Chapter 2

Safety Considerations in Process Industries

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2.1 Introduction

The misuse or the mishandling of a simple instrument such as a knife, hammer, or sickle may result in an injury to the holder. Workers in a factory, a manufacturing plant, or a chemical plant remain exposed to moving conveyers, machines, dangerous chemicals, heat, pressures, high electric fields, accelerating objects, and other sources of hazards. If workers are not protected from these hazards, there is the chance of incidents ranging from simple injuries to death of personnel. In addition, the damage can reach the whole manufacturing plant and its surrounding environment, causing much loss of life if the facilities or equipment are not properly controlled. These types of incidents have taken place since the beginning of the Industrial Revolution.

On December 26, 1984 at 11:30 p.m, when the people of Bhopal, India, were preparing for sleep, a worker detected a water leak in a storage tank containing methyl isocyanate (MIC) at the Union Carbide Plant. About 40 tons of MIC poured from the tank for nearly 2 hours without any preventive measures being taken. The night winds carried the MIC into the city of Bhopal. Some estimates report 4000 people were killed, many in their sleep; and as many as 400,000 more were injured or affected.

On April 26, 1986 at Chernobyl, Ukraine, a nuclear reaction went wrong and resulted in the explosion of one of the reactors in a nuclear power plant. These reactors were constructed without containment shells. The release of radioactive material covered hundreds of thousands of square kilometers. More than 3 million people in the surrounding suburbs suffered from this disaster. While 36 people died in the accident itself, the overall death toll has been estimated at 10,000.

In another incident, on January 29, 2003, an explosion and fire destroyed the West Pharmaceutical Services plant in Kinston, North Carolina, causing six deaths, dozens of injuries, and hundreds of job losses. The facility produced rubber stoppers and other products for medical use. The investigators found that the fuel for the explosion was a fine plastic powder used in producing rubber goods. Combustible polyethylene dust accumulated above a suspended ceiling over a manufacturing area at the plant and was ignited by an unknown event (Fig. 2.1).

Furthermore, on October 29, 2003, a series of explosions killed one person, severely burned another worker, injured a third, and caused property damage to the Hayes Lemmerz manufacturing plant in Huntington, Indiana. The Hayes Lemmerz plant manufactures cast aluminum automotive wheels, and the explosions were fueled by accumulated aluminum dust, a flammable by-product of the wheel production process (Fig. 2.2).

Figure 2.1 Dust explosion kills six, destroys West Pharmaceutical Services Plant, Kinston, NC (January 29, 2003). (*Source: www.chemsafety.gov/index.cfm?*)

These examples along with others show that the causes of these incidents were not only because of ergonomic factors but also because of the failure of the equipment or some other unknown reasons. The breakdown of these incidents was probably a lack of safety measures for the plant workers and also to the nearby communities.

Figure 2.2 Aluminum dust explosions at Hayes Lemmerz Auto Wheel Plant (October 29, 2003). (*Source: www.csb.gov/index.cfm?folder=current_investigations&page=info&INV_ID=44*)

The significance of safety measures is indicated in the proper operation of the plant, its regular checkups, overhauling, repair and maintenance, regular inspection of moving objects, electrical appliances, switches, motors, actuators, valves, pipelines, storage tanks, reactors, boilers, and pressure gauges. At the same time, the proper training of workers for running the operations and dealing with emergencies, spills, leaks, fire breakouts, chemical handling, and electrical shock avoidance should not be ignored.

2.2 OSHA (Occupational Safety and Health Administration), and PSM (Process Safety Management)

The release of toxic, reactive, or flammable liquids and gases in processes involving highly hazardous chemicals has been reported for many years. While these major incidents involving the hazardous chemicals have drawn the attention of the public to the potentials for major catastrophes, many more incidents involving released toxic chemicals have occurred in recent years. These chemicals continue to pose a significant threat to workers at facilities that use, manufacture, and handle these materials. The continuing occurrence of incidents has provided the impetus for authorities worldwide to develop or consider legislation and regulations directed toward eliminating or minimizing the potential for such events.

One such effort was the approval of the Sevaso Directive (Italy) by the European Economic Community after several large-scale incidents occurred in the 1970s. This directive addressed the major accident hazards of certain industrial activities in an effort to control those activities that could give rise to major accidents, as well as to protect the environment, human safety, and health. Subsequently, the World Bank developed guidelines for identifying, analyzing, and controlling major hazard installations in developing countries and a hazardous assessment manual that provides measures to control major fatal accidents.

