Schematically, this can be represented as follows: Two molecules A and B are reacting in the gas phase to form a new substance AB by the reaction  $A + B = AB$ . The activation energy of the reaction is high and therefore it proceeds very slowly.

If a catalyst is used, the reaction will proceed in a different way:



Where K is the catalyst

## CHAPTER THREE: SYSTEMATIC ANALYSIS OF CHEMICAL PROCESS

### 3.1 Introduction

Early chemical process usually involved a few simple steps. Materials were processed in small batches. Process improvements evolved slowly from experience gained by the operators. As the demand for chemical products increased and the chemical industry grew, processes had to be developed to produce large quantities at the lowest possible cost.

Improvements based on experience were no longer sufficient; it became necessary to build new plants for products never before produced. Systematic analysis of chemical processes elucidated many underlying principles which could be used in the synthesis of new processes.

Modern chemical processes are often extremely complex operations involving hundreds of pieces of equipment. Without a systematic approach, it would be impossible to analyse an existing process or to design a new process. Therefore, chemical processes are broken down into individual steps that recur in many other processes. The general principles of these steps have been carefully studied and are frequently well understood. If the principles are known, it is possible to design the step to do the best possible job. The typical chemical process is analysed with the following interdependent considerations:

### 3.2 Mass and energy balances;

The fundamental principles that engineers and scientist employ in performing design calculations and predicting the performance of plant equipment are discussed here. Topics include the **conservation laws for mass and energy**, thermochemistry, chemistry reaction equilibrium, chemical kinetics, the ideal gas law, and phase equilibrium.

### 3.3 Thermochemistry;

Considering the energy effects associated with a chemical reaction, it has been found in measuring energy changes for systems that the enthalpy is the most convenient term to work with. There are many different types of enthalpy effects; these include sensible heat, latent heat, and heat of reaction.

### 3.4 Unit operations;

In the chemical and other physical processing industries, including the food and biological processing industries, there are many similarities in the manner in which the entering feed materials are modified or processed into final products.

Unit operations deal mainly with the transfer and change of energy and the transfer and change of materials, primarily by physical means but also by chemical means.

### 3.5 Plant equipment;

The plant equipment provides details on a number of commonly used process units: reactors, heat exchangers, columns of various types (distillation, absorption, adsorption, evaporation, extraction), dryers, and grinders.

### 3.6 Ancillary equipment;

This section considers devices for transporting gases and liquids to, from or between units of process equipment. Some of these devices are simply conduits for the moving of material (pipes, ducts, fittings); others control the flow of material (valves); still others provide the mechanical driving force for the flow (fans, pumps, and compressors). This also covers storage facilities, holding tanks, materials-handling devices and techniques, and utilities along with air, water, and solid waste control equipment.

### **3.7 Process flow diagrams;**

The process flow sheet is the key instrument for defining, refining and documenting a chemical process. The process flow diagram is the authorised process blueprint, the framework for specifications used in equipment designation and design; it is the single, authoritative document employed to define, construct, and operate the chemical process.

### **3.8 Instrumentation and control;**

In a typical chemical process many instruments are used to measure, indicate and record the necessary process data. It is necessary to know such process data as flow rates, compositions, pressure and temperatures, so that the operator and production engineer can tell that process is functioning properly.

### **3.9 Economics**

When a plant is designed, many economic analyses are made to determine the least expensive design which will produce the desired quantity of product at a minimum price. If the cost of manufacture is sufficiently below the selling price to give an attractive profit, the plant will be built.

## CHAPTER FOUR: RAW MATERIAL, FUEL AND POWER FOR CHEMICAL PROCESS INDUSTRY

### 4.1 Introduction

The expenditures directly involved in the manufacturing process alone are known as the plant cost. The principal items of expenditure which together make up the plant cost are:

1. The raw materials, semi-products and basic materials
2. Fuel and power for technological uses.
3. Salaries and wages of basic employees.
4. Sinking-funds set aside to cover wear of basic items of capital investment (buildings, structures, equipment, etc.)
5. Shop costs- expenditure on maintenance and current repairs of the basic items of capital investments.
6. General plant expenditures.

### 4.2 Materials for Chemical Processes

The materials used in manufacturing chemical products can be divided into the categories of raw materials, semi-products, basic materials and waste products of other processes.

Raw materials are naturally occurring substances which have not been subjected to industrial processing. Semi-products are materials which have undergone some form of preliminary processing at the plant where they are used. A material processed at another plant prior to its use in the chemical process is known as a basic material. Waste products are by-products of other processes.

The raw material used in the chemical industry can be divided into the following categories:

1. Raw materials won from upper layers of the earth
  - a. Naturally occurring fuels, employed either as a chemical material or as a source of power (coal, petroleum, natural gas);
  - b. Ores - rock-like materials containing metal which can be economically isolated in the form of a technically pure product (iron ores such as magnetite, red and brown haematites, etc.)
  - c. Non-metallic - inorganic naturally occurring which are utilised otherwise than as a source for producing metals, although many of them contain one or more

metal constituents; examples are common salt and other chlorides, sulphides, carbonates, phosphates, alumina-silicates;

2. Vegetable and animal materials – wood, cotton fibre, leather, wool; and
3. Water and air

## CHAPTER FIVE: CATALYST AND CATALYSIS

### 5.1 Introduction

A catalyst is a substance that alters the velocity of a chemical reaction without appearing in the products. Catalysts accelerate reactions but do not change equilibria; both forward and backward reactions are catalysed to the same extent. Increasing the velocity of a desired reaction relative to unwanted reactions maximises the formation of a desired product. E.g. Platinum/rhodium catalyst, Platinum/palladium catalysts.

### 5.2 Chemical and Physical Aspects

The rate of a chemical reaction is proportional to a rate constant:

$$k = Ae^{-E/RT}$$

Because of the exponential form of the equation, even a small decrease in  $E$ , the activation energy, can bring about a large increase in velocity. The catalytic pathway is a series of three chemical reactions: formation of the complex ( activated adsorption), surface reaction and desorption.

### 5.3 Techniques

The following factors are considered when choosing a catalyst for a specific reaction: selectivity, or the efficiency in catalysing a desired transformation; activity, or the overall conversion, expressed as the amount of reactant in contact with the catalyst under a given set of conditions converted to all products; stability, the ability to retain initial activity and selectivity over the catalyst's lifetime; physical suitability; regenerability; and cost

### 5.4 Preparation

Properties of a catalyst are determined by its preparation, with care taken to ensure duplication of characteristics. Colloid chemistry is important, including gel preparation, leaching selected components from solids, or decomposition of salts or hydrates with gas evolution.

Organic and inorganic chemicals

## CHAPTER SIX: INDUSTRIAL GASES

### 6.1 Introduction

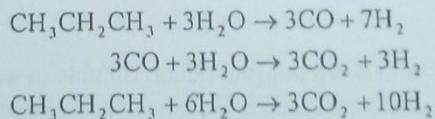
Those of the gases which are required in large quantities for industrial purposes are termed as industrial gases. The most important and largely used industrial gases are:

- i. Hydrogen
- ii. Oxygen
- iii. Nitrogen
- iv. Carbon dioxide
- v. Acetylene
- vi. Ethylene and
- vii. Helium

Industrial gases have a large variety of essential functions: some are used as raw materials for the manufacture of other chemicals; some are essential medicaments like oxygen and helium. Nitrogen is mainly used for blanketing. CO<sub>2</sub> and argon are occasionally used. CO<sub>2</sub> is more reactive and argon five to ten times expensive.

### 6.2 Hydrogen

The largest quantities of hydrogen are manufactured by catalytically reacting hydrocarbons and steam, to yield hydrogen and carbon oxides, followed by the water-gas shift reaction. The most commonly used raw material is natural gas, although other natural and refinery hydrocarbons, including naphtha cuts may be used. The following description is based on propane as a raw material.



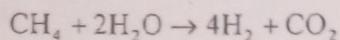
**Uses:** The manufacture of hydrogen is largely an integral part of other chemical manufacturing processes, the production of ammonia and methanol.

### 6.3 Carbon Dioxide

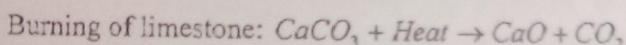
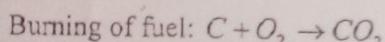
#### From Steam and Natural Gas

##### Process

Most of merchant carbon dioxide is a by-product of the production of ammonia, which in turn is produced by the reaction of nitrogen and hydrogen. Hydrogen for this reaction is produced in several ways, but primarily by the steam reforming process summarised in the equation. Most new producers of carbon dioxide make use of this by-product as their source of product.

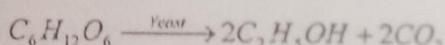


#### From Flue or Kiln Gases



#### From fermentation

**Process:** The fermentation of grain to produce ethyl alcohol also produces a stoichiometric quantity of carbon dioxide.



**Uses:** Refrigeration, carbonated beverages, chemical, inerting and pressure.

### 6.4 Sulphur Dioxide

#### Properties

Colourless gas or liquid with sharp pungent odour. Soluble in water, alcohol, and ether.

#### Preparation

1. By roasting pyrites in special furnaces. The gas is readily liquefied by cooling with ice and salt, or at a pressure of 3 atm.
2. By purifying and compressing sulphur dioxide gas from smelting operations.
3. By burning sulphur.

**Uses:** chemicals (sulphuric acid); sulphite paper pulp; ore and metal refining; soybean

protein; solvent extraction of lubricating oils; bleaching agent for oils and starch.

### 6.5 Carbon Monoxide

#### Properties

Colourless gas or liquid; practically odourless. Burn with a violet flame. Slightly soluble in water; soluble in alcohol and benzenes.

#### Preparation

1. Action of steam on hot coke or coal (water gas) or on natural gas.
2. By-product in chemical reactions
3. Dehydration of formic acid
4. Combustion of organic compounds with limited amount of oxygen as in automobile cylinders.

Uses: organic synthesis; metallurgy; zinc white pigments

### 6.6 Nitrous Oxide

#### Properties

Colourless, sweet-tasting gas; non-combustible; soluble in alcohol, ether and concentrated sulphuric acid; slightly soluble in water.

#### Preparation

Thermal decomposition of ammonium nitrate; controlled reduction of nitrates or nitrites.

#### Uses

Anaesthetic in dentistry and surgery; propellant gas in food aerosols; leak detection.

## CHAPTER SEVEN: ENERGY CONSERVATION IN CHEMICAL PROCESS INDUSTRIES

### 7.1 Introduction

Energy is one of the most vital inputs for economic development of any nation. Per capita consumption of energy is an index which refers to the economic development of any country.

Chemical industry is the fountainhead for the manufacture of a variety of chemical products beginning with products like soda ash, paper, plastics, pharmaceuticals and some specialty chemicals like isotopes.

### 7.2 Process Design and Energy Consumption

The concept of maximization of production with lower energy consumption is catching on. The basic process in chemical industry is the separation process and separation based on difference in volatility accounts for more than 80 percent.

The energy consumption of any process is required to be looked at from the overall thermodynamics. For example, a typical distillation process shows the thermodynamic efficiency to be less than 10 percent and this means that a large amount of energy is merely wasted.

### 7.3 Energy Management Principles

The energy management principles followed in Heavy Water Board (HWB) are applicable to other chemical industries as well and are illus trusted below. The energy management must begin form the very top and should have the following six essential elements:

1. A well defined energy policy
2. Organizational structure to implement the policy
3. Methodology for energy management
4. A motivated staff
5. Comprehensive information systems
6. Investment

## CHAPTER EIGHT: ENVIRONMENTAL PROTECTION, REGULATIONS AND POLLUTION CONTROL

### Water Laws

- CWA – Clean Water Act
- SDWA – Safe Drinking Water Act
- NPDES – National Pollution Discharge Elimination Systems

### Air Pollution Law

- CAA - Clean Air Act

#### **9.1 Introduction - Pollution Control**

Pollution control is recognised as an important aspect of chemical engineering. Due to lack of development of a culture of pollution control, a heavy backlog of gaseous, liquid and solid pollution in our country has resulted. Pollution is a man-made problem, mainly of affluent countries.

Pollution is an undesirable change in the physical, chemical or biological characteristics of air, water and soil that may harmfully affect the life or create a potential health hazard of any living organism. Pollution is thus direct or indirect change in any component of the biosphere that is harmful to the living component(s), and in particular undesirable for man, affecting adversely the industrial process, cultural and natural assets or general environment.

#### **9.2 Environmental Pollutant**

Any substance which causes pollution is called a pollutant. A pollutant may thus include any chemical or geochemical (dust, sediment, grit, etc.) substance, biotic component or its product, or physical factor (heat) that is released intentionally by man into the environment ~~in~~ such a concentration that may have adverse harmful or unpleasant effects on human health.

- The various principal pollutants which pollute air, water, land are as follows:
  1. Deposited matter- soot, smoke, tar, dust, grit etc.
  2. Gases- oxide of nitrogen ( $\text{NO}$ ,  $\text{NO}_2$ ), sulphur ( $\text{SO}_2$ ), carbon monoxide, halogens,

#### **9.4 Water Pollution**

Water pollution is defined as "the addition of any substance to water or changing of water's physical and chemical characteristics in any way which interferes with its use for legitimate purposes". It contains impurities of various kinds-dissolved as well as suspended. These include dissolved gases ( $H_2S$ ,  $CO_2$ ,  $NH_3$ ,  $N_2$ ), dissolved minerals (Ca, Mg, Na salts), suspended matter (clay, silt, sand) and even microbes.

#### **Sources of Pollution and the Pollutants**

The chief sources of water pollution are as follows:

1. Sewage and other waste
2. Industrial effluents
3. Agricultural discharges
4. Industrial wastes from chemical industries, fossils fuel plants and nuclear power plants.

#### **Prevention and Control of Water Pollution**

Biodegradable pollutants alone are not responsible for water pollution, though these indicate level of pollution (through BOD values). Besides these a substantial pollution load is contributed by non-degradable or slow degrading pollutants, such as heavy metals, minerals oils, biocides, plastic materials etc. that are dumped into water. For biodegradable pollutants, pollution may be controlled at source by their treatment for reuse and recycling.

#### **9.5 Solid Waste**

The solid waste includes glass containers as bottles, crockeries, plastic containers, polythene and other packing materials that are used and then thrown away as garbage. These pile up at public places and cause obstruction in daily life. Besides these there are also other used things like automobile spares, machines, cycle parts etc. that are thrown as junk. The wastes from building material, sludge, dead animal skeletons, heaps of crop residues also contribute to solid waste.

To solve these problems technologies have been developed to recycle most of the solid waste items. Thus paper cans, newspapers and other waste paper may be easily recycled.

Metallic component of vehicles spares may be recycled by cheap methods. However, there is problem of recycle of heavy metals, plastics, nylon, polythene, etc.

To control solid waste pollution, the following methods have been suggested:

1. Recycling
2. Burning of waste and utilising heat to warm residual units, generation of electricity.
3. Composting of organic waste for preparation of manures and biogas.

#### **9.6 Radioactive Pollution**

Discharge of potentially noxious materials into the environment involves some risk, which may or may not be measurable. Among the hazardous substances, radioactive substances are most toxic. As compared to organic poisons, injurious effects of radio-nuclides are exceedingly high.

##### **Sources of Wastes or Nuclear Pollutants**

Some of the sources which can cause radioactive pollution and radioactive wastes are listed below:

1. Uranium mining and milling
2. Processing of uranium oxide
3. Fuel fabrication
4. Reactor wastes
5. Spent fuel processing
6. Research and development
7. Hospitals and biological laboratories
8. Industrial application

#### **9.7 Noise Pollution**

The human ear is constantly being assailed by man-made sounds from all sides and there remain few places in populous areas where relative quiet prevails.

Aeroplanes, trains, cars and pneumatic drills and radio and television sets, all produce noise, the most dangerous pollutant of man's environment. Noise harms the body and mind. It not only causes irritation or annoyance but is constricts arteries, increases the flow of adrenaline and forces the heart to work faster.

## **SECTION II**

### **1.1 WASTE WATER ENGINEERING**

It is the branch of environmental engineering in which the basic principles of science and engineering are applied to solving the issues associated with the treatment and reuse of waste water. The ultimate goal of waste water engineering is the protection of public health in a manner commensurate with environmental, economic, social and political concerns. To protect public health and the environment, it is necessary to have the basic knowledge of:

1. Constituents of concern in waste water
2. Impact of these constituents on the environment
3. Transformation and long term fate of constituents in treatment process
4. Treatment methods to modify or remove constituents found in wastewater
5. Methods for the beneficial use or disposal of solids generated by the treatment systems

#### **Waste water**

Waste water can be defined as a combination of the liquid or water carried-waste removed from residencies, institutions and commercial and industrial establishments, together with such groundwater, surface water and storm water as may be present.

The principal constituents of concern in waste water are

1. Suspended solids
2. Biodegradable organic matter
3. Pathogens
4. Dissolved inorganic matter
5. Heavy metals

When untreated waste water accumulates and its allowed to go septic, the decomposition of the organic matter it contains will lead to the production of unpleasant smell and other nuisance conditions. In addition waste water contains numerous pathogenic microorganisms that dwell in the human intestinal tract causing diseases. It may also

toxic compounds that may be potentially mutagenic or carcinogenic.

For these reasons the immediate nuisance-free removal of waste water from its sources of generation followed by treatment, reuse or dispose into the environment is necessary to protect public health and the environment.

Organic compounds that contain C, H, N, O are primarily found in:

Proteins (40-60%)

Carbohydrate (25-50%)

Oils and fats (8-12%)

Laboratory methods commonly run to measure gross amount of organic matter (greater than  $1\text{g/m}^3$ ) include tests for:

1. Biological oxygen demand (BOD)
2. Chemical oxygen demand (COD)
3. Total organic carbon (TOC)
4. Total oxygen demand (TOD)

The COD test is a chemical test, the TOC and TOD tests are instrumental tests, and the BOD test is a biochemical test involving the use of microorganisms.

In addition to the above tests, if the chemical formula of the individual compounds is known, the Theoretical oxygen demand (ThOD) can be computed from stoichiometric considerations.

#### BOD

Most widely used parameter of organic pollution applied to both waste water and surface water, normally written as  $\text{BOD}_5$  because it is based on a 5-day analysis. BOD is the amount of oxygen used in the metabolism of biodegradable organics. The determination of BOD involves the measurement of dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. The principal end products of the carbonaceous oxidation of the organic matter are carbon dioxide ( $\text{CO}_2$ ), ammonia ( $\text{NH}_3$ ), and water ( $\text{H}_2\text{O}$ ). Unless otherwise noted, reported BOD values are only for the biodegradation of

Bar Screen: It is used to remove total suspended solids (TSS).  
Grit removed unit removes much smaller particles.

carbonaceous materials. Hence governmental agencies are encouraging the use of CBOD instead of BOD to denote carbonaceous biochemical oxygen demand, to avoid confusion.

#### BOD tests are used:

- To determine the approximate quantity of oxygen that would be required to biological stabilize the organic matter present
- To determine the size of waste treatment facilities
- To measure the efficiency of some treatment process
- To determine compliance with waste water discharge

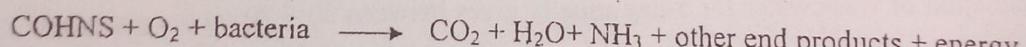
#### Basis for BOD test

If sufficient oxygen is available the aerobic biological decomposition of organic waste will continue until all of the waste is consumed. Three (3) more or less distinct activities occur:

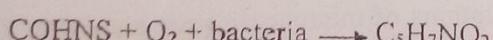
- A portion of the waste is oxidized to end product to obtain energy for cell maintenance and synthesis of cell tissue.
- Simultaneously some of the waste is converted into new cell tissue using part of the energy released during oxidation.
- When organic matter is used up, the new cells begin to consume their own cell tissue to obtain energy for cell maintenance. This third process is called endogenous respiration.

The 3 processes are defined by the following generalized chemical reactions:

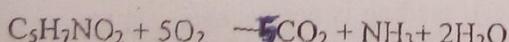
#### Oxidation:



#### Synthesis for formation of cell tissue



#### Endogenous respiration



If only the oxidation of the organic carbon that is present in the waste is considered, the ultimate BOD is the oxygen required to complete the three reactions given above. This

oxygen demand is known as the ultimate carbonaceous BOD, usually denoted by UBOD.