By 1985, in the United States, the U.S. Congress, federal agencies, industry, and unions became actively concerned and involved in protecting the public and the environment from major chemical accidents involving highly hazardous chemicals. In response to the potential for catastrophic releases, the Environmental Protection Agency (EPA) was seriously involved in community planning and preparation against the serious release of hazardous materials.

Soon after the Bhopal incident, the Occupational Safety and Health Administration (OSHA) determined the necessity of investigating the general standards of the chemical industry and its process hazards, specifically the measures in place for employee protection from large releases of hazardous chemicals.

OSHA has introduced certain standards regarding hazardous materials, flammable liquids, compressed and liquefied petroleum gases, explosives, and fireworks. The flammable liquids and compressed and liquefied petroleum gas standards were designed to emphasize the specifications for equipment to protect employees from other hazardous situations arising from the use of highly hazardous chemicals. In certain industrial processes, standards do exist for preventing employee exposure to certain specific toxic substances. They focus on routine and daily exposure emergencies, such as spills, and precautions to prevent large accidental releases.

Unions representing employees who are immediately exposed to danger from processes using highly hazardous chemicals have demonstrated a great deal of interest and activity in controlling the major chemical accidents. The International Confederation of Free Trade Unions (ICFTU) and the International Federation of Chemical, Energy and General Workers' Union have issued a special report on safety measures.

The objectives of the process safety management of highly hazardous chemicals were to prevent the unwanted release of hazardous chemicals, especially into locations that could expose employees and others to serious harm. An effective process safety management requires a systematic approach to evaluating the whole process. The process design, process technology, operational and maintenance activities and procedures, nonroutine activities and procedures, emergency preparedness plans and procedures, training programs, and other elements that have an impact on the process are all considered in the evaluation. The various lines of defense that have been incorporated into the design and operation of the process to prevent or mitigate the release of hazardous chemicals need to be evaluated and strengthened to assure their effectiveness at each level. Process safety management is the proactive identification, evaluation and mitigation, or prevention of chemical releases that could occur as a result of failure in the procedures or equipment used in the process.

These standards also target highly hazardous chemicals and radioactive substances that have the potential to cause catastrophic incidents. This standard as a whole is to help employees in their efforts to prevent or mitigate the episodic chemical releases that could lead to a catastrophe in the workplace, and the possibility of the surrounding community to control these types of hazards. Employers must develop the necessary expertise, experience, judgment, and proactive initiative within their workforce to properly implement and maintain an effective process safety management program as envisioned in the OSHA standards.

2.3 Incident Statistics and Financial Aspects

Normally the management of any production plant is not very concerned about the safety of employees. Moreover, it is financially reluctant to engage in extensive safety planning until and unless it is very imperative or is required by some monitoring agencies that inspect the safety procedures and facilities. The situation is worse in the third world countries. There is a need to develop a culture in an organization that is safety and health oriented. The duty of the supervisors or safety managers is to realize the need for safety measures in terms of financial loss to the producer. It can be highlighted for management by bringing the information on the loss of working hours, employee injuries, property damage, fires, machinery breakdown, public liabilities, auto accidents, product liabilities, fines, costly insurance, and such to their attention.

The varying estimates of the annual cost of industrial accidents are stated in terms of millions of dollars and are usually based on the lost time of the injured worker. This is largely an employer's loss, but is far from being the complete cost to the employer. The remaining incidental cost is four times as much as the compensation and the medical payments.

2.4 Safety Decision Hierarchy

The set of commands and actions that follow a sequence of priority to reach a conclusion is called hierarchy. Hierarchy identifies the actions to be considered in an order of effectiveness to resolve hazard and risk situations. It helps in locating a problem of risk, its analysis and approaches to avoid this risk, a plan for action, and its effects on productivity.

The different sequences of a safety plan are given in Fig. 2.3.

In the first stage of risk assessment hierarchy, identify and analyze the hazard and follow up with an assessment of the risk. The alternative approaches are carried out to eliminate the hazards and risks through system design and redesign. Sometimes the risk can be reduced by substituting less hazardous materials or by incorporating new safety devices, warning systems, warning signs, new procedures, training of employees, and by providing personnel protecting equipment. A decision is normally taken after the evaluation of the various alternatives followed by the reassessment of the plan of action.