#### BOD Test Procedure

In a standard BOD test, a small sample of the wastewater to be tested is placed in a BOD bottle that has a volume of 300 ml. The bottle is then filled with dilution water saturated in oxygen and containing the nutrients required for biological growth. After bottle is incubated for 5-days at 20 °C the dissolved oxygen is measured again. The BOD of sample is calculated as follows:

- (i) For an unseeded dilution water,

$$BOD, \text{mg/L} = \frac{D_1 - D_2}{P}$$

where  $P = \text{fraction of wastewater sample volume to total combined volume, } \frac{V_s}{300\text{mL}}$

- (ii) For a seeded dilution water

$$BOD, \text{mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where  $D_1 = \text{dissolved oxygen of diluted sample immediately after preparation}$

$D_2 = \text{dissolved oxygen of diluted sample after 5-day incubation at } 20^\circ\text{C, mg/L}$

$B_1 = \text{dissolved oxygen of seed control before incubation, mg/L}$

$B_2 = \text{dissolved oxygen of seed control after incubation, mg/L}$

$f = \text{fraction of seeded dilution water volume in sample to volume of seeded dilution}$

$\text{water in seed control. (or } f = \frac{\% \text{ seed in } D_1}{\% \text{ seed in } B_1} = \text{ratio of seed in sample to seed in control)}$

#### Note:

- a. Incubation of wastewater for 5-day usually gives between 60 – 70% conversion of Carbonaceous Organic Matter. For 20-day conversion, it is between 90 – 95%.
- b. Also, when testing waters with low concentrations of microorganisms, a seeded BOD test is conducted (FIG. 2-19b). When the sample contains a large population of microorganisms (e.g. untreated wastewater), seeding is not necessary (FIG. 2-19a).

### Question 3.1

The following information is available for a seeded 5-day BOD test conducted on a wastewater sample. Fifteen (15) mL of the wastewater sample was added directly into 300mL BOD incubation bottle. The initial DO of the diluted sample was 8.8mg/L and the final DO after 5 days was 1.9mg/L. the corresponding initial and final DO of the seeded dilution water was 9.1 and 7.9mg/L respectively. Determine;

- The 5-day BOD (BOD<sub>5</sub>) of the wastewater sample.
- The 5-day BOD of the wastewater sample assuming dilution water was not seeded.

### Modeling of BOD Reaction (First Order Rate Model for BOD)

If a closed system is observed for a long enough period of time, nearly all of the degradable organic matter, including that in cell tissue will be converted to CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O, and the ultimate BOD will be approached. Because of complications induced by the oxidation of NH<sub>3</sub> to NO<sub>3</sub><sup>-</sup>, the BOD<sub>u</sub> is very difficult to measure. For the reaction that occurs in the BOD bottle,

$$\frac{d(BOD_r)}{dt} = -k(BOD_r)$$

where

BOD<sub>r</sub> = BOD remaining at time t, g/m<sup>3</sup>

k = reaction rate constant, t<sup>-1</sup> (base e)

integrating between limits of UBOD and BOD<sub>r</sub> at t = 0 and t = t yields

$$\ln \frac{BOD_r}{BOD_u} = -k_1 t$$

$$BOD_r = BOD_u e^{-k_1 t}$$

but      BOD<sub>t</sub> = BOD<sub>u</sub> - BOD<sub>r</sub>

therefore    BOD<sub>t</sub> = BOD<sub>u</sub> - BOD<sub>u</sub> e<sup>-k<sub>1</sub> t</sup>

$$BOD_t = BOD_u (1 - e^{-k_1 t})$$

where BOD<sub>t</sub> is the desired BOD value that has been exerted up to time t.

NOTE:

The value of k for untreated wastewater is generally about 0.12 to 0.46d<sup>-1</sup> (base e) with a

typical value of  $0.23\text{d}^{-1}$ .

$$K_1(\text{base } 10) = \frac{K_1(\text{base e})}{2.303}$$

### Temperature Effects of BOD

It is possible to determine the reaction constant  $k$  of wastewater at a temperature other than  $20^\circ\text{C}$ .

$$K_{1_T} = K_{1_{20}} \theta^{T-20}$$

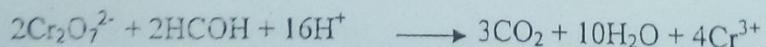
use of  $\theta = 1.056$  for  $T > 20^\circ\text{C}$  and  $\theta = 1.135$  for  $4 < T < 20^\circ\text{C}$  has been suggested.  
The most commonly used value of  $\theta = 1.047$

### Question 3.2:

Determine the 1-day BOD and Ultimate first-stage BOD for a wastewater whose 5-day  $20^\circ\text{C}$  BOD is 200mg/L. The reaction constant  $k(\text{base e}) = 0.23\text{d}^{-1}$ . What would have been the 5-day BOD if the test had been conducted at  $25^\circ\text{C}$  and take  $\theta=1.047$ .

### COD

The COD test is used extensively because it takes less time (about 3 hours) for nearly all the organic compound to be oxidized. It is used to measure the organic content of natural waters, municipal wastewaters, and industrial wastes. The oxygen equivalent of the organic matter is measured using a strong oxidizing agent (potassium dichromate) in an acidic (e.g.  $\text{H}_2\text{SO}_4$ ) medium. The test is performed at elevated temperatures, using a catalyst (silver sulphate) to help in the oxidation of certain resistant classes of organic compounds. The reaction involved in the test



After boiling, remaining  $\text{Cr}^{3+}$  is titrated against a reducing reagent. Difference between the original chromium and the one after titration = COD

Disadvantages of COD tests

- COD test cannot be used to differentiate between biologically oxidizable and inert organic matter
- No information is provided about the rate at which the organic material will be oxidized biologically
- Certain inorganic constituents such as chloride can interfere with the tests

### TOC

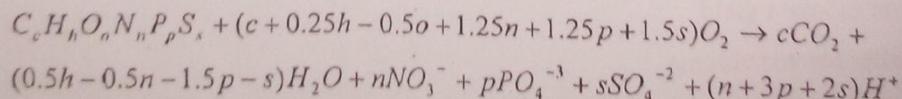
For smaller amounts of organic matter, the instrumental TOC test has proved to be satisfactory. In one form of this test, a sample is evaporated and oxidized catalytically to carbon dioxide. The amount of carbon dioxide released is measured with an infra-red analyzer. To ensure that only organic carbon is measured, the samples to be tested are acidified and aerated to remove the inorganic forms of carbon. In some cases, certain organic compounds may be oxidized completely and the measured TOC value will be slightly less than the actual value in the sample.

### TOD

In the instrumental TOD test, organic and some inorganic compounds are converted to stable end products, such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , in a platinum-catalyzed combustion chamber. The TOD is determined by the loss of oxygen in the nitrogen-carrier gas. Temperature range is around  $680\text{-}950^\circ\text{C}$ .

### ThOD

Where the chemical formula of the organic compound is known, the ThOD can be estimated from stoichiometric considerations. The amount of oxygen required for complete oxidation of an organic compound is equal to the amount required for the oxidation of each element minus the amount of oxygen present initially in the organic compound. Thus:



Because phosphorus and sulfur are present in small amounts in most organic compounds,

they can be neglected without serious error. If the nitrogen in the organic compound is not oxidized but it is converted to ammonia, the resulting oxygen requirement is essentially equal to the COD and to the BOD<sub>u</sub>, or the ultimate carbonaceous biochemical oxygen demand. The theoretical stoichiometric amount of oxygen required to oxidize the ammonia to nitrate is essentially the same as that required for the biological oxidation of ammonia to nitrate.

*Nitrification* is the term applied to the biological oxidation of ammonia to nitrate, and the oxygen required is termed the nitrogenous biochemical oxygen demand (NBOD).

## 1.2 TREATMENT OF WASTE WATER (ANAEROBIC WASTEWATER TREATMENT)

It is for the treatment of waste sludge and dilute waste streams.

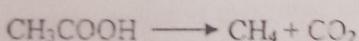
### Process description

There are three stages and they are hydrolysis, fermentation and methanogenesis.

**Hydrolysis:** particulate matter are converted to soluble compounds that can be hydrolyzed further to simple monomers that are then acted upon by bacteria for the fermentation process

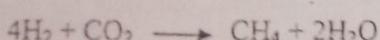
**Fermentation:** amino acids, sugars and fatty acid are degraded further. In the degradation we have propionate that are further fermented to produce H<sub>2</sub>, CO<sub>2</sub> and acetate

**Methanogenesis:** methanogens are the bacteria that acts on these building blocks (H<sub>2</sub>, CO<sub>2</sub> and acetate)



Aceticlastic methanogens act on the acetate

**Hydrogen utilizing methanogens:** they convert the hydrogen and CO<sub>2</sub> into methane.



**Advantages of anaerobic water treatment over aerobic**

- energy recovery
- lower biomass yield
- smaller reactor volume

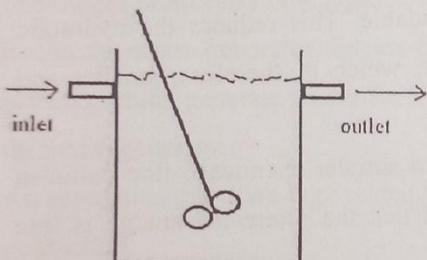
### 1.3 REACTORS USED IN WASTE WATER TREATMENT

#### Batch reactor

Flow neither enters nor leaves the reactor (on a continuous basis). material enters, treated and is discharged and the cycle goes on. Used when we want to blend chemicals and dilute concentrated chemicals.

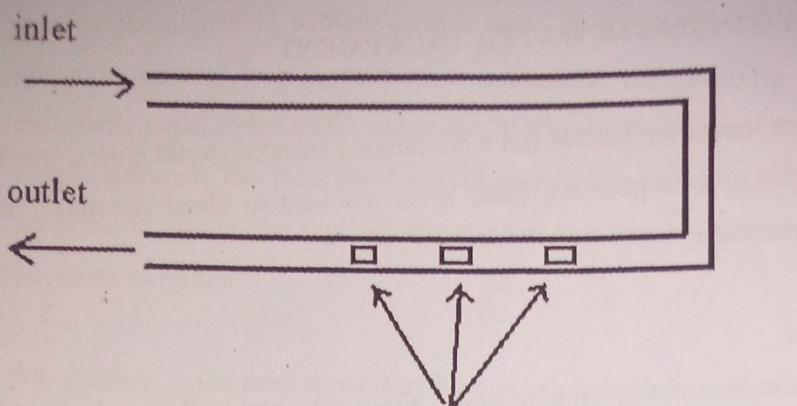
#### Complete mix reactor

It is also called continuous stirred tank reactors. Flow rate out = flow rate in, but concentration changes. There is complete and instantaneous mixing and this is uniform throughout the reactor. Fluid particles leave reactor in proportion to their statistical population. CSTR or well mixed reactors are easily visualized as vessels or tanks that are stirred to achieve uniformity throughout the tank. A very important characteristic of the CSTR is that the concentration of the reactants in the outlet is equal to the concentration of the reactants in the vessel regardless of the concentration of the reactants in the inlet.



#### Plug flow reactor

The fluid particles pass through the reactor with little or no longitudinal mixing and exit from reactor in the same sequence in which they entered. Application is in pipes/pipelines. Plug flow reactors can be modeled as a pipe where the reactants move as a plug along the pipe. The concentrations of the reactants will vary along the pipe and there is no mixing between the beginning and the end of the system.



No mixing between flowing "plugs"

### Complete mix reactors in series

Used to model flow regimes in ideal hydraulic flow patterns corresponding to a complete mix and plug flow reactors.

#### Purpose of the Hydrolysis of wastewater

The objective of the hydrolysis process is to hydrolyse organic solids, to solubilise them, and by so doing make them more readily biodegradable. This reduces the hydraulic retention time in the downstream anaerobic digester, which is, therefore, smaller and lower in capital cost.

Hydrolysis breaks up long chain cellular material into simpler chemicals, floc particles and organic macromolecules, with the added benefit that the pretreated sludge is less viscous and easier to pump.

In addition, the greater biodegradability of hydrolysed sludge improves removal of volatile suspended solids, which increases the biogas yield and reduces the quantity of sludge for final disposal.

Thermal hydrolysis is carried out at temperatures in the range of 140-170°C, so the first step of treatment is to dewater the raw sludge to about 30%. This is done using a centrifuge, or belt-filter, in order to minimise the energy required for heating.

The Biothelys system consists of two or more batch hydrolysis reactors working in parallel, out of phase with each other. Each reactor, in turn, goes through a multi-step cycle, taking between 120 to 165 minutes, depending on the configuration.

First, the reactor is filled with raw sludge and this is preheated with recycled flash steam

from the other reactor. Heating to hydrolysis temperature is completed by injecting live steam into the sludge from a steam generator fired with biogas.

Once the required temperature for hydrolysis has been reached it is maintained for a preset time before the steam is released as flash steam. This is recovered for preheating another reactor. Finally, the reactor is emptied using the residual pressure inside it to aid discharge to a buffer tank. Here the hydrolysed sludge is stored and cools prior to being transferred to the anaerobic digester.

Mesophilic anaerobic digestion and final dewatering are followed by storage in covered cells for nine months. After this, the sludge is completely safe and provides an excellent compost when spread on agricultural land.

There are no mechanical rotating parts in the thermal hydrolysis reactors - mixing of raw sludge is achieved by steam injection through the treatment cycle. Hydrolysis is at a temperature of 160°C, held for at least 30 minutes.

The biogas produced in the digester is stored in a double-membrane gas holder for use as fuel in the steam generator. Excess biogas is fed to the combined heat and power (CHP) plant(s), which generate power for the works and also preheat the softened-water feed to the steam generator.

An emergency gas flare is provided for periods when the biogas consumption is less than production.

The Biothelys process, together with mesophilic anaerobic digestion, at is reported to be achieving about 45-50% removal of volatile suspended solids. This is compared with 30-35% removal typically achieved by a single-stage mesophilic digester treating extended-aeration sludge.

The biogas production is reported to be increased in the same proportion. The Veolia Water Solutions & Technologies, Saumur Plant produces a biogas which is also of higher calorific value than would be expected from AD alone, at 75% methane and only about 24% carbon dioxide.

The thermal hydrolysis process can be self-sufficient in energy, using some of the biogas produced by the anaerobic digestion. The remaining biogas is used to fuel a CHP plant. In the case of larger installations, further improvements to efficiency can be made by

using all the biogas in CHP plants with steam generation in a waste-heat boiler.

The AD reactor size can reportedly also be reduced when there is a good hydrolysis stage up-front. Without the thermal hydrolysis step, the digester volume would have been almost about three times that of the installed plant. This means retrofitting thermal hydrolysis as a pretreatment for existing digesters could increase their capacity by up to three times.

The reduction in digester cost resulting from systems like Biothelys - combining thermal hydrolysis with anaerobic digestion – is reported to make them economically viable for the treatment of various sludge types, including primary, biological and blends of primary and biological sludges.

Veolia says it provides benefits in terms of volatile solids removal, better sludge dewaterability and a reduction in the quantity of sludge for disposal. The firm says it also optimises energy recovery in the form of biogas from sludge digestion, while producing a high-quality sludge that is free of pathogens, stabilised, odourless and with good fertilising characteristics - making disposal to agriculture a practicable option.

#### **Objective for the Fermentation Process**

Further characteristic of our fermentation system lies in the acceleration of the biological conversion to biogas. An important factor in anaerobic degradation is the size the organic fraction that biologically, is easily accessible, since this can offer significant economic advantages with regards to the size of the plant. Depending on the task at hand, our fermentation systems comprise of an upstream hydrolysis stage which can, if required, be operated under aerobic conditions. The fermentation process reduces the organic loading of the wastewater (BOD<sub>5</sub>, COD, organic acids, etc.). Often however, further groups of pollutants (e.g. Nitrogen compounds, hard COD) that are present in the wastewater are not sufficiently degraded. Further treatment for the removal of nitrogen compounds and the remaining organic contamination is therefore installed subsequent to the fermentation process. The combination of anaerobic and aerobic wastewater treatment has been successfully implemented in our company for many years.

## CHAPTER TWO! WATER TREATMENT AND PURIFICATION

### 2.1 Introduction

Water treatment describes the process used to make water acceptable for a desired end use. This can include use as drinking water, use in industrial process or to allow discharge into the environment without adverse ecological impact. The processes may be physical such as sedimentation, chemical such as disinfection or coagulation or biological such as slow sand filtration.

Water purification is the removal of contaminants from untreated water to produce water that is pure enough for human consumption. Substances removed during the process of drinking water treatment include bacteria, algae, viruses, fungi and manmade pollutants. There is no such thing as pure water. As the universal solvent, the moment purified is exposed to the environment it interacts with carbon dioxide in the air.

### 2.2 Methods and Processes of Water Treatment

Water treatment methods can be divided into the following main groups

1. Those aimed at improving the organoleptic properties of water i.e. clarification, discoloration, deodorization.
2. Those which ensure epidemiological safety i.e chlorination, ozonation, ultraviolet irradiation
3. Those by which the mineral composition of water is conditioned i.e fluorination, defluorination, deironing, deferrization, demanganization, softening, desalination.

A particular method of water treatment is chosen upon preliminary examination of the properties of the composition and properties of the water source to be used and comparing it with the standard or consumer requirements. Other processes employed in preparation of potable water include:

- softening
- addition of alkaline reagents
- precipitation of hardness salts

-desalination either by distillation, ion exchange, hyperfiltration or electrodialysis

### Treatment of Water from Barekese Dam

The water treatment involves the following processes:

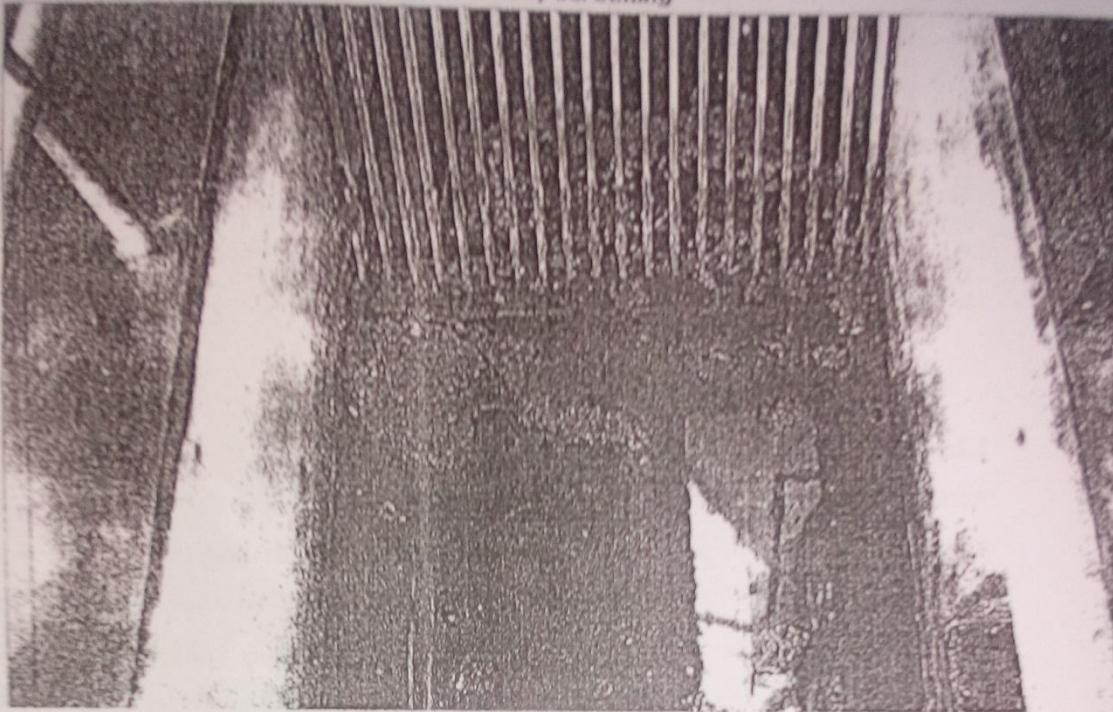
1. Screening
2. Grit removal
3. Aeration
4. Coagulation
5. Sedimentation
6. Filtration
7. Addition of hydrated lime
8. Disinfection
9. Laboratory analysis
10. Storage

#### 2.2.1. Screening

The first unit operation encountered in the treatment process is screening. A screen is a device with openings generally uniform in size that is used to retain large solids found in the influent raw water to the treatment plant. The water stream is reduced in speed to a range of  $0.3 \text{ m/s}^1$ . The principal role of the screen is to remove coarse material from the flow stream that could:

- damage subsequent process equipment by protecting pumps, valves, pipelines from damage or clogging
- reduce overall treatment reliability and effectiveness
- contaminate waterways

*Primary screening*



After the raw water is screened, it enters the grit removal chamber.