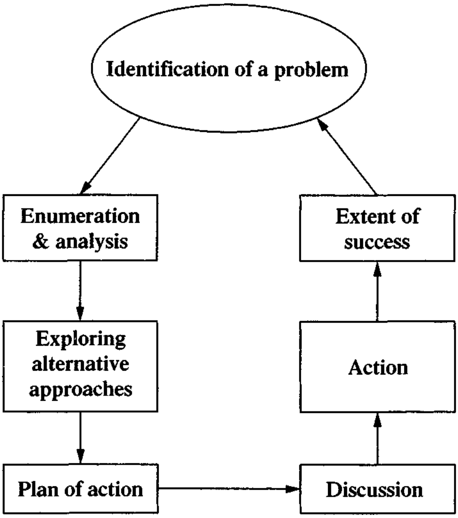

Figure 2.3 Risk assessment hierarchy.

2.5 Hazard Analysis and Risk Assessment (HARA)

The safety standards and guidelines issued from time to time are always under development regarding hazard analysis and risk assessment. The job of making a guideline becomes more difficult because of the varied nature of different industries, for example, machinery making; chemical production; manufacturing of semiconductors, pharmaceuticals, pesticides, construction materials, petroleum and refinery; and food and beverage. Each of these industries has its own hazards and risks. Therefore, it is not possible to apply a general HARA plan to all of these industries. However, this general plan can be modified for a particular process. The main features are discussed below.

- Specify the limits of the machine
- Identify the hazards and assess the risks
- Remove the hazards or limit the risks as much as possible
- Design guards and safety devices against any remaining risks
- Inform and warn the user about any residual risks of the process or machine
- Consider any necessary additional precautions

Considering all the above points, the risk management program can be started from a proper design of a machine, process, reactions, installation, operation and maintenance, and so forth.

2.6 Types of Hazards in Industries

2.6.1 Heat and temperature

In any manufacturing facility there are many sources of heat such as boilers, kilns, incinerators, evaporators, and cryogenic facilities. Extreme temperatures can lead directly to injuries of personnel and may also cause damage to the equipment. These factors can be generated by the thermal changes in the environment that lead to accidents, and therefore, indirectly to injuries and damages.

The immediate means by which temperature and heat can injure personnel is through burns that can injure the skin and muscles as well as other tissues below the skin. Continued exposure to high temperatures, humidity, or sun is a common cause of heat cramps, heat exhaustion, or heat stroke. The same degree of exposure may produce different effects, depending on the susceptibility of the person exposed.

Temperature variations affect personnel's performance. Stress generated by high temperature may degrade the performance of an employee. There are no critical boundaries of temperatures for degraded performance. Other factors that may also affect performance are the intensity of heat, duration of the exposure period, task involved, personal physical conditions, and stresses such as humidity and hot wind. There is a report indicating that the performance at high humidity is doubly lower than at high temperature. The duration of heat exposure also affects human performance. Volunteers were exposed to less than 1 hour to ambient dry bulb temperature. No significant impairment of performance by a person was observed. Long exposure to high temperature affects human performance. Other factors such as humidity and odor, fatigue and lack of sleep, smoke, dust, or temporary illness also aggravate the performance.

The effects of heat and temperature not only affect workers but also equipment and processes. For example, certain chemicals that have a low boiling point can cause an explosion at higher temperatures. In a process where these chemicals are used, they should be kept at low temperature.

The effect of excessive heat results in the degradation of the equipment by corrosion and weathering of polymer and plastic materials used in the plant. The corrosion reactions are very rapid at elevated temperatures.

The reliabilities of electronic devices are also degraded at high temperatures so that the failure of a part and thus the particular equipment becomes more frequent. The hydraulic materials or fluids generate pressures at elevated temperatures and may also cause a failure of the equipment.

The increased pressure of gas in a closed container at high temperature can cause rupture of a tank. Even a small rise in temperature of a cryogenic liquid could produce a sharp increase in vapor leading to an increase in the pressure of the container so that the container bursts.

A liquid may also expand with rise in temperature. Hence, if a tank is completely filled, the liquid will expand and overflow. An overflowing flammable liquid would then generate a severe fire hazard.

The strength of most common metals is generally reduced with increase in temperature. Most metals expand and change dimensionally on heating. This is a common cause of deformation and damage leading to the collapse of welded materials. On the other hand, reduced temperatures can cause a loss of ductility of metals and can increase their brittleness. The brittle failure of steel may seriously affect structures such as bridges causing them to collapse, ships and heavy equipment to break up, and gas transmission lines to crack. The above-mentioned facts demand a thorough inspection of the process, technical design, and regular checking of the equipment as to their safe working temperatures.

2.6.2 Pressure hazards

It is sometimes necessary to work at lower pressure to avoid serious injuries and damage. It is also commonly and mistakenly believed that injury and damage will result only from high pressures.