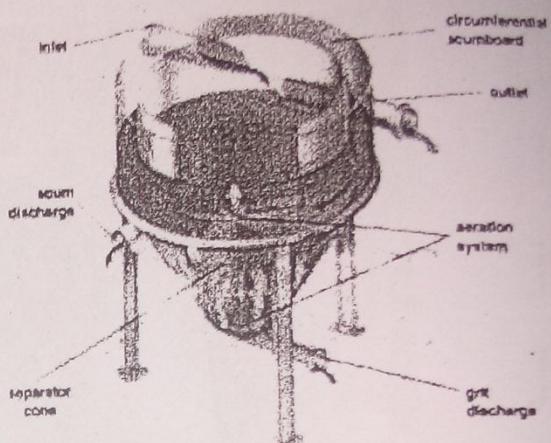
#### 2.2.2. Grit Removal

Grit consists of sand, gravel, pieces of glass, stones or heavy solid materials having specific gravities substantially greater than those organic putrescible solids in the water. They are generally located after the bar screens. Grit chambers are usually long rectangular open chambers or tanks designed to remove grit from the raw water by allowing them to settle at the bottom and are provided to:

- protect mechanical equipment from abrasion and accompanying abnormal wear
- reduce formation of heavy deposits in pipelines, channels and conduits
- reduce frequency of cleaning caused by excessive accumulation of grit

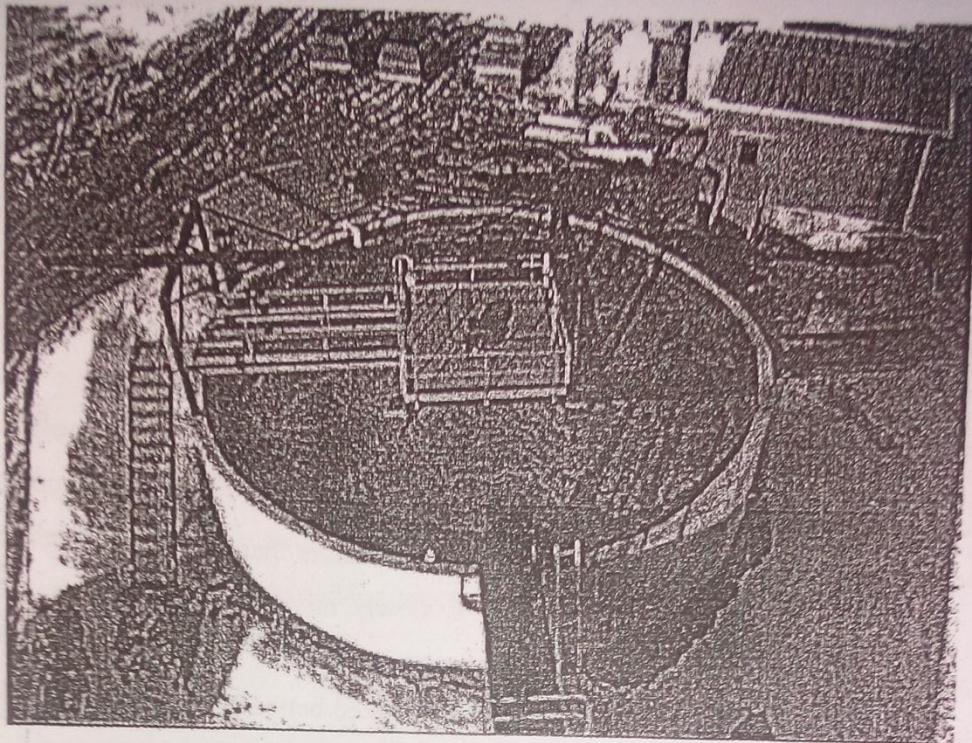
### Circular Grit Chambers

The Circular Grit Chamber is a high efficiency grit removal system. The unit can separate grit particles from sewerage or industrial waste water. Flow range is between 10 - 200 L/s. Settled grit is pumped with a rubber lined slurry pump to a the Grit Classifier system for final treatment.



### 2.2.3. Aeration

Aeration is a process to remove excess gases or to cure oxygen deficiency. The primary purpose is to improve taste by removing hydrogen sulphide and the volatile taste and odour waste of algae or decomposition of organic matter. Aeration makes water more palatable, as unaerated water has 'flat' taste. Aeration makes water less corrosive by removing carbon dioxide. In water supersaturated with oxygen, aeration causes oxygen to be released thus avoiding possible lifting of the surface in filters. On the other hand, increasing the oxygen content of oxygen deficient water results in the oxidation of ferrous and manganese ions. When water is alkaline, ferrous bicarbonate or sulphate is reduced in the presence of oxygen to ferric oxide which is insoluble.



#### 2.2.4 pH Adjustment

If water is acidic, lime or soda ash is added to raise the pH. Lime is cheaper but adds to water hardness. Making water slightly alkaline ensures coagulation and flocculation processes work effectively and help minimize the risk of lead being dissolved from lead pipes.

#### 2.2.5 Coagulation

Purification method using chemical which effectively glue small suspended particles so that they settle out of the water or stick to sand or other granules in a granules media filter. They work by eliminating natural electrical charge of suspended particles so that they attract and stick to each other. The joining of particles so that they form larger settleable particles is COAGULATION. A coagulant is the chemical that is added to destabilize the colloidal particle in water so that floc formation can result.

Coagulants:

- a) Aluminium sulphate also called filter alum. It reacts with water to form flocs of aluminium hydroxide. This leaves residue of aluminium in finished water 0.1-0.15 mg/l. Higher concentration can be toxic.

- b) Iron sulphate: coagulant work over larger pH range than alum but is not so effective. It has lower costs, slightly better in the removal of natural organic contaminants and leaves a residue of iron in the finished water, causing brownish stains on porcelain fixtures.
- c) Polymers are also used as coagulants aids. The long chains help strengthen the flocs, making it larger ensuring faster settling and easier to filter out. They are however expensive, can blind sand filters and have narrow range of effective doses.

#### 2.2.6 Flocculation

Flocculation is the process whereby particle size increases as a result of particle collision. A flocculant is a chemical, typically organic, added to enhance the flocculation process. Here coagulants are used but resultant floc is settled out rather than filtered through sand filters. The chosen coagulants and raw water is slowly mixed in a large tank called flocculation basin. Flocculation paddles turn very slowly to minimize turbulence. Retention time of flocculation is at least 30 min with speed between 15-45 cm/min. Flow rate less than 15 cm/min cause undesirable floc settlement within the basin.

#### 2.2.7 Sedimentation

The objective of this treatment is the separation of readily settleable solids and suspended particles that are heavier than water from water through gravitational settling and thus reduce suspended solid content. Water exiting the flocculant basin enters the sedimentation basin also called clarifier or settling basin. This is located close to the flocculation basin so that the flocs do not break up. The basins are either rectangular where water flows from end to end or circular, where flow is from centre outward. Minimum retention time is usually 4 hrs. A deep basin will allow more flocs to settle than a shallow basin. This is because large particles settle faster than small ones so large particles pump and integrate smaller ones to settle. At the bottom a layer of sludge is formed on the floor of the tank. About 3-5% of total volume is treated as sludge. An increasing popular method of floc removal is by dissolved air floatation. A proportion of clarified water is 5-10% of throughput is recycled and air is dissolved in it under pressure. This is injected into the bottom of the clarifier tanks where tiny air bubbles are formed which attach themselves to the floc particles and float them to the surface.

### **2.2.8 Filtration**

#### **a) Rapid Sand Filter**

After the floc separation, the water is filtered as the final step to remove remaining suspended particles and unsettled flocs. Most common type of filter is rapid sand filter. Water moves vertically through sand which often has a layer of activated carbon or anthracite carbon above the sand. Top layer removes organic compounds including taste and odour. Most particles pass through surface layers and are trapped in pore spaces or adhere to sand particles. To clean the filter, water is passed quickly upward through the filter opposite the normal direction to remove embedded particle. Prior to this compressed air may be blown up through the bottom of the filter to break p compacted filter media to aid backwashing process. This is known as AIR SCOURING

#### **b) Slow Sand Filter**

This is used where there is sufficient land and space .These rely on biological treatment rather than physical filtration. Slow sand filters are carefully constructed using graded layers of sand with the coarsest at the base and the finest at the top. Drains at the base convey treated water away for disinfection. Filtration depends on the development of a thin sticky biological layer at the surface of the filter known as Schemutzdecke and consists of algae, plankton, bacteria and protozoa. In the schemutdecke microorganisms break down organic matter and a great deal of inorganic suspended matter. In the filter, minute particles are acted upon by a variety of forces:

-Adsorption (space between sand grains reduced by sticky layer)

-Centrifugal forces-change of direction

-Sedimentation-between grain pockets that act as tiny sedimentation basins.

As water goes through bed it is constantly changing directions by the forces so that particles come into contact grains. Active microscopic and other organisms, bacteria and protozoa feed on impurities and on themselves thus converting organic matter and microorganisms into simple and harmless inorganic salts. 90-99.9 of bacteria are removed through this process.

#### **2.2.9 Disinfection (Tertiary Treatment)**

Disinfection is normally the last step in purifying drinking water. Water is disinfected to destroy any pathogens including viruses and bacteria. Chemicals used are chlorine or compounds such as chloroamine or chlorine dioxide which are strong oxidants that kill many microorganisms. Due to its germicidal activity, it ensures the destruction of enzymes essential for existence of microorganisms. Chlorine oxidizes iron, manganese and hydrogen sulphide. It also aids coagulation. Chlorine dioxide may create excessive amount of chlorate and chlorite. This poses extreme risk in handling and may spontaneously detonate upon release to the atmosphere in an accident. Chloamines are not very effective disinfectants but water may experience nitrification, where in ammonia as a source for bacterial growth.

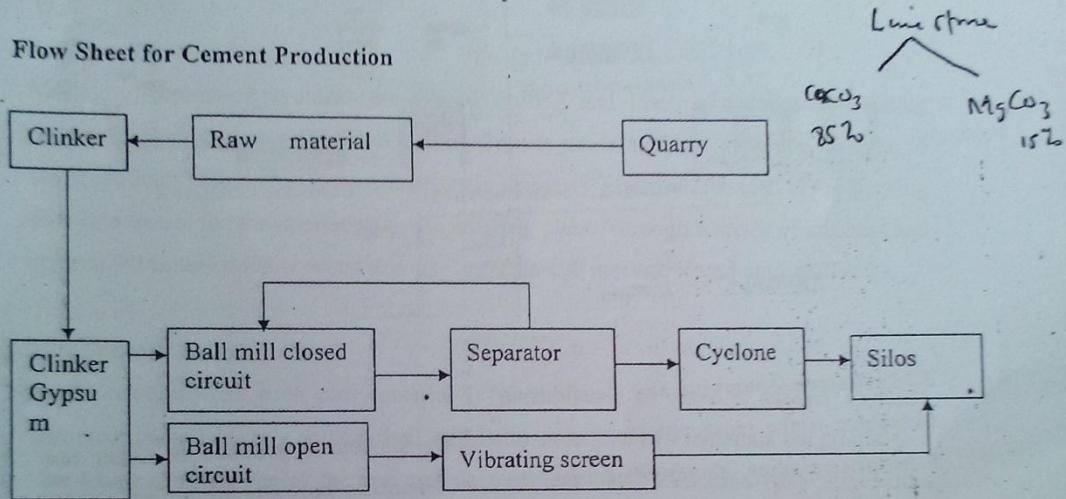
In Barekese, bleaching powder is used instead of chlorine and associated compound, since it is cheaper and easier to handle. Bleaching powder is a mixture of calcium hydroxide, calcium chloride and calcium hypochlorite. This combination has 20-35 % available chlorine.

## CHAPTER THREE: CEMENT PRODUCTION

### 3.1 Introduction

The raw materials used in the cement manufacturing process are limestone, sand, shale, clay and iron ore. The main material, limestone, is mined at site while the other minor materials may be mined either on site or nearby quarries. Another source of raw materials is industrial by-products. The use of by-product materials to replace natural raw material is a key element in achieving sustainable development.

Flow Sheet for Cement Production



Portland cement manufacturing requires a precise mix of raw materials. This mix is commonly called the raw mix and consists of two main natural materials; limestone (calcium carbonate) and argillaceous materials (alluminosilicates). The cement industry must therefore start by quarrying limestone and clay. The main objective of raw material control is to produce a kiln fed that will allow the production of a quality cement clinker, while conserving as much energy.

The cement clinker requires a defined proportion of the elements calcium, silicon, aluminium and iron, all these raw materials together with fuel ash must combine and form the typical clinker composition:  $\text{CaO} = 65 \pm 3\%$ ,  $\text{SiO}_2 = 20\%$ ,  $\text{Al}_2\text{O}_3 = 5 \pm 1.5\%$  and  $\text{Fe}_2\text{O}_3 = 3 \pm 1\%$ . (Bhatty 2005).

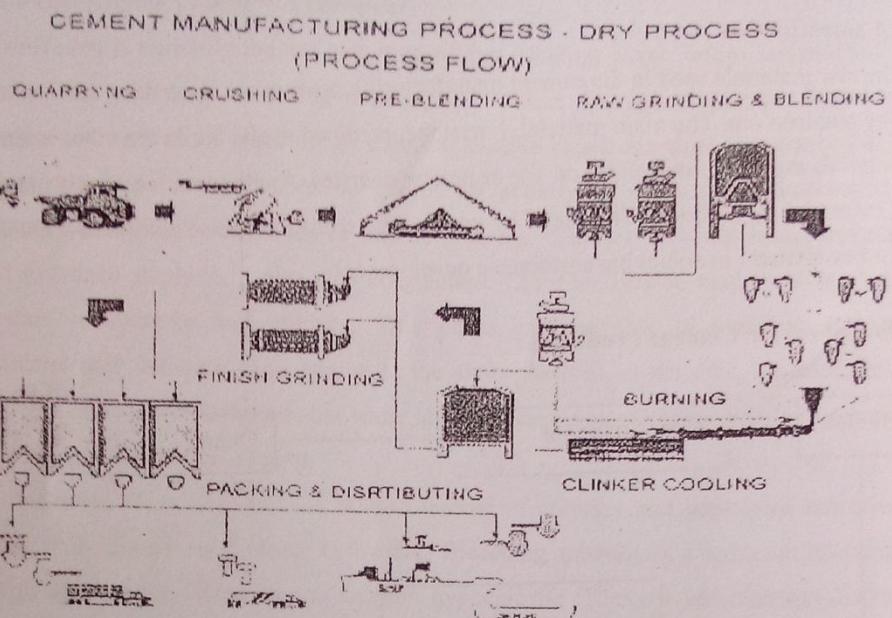
Instrument for particulate ctrl  
① Electrostatic precipitator (ESP)  
bag house

51

Calcinatory - is where there is  
burning & mixing of chemicals

Gypsum -  $\text{CaSO}_4$

Figure 1 Shows A Cement Manufacturing Process.



### 3.2 Limestone Quarrying and Crushing

Limestone is the most suitable source of  $\text{CaCO}_3$  for cement production. Other raw materials are silica, alumina and iron. Raw feed consists basically of limestone; the typical limestone used in cement production has 75-90 %  $\text{CaCO}_3$ . The remainder is magnesium carbonate and impurities. Typically cement plants are located close to the limestone source. The quarrying operations are done using the open mining process. Quarrying is done through drilling, blasting and using heavy moving equipment such as bulldozers and dump trucks. The quarried raw material is then transported to the cement plant using mechanical conveying equipment such as conveyor belts. The main steps to produce crushed limestone are:

- overburden removal-remove soil, clay and loose material and vegetation
- blasting of the limestone deposit
- transport of the blast limestone to the primary crusher
- Crushing of the limestone at the primary crusher to reduce stone size to about 25 cm and then through the secondary crusher to reduce stones to approximate size of 5-10

Calcination  
involves  $\text{H}_2\text{O}$   
✓  $\text{CO}_2$   
involves combustion

The quarried limestone normally is in the form of large boulders ranging from a few centimeters to several meters in diameter. These varying sizes of limestone need to be crushed to about 4 cm in order to be used in the next step for a raw feed preparation. Limestone quarrying will consume approximately 85% of the total energy used in mining process. The other 15% will be consumed by the crushing process and limestone transport system composed of a sequence of conveyor belts and dust collectors.

### **3.3 Raw Material Preparation**

Mining of limestone requires the use of drilling and blasting techniques. Blasting produces materials in a wide range of sizes from approximately 1.5 meters in diameter to small particles less than a few millimeters in diameter. Material is loaded at the blasting face into trucks for transportation to the crushing plant. Through a series of crushers and screens the limestone is reduced to a size less than 100 mm and stored until required.

#### **Wet Process**

In the wet process each raw material is proportioned to meet a desired chemical composition and fed to a rotating ball mill with water. The raw materials are ground to a size where the majority of the raw materials are less than 75 microns. Materials exiting the mill are called slurry and have flow characteristics. This slurry is pumped to blending tanks and homogenized to ensure the chemical composition of the slurry is correct. Following the homogenization process, the slurry is stored in tanks until required.

#### **Dry Process**

In the dry process each raw material is proportioned to meet a desired chemical composition and fed to either a rotating mill or vertical roller mill. The raw materials are dried with waste process gases and ground to a size where the majority of the materials are less than 75 microns. The dry materials exiting either type of mill are called kiln feed.

### **Pyroprocessing**

Whether the process is wet or dry the same chemical reactions take place. Basic chemical reactions are: evaporating all moisture, calcining the limestone to produce free calcium oxide and reacting the calcium oxide with minor materials (sand, shale, clay and iron). This results in a final black nodular product known as clinker which has the desired hydraulic properties. In the wet process, the slurry is fed to a rotary kiln which can be from 3-5 m in diameter and from 120- 165 m in length. The rotary kiln is made of steel and lined with special refractory materials to protect it from the high process temperatures. Process temperatures can reach as high as 1450 °C during the clinker making process. In the dry process kiln, material is fed to a preheater tower, which can be high as 150 m. Material from the preheater tower is discharged to a rotary kiln which can have the same diameter as a wet process kiln but the length is much shorter at approximately 45 m. The preheater tower and rotary kiln are made of steel and lined with special refractory materials to protect from high process temperature. Regardless of the process the rotary kiln is fired with intense flame produced by burning coal, coke, gas or waste fuels. Preheater towers can be equipped with firing as well. The rotary kiln discharges the red hot clinker under the intense flame into a clinker cooler. The clinker cooler recovers heat from the clinker and returns the heat to the pyroprocessing system, thus reducing fuel consumption and improving energy efficiency. Clinker leaving clinker cooler is at a temperature conducive to being handled on standard conveying equipment.

### **3.4 Finish Grinding and Distribution**

The black nodular clinker is stored on site in silos or clinker domes until needed for cement production. Clinker, gypsum and other process additives are ground together in ball mills to form the final cement product. Fineness of the final products, amount of gypsum added, and the amount of final cement products.

Each cement product is stored in an individual bulk silo until needed by the customer. Bulk cement can be distributed in bulk by trucks, rail or water depending on the customers' needs. Cement can be packaged with or without colour addition and distributed by truck or rail.

TABLE 1 Describes the sequence of chemical and physical changes that take place in the preheater tower and inside the kiln

Temperature °C	Process Description	Chemical reaction
HEATING PROCESS		
>200	Water evaporation	
>500	Decomposition of mineral structures and oxide formation	$\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3 = \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ $\text{Al}_2\text{O}_3.\text{SiO}_2 = \text{Al}_2\text{O}_3 + \text{SiO}_2$
>800	Belite formation	$\text{CaO} + \text{SiO}_2 = \text{CaO}.\text{SiO}_2$ $= 2\text{CaO}.\text{SiO}_2$
800-900	Limestone calcinations	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$
>1260	Liquid phase formation	*
1450	Tetracalcium aluminoferrates	$2\text{CaO}.\text{SiO}_2 + \text{CaO} = 3\text{CaO}.\text{SiO}_2$ $3\text{CaO}.\text{Al}_2\text{O}_3 + \text{CaO} + \text{Fe}_2\text{O}_3 =$ $4\text{CaO}.\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$
COOLING PROCESS		
1300-240	Cooling and crystal formation	

The clinker coming out of the kiln is approximately 1500 °C. It is cooled in an air cooled cooler. Ambient air is blown into the cooler to exchange heat between the hot clinker and the ambient air. After cooling the clinker temperature drops to approximately 170 °C.

### 3.5 Energy Use in the Cement Manufacturing Process

Portland cement production is a high energy demand process. The U.S average kiln fuel energy consumption in 1973 was 7 GJ/t. In the mid 1990 it was about 25% above what the best available technology would require which was about 3GJ/t (Choate 2003). The main reason for the energy consumption reduction is the conversion from the wet process to the dry process. However the new dry process requires less energy overall. The energy used for manufacturing is distributed as follows:

92.7 % pyroprocessing, 5.4 % finishing grinding, 1.9 % Raw materials (Choate 2003)

Cement kilns use a large variety of fuel sources to provide the energy required to produce the high temperatures necessary for the clinker formation. Fuel is fed into the rotary kiln mainly on the back end and raw material flows counter current to a stream of hot gases. The energy generated by the fuel combustion will evaporate any water from the raw materials, calcine the limestone and finally form the clinker. Calcination takes place between 700-900°C and the clinker formation will occur at approximately 1500°C. Carbon dioxide formed during the pyroprocesssing is a direct consequence of the type of fuel used. The most common fuel sources for the cement industry are: coal, fuel oil and petroleum coke.

TABLE 2 Typical data on energy content and CO<sub>2</sub> emission for frequent fuels

Fuel	Energy content(MJ/kg)	CO <sub>2</sub> emission factor(kg/MJ)
Coal	32	0.103
Fuel oil	40	0.077
Natural gas	36	.056
Petroleum coke	34	0.073-0.095

The amount of CO<sub>2</sub> generated by waste fuels is considered to be zero as shown in the table. This is based on the argument that the CO<sub>2</sub> generated by waste fuels would be released into the atmosphere by natural degradation and during the natural process the energy content would not be applied in any manufacturing process.

TABLE 3 Typical data on energy content and CO<sub>2</sub> emission for waste fuels

Fuel	Energy content(MJ/kg)	CO <sub>2</sub> emission factor(kg/MJ)
Scrap tries	21	NA
Plastics	33	NA
waste oil	38	NA
paper residue	6	NA
waste solvents	18-23	NA

### 3.6 Calcination

Calcination is a process of heating, without fusion, to change the physical or chemical constitution of substances. Calcining process consists of 3 main objectives: The first objective is to remove water which is absorbed as water of crystallization or water of constitution. The second objective of calcining is to remove CO<sub>2</sub>, SO<sub>2</sub> and other volatile substances. The third objective of calcination is the oxidation of the substance completely or partially.

#### Carbon Dioxide Formed by Calcinations

A large percent of cement plants are located close to their source of calcium oxide. This is an essential requirement since limestone represents about two-third of the clinker composition by mass. A typical clinker raw mix is made up of approximately 80% limestone. During the clinker process, limestone will suffer calcinations and CO<sub>2</sub> will be formed. The limestone chemical reaction can be expressed by the equation below:



The percentage of the calcium oxide in clinker is usually between 62 and 67 %. The complement comprised of iron oxides, silicon oxides and aluminium oxides. The amount of carbon dioxide generated by the process varies based on the specific loss of the raw materials (limestone) on ignition.

## CHAPTER FOUR: PETROLEUM REFINERY AND PETROCHEMICALS

### 4.1 Nomenclature in the Petroleum Industry

Most petroleum types are complex mixtures that are difficult to characterize in detail, and therefore, many definitions used by the exploration, production and refining sectors of the industry to describe petroleum and its products lack precision. Traditionally, the unit of crude oil production has been the barrel, equal to  $0.159 \text{ m}^3$ , or  $5.61 \text{ ft}^3$ . Today, however, petroleum reserves are often given in metric tons. Density may be reported in metric units but is more often in degrees API (American Petroleum Institute). The relationship between specific gravity and API, also called API gravity, is defined by

$$\text{Sp gr. (at } 16^\circ\text{C}) = \frac{141.5}{(\text{API} + 131.5)} \text{ or} \quad \text{API} = \frac{141.5}{\text{Sp gr. (at } 16^\circ\text{C})} - 131.5$$

### 4.2 Origin of Petroleum

Petroleum is naturally occurring complex mixture consisting predominantly of hydrocarbons, frequently with other hydrogen and carbon compounds containing significant amounts of nitrogen, sulphur and oxygen as well as amounts of nickel, vanadium, and other elements. It can occur in solid, liquid, or gaseous form as asphalt, crude oil, gas, respectively.

Organic matter is incorporated into sediments as they are deposited and some biogenic gas may be generated; with increasing depth of burial, temperature converts the organic matter to petroleum-like material; part of this material migrates from the source rock through carrier beds to the reservoir; here, compositional changes may be produced by increasing temperature, water washing, and bacterial degradation.

### 4.3 Composition of Petroleum

The term petroleum, literally, rock oil, is applied to the deposits of oily material found in the upper strata of the earth's crust, where they were formed by a complex series of chemical reactions from organic materials laid down in previous geological eras.

The elemental composition of petroleum varies greatly from one deposit to another. Carbon and hydrogen make up the bulk, but other elements present include sulphur (trace

Fossil Fuels  
crude oil (petroleum)  
Coal  
Natural gas

to 8%), nitrogen (trace to 6%), oxygen (trace to 1.8%), and nickel and vanadium.

#### 4.4 Resources

Petroleum resources are distributed widely in the earth's crust as gases, liquids, and solids. The product derived from these naturally occurring resources are used mainly as energy sources, although substantial volumes serve as feedstock in the plastic, chemical, and other industries.

Petroleum resources are classified as follows: the *resource base* is the total amount present in a specific volume of the earth's crust; *resources* represent the total amount of petroleum, including reserves, that is expected to be produced in the future; *reserves* constitute the petroleum that has been discovered and can be produced at the prices and technology that existed when the estimated was made; *proved reserves* are estimates of reserves contained primarily in the drilled portion of the fields; *indicated reserves* constitute known petroleum that is currently producible but cannot be estimated accurately enough to qualify as proved; *inferred reserves* are producible but the assumption of their presence is based upon limited physical evidence and considerable geological extrapolation; sub-economic resources constitute the petroleum in the ground that cannot be produced at present prices and technology but may become producible; undiscovered resources are estimated totally by geological speculation with no evidence by drilling available.

#### 4.5 Drilling Fluids

Drilling fluids and muds perform a variety of functions that influence the drilling rate, cost, efficiency, and safety of the drilling operation. They are pumped down a hollow drill string through nozzles in the bit at the bottom and up the annulus formed by the hole or casing and the drill string to the surface. The bit is turned by rotating the entire string from the surface or by using a down-hole motor. After reaching the surface, the drilling fluid is passed through a series of screens, settling tanks or pits, hydroclones, and centrifuges to remove formation material brought to the surface. It is then treated with additives to obtain the desired properties. Once treated, the fluid is pumped back into the well and the cycled repeated.

## Properties

The density is adjusted with dissolved salts or powdered high density solids to provide a hydrostatic pressure against exposed formations in excess of the pressure of the formation fluids. In addition, the hydrostatic pressure of the mud column prevents collapse of weak formations into the borehole. The hydrostatic pressure imposed by a column of drilling fluid is expressed as follows:

$$P = 0.098L_m (0.052L_m)$$

$$P = \frac{distance (ft)}{density (lbm/gal)}^m$$

### Density control

Mud density is controlled accurately by suitable weighting material that does not adversely affect the other properties. Most important is the specific gravity of the weighting agent as well as its chemical inertness. Barite meets these requirements; it is virtually insoluble in water and does not react with other mud constituent.

The drilling rate is improved by solids-free fluids, which are designed for work-over and completion operation to avoid formation damage. Weighted fluids without solids are provided by solutions of various water-soluble salts below. **Table 2.1**

### Viscosity

The type of solids and the solids content of water based muds control the viscosity. The reactive solids are composed of commercial clays, of which bentonite, attapulgite, and sepiolite are the most important; organophilic clays, prepared from bentonite or attapulgite and aliphatic amine salts are used for oil-based muds.

Viscosity is decreased by a reduction of solids, or deflocculation or clay water suspensions. Thinning is obtained by reducing plastic viscosity, yield point, or gel strength, or a combination of these properties. Typical mud thinning chemicals are polyanionic materials that are absorbed on the positive-edge sites of the clay particles, thereby reducing the attractive forces between the particles without affecting clay hydration.

### Filtration control

Filtration control is particularly important in permeable formations where the mud hydrostatic pressure exceeds the formation pressure. It reduces drill string sticking, torque, and drag due to filter-cake development; minimises damage to protective formations; and in some areas, improves boreholes stability. Materials for this purpose

include clays, organic polymers, and lignite derivatives. The bentonite present in freshwater systems acts as the primary filtration agent; concentrations vary widely, but may range up to 100 kg/m<sup>3</sup>.

#### 4.6 Refinery Processes

Petroleum products derived from crude oil are a convenient source of energy. Since petroleum liquids are easy to handle and store, they are well suited for transformation fuel, e.g. for cars and airplanes. Other refinery products include lubricants, waxes, asphalt, solvents and specialities such as liquefied petroleum gas (LPG), hydraulic fluids, and others. Petroleum is the principal raw material source for petrochemicals such as plastics, synthetic elastomers, certain alcohols and other important products.

Crude petroleum contains a wide range of hydrocarbons from light gases to residuum that is too heavy to distil even under vacuum. Crude oil is primarily made up of paraffins, cycloparaffins and aromatic compounds in varying proportions, some sulphur compounds, a small amount of nitrogen, but no appreciable amount of oxygen or olefins. Refining processes can be grouped into three classes; separation, usually distillation to give the desired type of compounds; conversion, usually cracking, to change molecular weight and boiling point; and upgrading, e.g. hydrotreating to meet product-quality specifications.

#### 4.7 Processing Steps

##### Desalting

Salt and clay or other suspended solids are removed by washing with water at 65-90 °C to reduce viscosity. Typical salt content of crude may be 280 g/100m<sup>3</sup>; desalting may remove over 90% without the loss of oil.

##### Distillation

The crude is separated in continuous-fractionation plate towers, as shown in the figure below. Primary distillation takes place at atmospheric pressure and the bottom temperature is limited to 370-400 °C to prevent thermal cracking.

### **Hydro-processing**

Hydroprocessing improves the quality of various products or cracks heavy carbonaceous materials to lower-boiling, more valuable products. Mild hydrotreating removes sulphur, nitrogen, oxygen and metals and hydrogenates olefins.

Hydrogen consumption increases with severity and depends on the amount of sulphur removed and the feed content of aromatic materials and olefins, which also consume hydrogen.

### **Hydrocracking**

In hydrocracking, high molecular weight compounds are cracked to lower boiling materials. Severity is increased by operating at higher temperatures and longer contact time than in hydrotreating. Hydrocracking is used extensively on distillate stocks. It is of increasing importance in view of the trends to heavier crudes and the need for processing synthetic crudes.

### **Catalytic cracking**

In catalytic cracking, heavy distillate oil is converted to lower molecular weight compounds in the boiling range of gasoline and middle distillate. Gasoline yield is high and so is the octane number.

### **Coking**

Coking can be considered as high severity thermal cracking or destructive distillation. It is generally used on vacuum residuum to deposit coke while cracked vapours are taken overhead. Fluid coking is a continuous process similar in design to fluid catalytic cracking.

### **Visbreaking**

Viscosity breaking is one of the few thermal-cracking processes still used in refining other than coking. It reduces the viscosity of heavy fuel oil and permits handling at lower temperature. Vacuum residuum can usually be burned directly but would require perhaps 200 °C for proper atomisation in burners. After visbreaking, a temperature of 100 °C or less adequate which gives a fuel oil suitable for large commercial buildings.

### **Steam-cracking**

Steam-cracking is used primarily to produce olefinic raw materials for petrochemicals manufacture. It plays such an important role in refining, however, that the planning and operation of a large stream-cracking plant is usually closely integrated with a large refinery. Steam-cracking is carried out at ca 8000-850 °C and slightly above atmospheric pressure.

### **Alkylation**

In alkylation, olefins of 3,4 and 5 carbon atoms react with isobutene to give higher molecular weight products of high octane. Thus, alkylation increases the high octane component in the gasoline pool.

### **Extraction**

Extraction separates by chemical type rather than by boiling point and is much more expensive than distillation. It is used primarily for removal of aromatic material from naphtha fractions, upgrading middle distillates, and preparation of high quality lubricating oils

### **Lubricants**

Petroleum is the main source of lubricants for a wide range of uses. Lubricants are derived from distillates boiling above 370 °C and they are separated by vacuum distillation and refined to meet specifications.

### **4.8 Petroleum Products**

The importance of petroleum products is reflected in the great consumption of crude oil, the starting material for these products.

Petroleum products include power fuels for passenger cars, trucks, aircraft engines, and gas turbines (gasoline, jet fuels, diesel fuel and LPG); heating oils; illumination oils (kerosene); solvents (petroleum spirits, aromatic solvents); lubricants (engine oils, greases); building materials (asphalts); insulating and waterproofing materials; and other products, such as cutting oils, heat-treating oils, hydraulic oils, petroleum jelly etc.

#### **4.9 Petrochemicals**

Petrochemicals are essentially the chemical compounds derived from petroleum sources. Thus, cracking of petroleum produces ethylene which is converted to ethylene glycol, the latter being a typical petrochemical. The term is also applied to substances such as ammonia, because hydrogen used to form the ammonia is derived from natural gas. Thus synthetic fertilisers are considered to be petrochemicals. The bulk of petrochemicals obtained from common hydrocarbons are broadly grouped as under.

1. Paraffins (saturated): methane, ethane propane butanes (iso and normal), etc.
2. Olefins (unsaturated): ethylene, propylene, butylenes (butane 1 and 2 and isobutylene), etc.
3. Aromatics: benzene, toluenes, xylenes etc.

#### **Petrochemicals from methane**

Ammonia, nitric acid, ammonium nitrate, ammonium sulphate, urea carbon dioxide, methyl alcohol, neoprene rubbers, acetic acid, chloroform, methyl chloride, carbon disulphide, etc.

#### **Petrochemicals from Ethylene**

Ethylene oxide, ethylene glycol, monoethanolamine, diethanolamine, diethylene glycol, ethyl chloride, ethylene dichloride, acetic acid, ethyl alcohol, etc.

#### **Petrochemicals fro propane and propylene**

1. Propane: ethylene, methyl alcohol, formaldehyde, acetaldehyde, acetone.
2. Propylene: allyl chloride, allyl alcohol, glycerine, epoxy resins acrolein, cumenepheno, methyl styrene, polypropylene, etc.

#### **Petrochemicals from butanes and butylenes**

1. Butanes: acetic acid, propionic acid, butyric acid, isobutyl alcohol, etc
2. Butylenes: butadiene, synthetic rubber, butyl rubber, etc

#### **Petrochemicals from aromatics**

1. Benzene: ethyl benzene, styrene, synthetic rubber, phenol, cumene, methyl styrene, etc.
2. Toluene: trinitrotoluene, etc.

3. Xylenes: para-xylene, terephthalic acid, etc.

#### 4.10 Lubrication and Lubricants

The process of reducing friction between two surfaces moving tangentially with respect to one another by interposing a substance of low shear strength between them is called lubrication and the interposed substance is known as a lubricant.

#### Functions of lubricants

The main functions of the lubricants are as follows:

1. It reduces wear and tear by avoiding direct contact between the rubbing surfaces.
2. It reduces loss of energy in the form of heat by acting as coolant.
3. It increases the efficiency of the machine.
4. It minimizes the liberation of heat.
5. It reduces the maintenance as well as running cost of machine.
6. It also acts as a seal to internal combustion engines.

#### Substance used as lubricants

Vegetable oils and fatty acids are most important substances which are used as lubricants. Tallow, lard, whale oils, neat foot oil, rosin oil, castor oil, olive oil, coconut oil, palm oil, oleic acid, etc are the various substances used as lubricants.

#### Characteristics of good lubricating oil

The characteristics of good lubrication oil are:

1. High boiling point or low vapour pressure.
2. Suitable viscosity for particular service condition.
3. Low freezing point
4. High thermal stability
5. High oxidation resistance
6. Non-corrosive nature
7. Resistance to decomposition at higher or elevated temperatures.

## CHAPTER FIVE: SOAPS AND DETERGENTS

### 5.1 Introduction

Soap is actually a specific type of salt, the hydrogen of the fatty acid being replaced by a metal, which in common soaps is usually sodium. Soap lowers the surface tension of water and thus permits emulsification of fat-bearing soil particles. A typical commercial cleansing soap is made by reacting sodium hydroxide with a fatty acid. The lower the hydrogen contents of the acid, the thinner the soap. The by-product of the reaction is glycerol.

Detergent is a substance that reduces the surfaces the surface tension of water, specifically, a surface-active agent which concentrates at oil-water interfaces, exerts emulsifying action, and thus aids in removing soils. Detergents excel in possessing these special properties to effect soil removal. There are light and heavy-duty detergents.

### 5.2 Detergent raw materials

A large volume of active organic compounds, or surfactants, for both detergents and soaps are manufactured in final form by soap and detergent companies. The same is true for fatty acids, the basic material for soaps.

**Surfactants:** these embrace "any compound that affects (usually reduces) surface tension when dissolved in water or water solutions, or which similarly affects interfacial tension between two liquids.

**Suds regulators:** a suds regulator -either a stabiliser or suppressor- is often used with a surfactant. These materials have no common chemical relationship and are often specific for certain surfactants. Examples of stabiliser surfactant systems are lauric ethanolmaide-alkylbenzenene sulphonate and lauryl alcohol alkyl sulphate. Suds suppressors are generally hydrophobic materials, some examples of which are long-chain fatty acids, silicones.

raw materials for soap pds

= fatty + base

66

Df. b. detergent & soap  
Df. b. hard soap / soft soap

**Builders:** builders boost detergent power, and complex phosphates such as sodium tripolyphosphate, have been used most extensively. These are more than water softeners which sequester water-hardening calcium and magnesium ions. They prevent redeposition on fabric or soil from the wash water.

**Additives:** corrosion inhibitors, such as sodium silicate, protect metal and washer parts, utensils and dishes from the action of detergents and water.

### 5.3 Soap

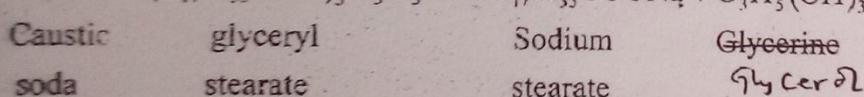
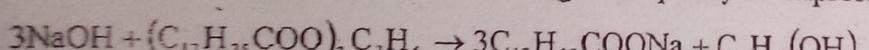
Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, palmitic, lauric and myristic acid.

#### Soap manufacture

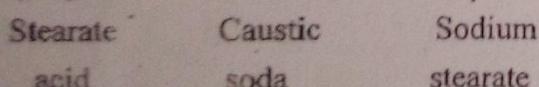
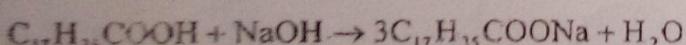
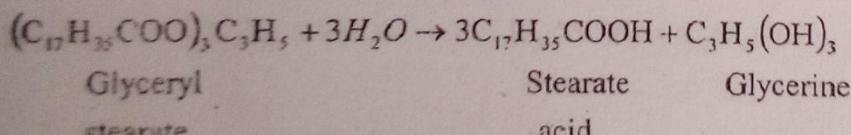
The present procedure involves continuous *splitting* or *hydrolysis*.

After separation of the glycerine, the fatty acids are neutralised to soap.

The basic chemical reaction in the making of soap may be expressed as *saponification*:



The procedure is to split or hydrolyse, the fat, and then, after separation from the valuable glycerine, to neutralise the fatty acids with a caustic soda solution:



**Washing:** Carcasses are washed with cold water to remove attached tissue, foreign materials, blood, etc.

**Chilling:** Chilling of carcasses is done to remove body heat and to protect from microbial action. Normally chilling is done below 40 °F.

**Packing:** Sometimes carcasses are cut into parts according to market demand otherwise they are packed in frozen form.