The damage caused by a slow-moving hurricane or wind blowing at 70 mi/h is enormous. Nevertheless, the expansive pressure exerted is in the range of 0.1 to 0.25 psi. Therefore, high pressure is a relative term. The pressures of boilers, cylinders, or compressors can be categorized in the following classes:

Low pressure	1 atmosphere (14.6 psi) to 500 psi
Medium pressure	500 to 3000 psi
High pressure	2000 to 10,000 psi
Ultra high pressure	above 10,000 psi

When the expansive force of a liquid inside a container exceeds the container's strength it will fail by rupturing. Rupturing may occur by the popping of rivets or by opening of a crack that provides a passage for fluid. When bursting is rapid and violent, the result will be destruction of the container. If employees are in the vicinity, injuries could result from impacts and from fragments. The rupture of a pressure vessel occurs when the total force that causes the rupture exceeds the vessel's strength. For example, boilers provide steam at high temperature and pressure and they are normally equipped with safety valves that permit pressures to be relieved if they exceed the set values to prevent rupturing. If the valves are not working properly, pressure from the steam may build up to a point whereby the boiler will burst.

The possibility of a rupture because of overpressurization can be minimized by providing safety valves. Possible discharges from such valves should be conducted in locations where they constitute no danger, especially if the fluid discharge is very hot, flammable, toxic, or corrosive.

Storage tanks and fermenter reactors should be pressure and temperature controlled. The high-pressure vessels should not be located near sources of heat, such as radiators, boilers, or furnaces; and if in an open area they should be covered.

Vessels containing cryogenic liquids can absorb heat from the normal environment that could cause boiling of liquids and very high pressures. Cans and other vessels used for volatile liquids should not be kept near heat or fire as they could explode violently.

The pressures in cylinders of compressed air, oxygen, or carbon dioxide are over 2000 psi. When these cylinders weigh about 200 lb, the force or thrust generated by the gas flowing through the opening when a valve breaks off a cylinder can be 20 to 50 times greater than their weight. Accidents have occurred when such cylinders were dropped or struck and the valve broke off. These cylinders sometimes took off, smashing buildings and machinery, and injuring personnel nearby. Safeguards should be used while handling, transporting, and using these cylinders.

Whipping of flexible gas lines can also generate injury and damage. A whipping line of any kind can tear through and break bones, metal, or anything else that it comes in contact with. All high-pressure lines and hoses should be restrained from possible whipping by being weighted with sand bags at short intervals, chained, clamped, or restricted by all of these means. Workers should be trained to never attempt to grab and restrain a whipping line.

A vacuum (the negative difference between atmospheric and below-atmospheric pressure) can be as damaging as the high-pressure systems. Sometimes a vacuum is more damaging to the structures that may not be built to withstand reversal stresses.

Most buildings are designed to take positive load but not to resist negative pressures. Such negative pressures might be generated on the lee side (the side opposite to the one that faces the wind) when a wind passes over. Although the actual difference is very small, the area over which the acting total negative pressure is very large so that the force involved is considerable. In most cases, the damage caused by high winds during hurricanes or tornadoes is the result of a vacuum.

The negative pressure can also be generated by the condensation of vapors that could cause a collapse of the closed containers. When vapors are cooled down to liquefy, the volume occupied by the liquid is far less than their vapors. As a result, the partial pressure inside the container decreases significantly. Vessels are designed to sustain the load imposed by the difference between the outside and inside pressures, or unless a vacuum breaker is provided.

2.6.3 Electrical hazards

The use of electricity and electrically operated equipment and appliances is so common in production and processing facilities that most persons fail to recognize the hazards involved. Electrical power is beneficial and at the same time hazardous if not properly used. The hazards involved are mainly:

1. Shock to personnel
2. Short circuiting and overheating
3. Ignition of combustible materials
4. Electrical explosions
5. Inadvertent activation of equipment
6. Electromagnetic effects on equipment and personnel

Electrical shock is initiated when a person comes into contact with a bare electrical wire and the current starts flowing through the body. This shock is a sudden and accidental stimulation of the nervous system by an electrical current. Although the potential difference determines the current flow through the body, the damaging factor and the chief source of injury and death in electrical shock is the current flow. Currents in the range of 1 to 75 mA is not damaging but above this range can be fatal.

There are many ways for a person to be shocked electrically including contact with a normally bare energized conductor or a conductor with deteriorated insulation, the equipment failure that causes an open and short circuit, static electrical discharge, and by lightning strike.

Accidents are frequent when a person is electrocuted because of lack of care near the energized bare conductor, the construction area, rooftops, or TV antennas, or working on live high-voltage lines.

Accidents may occur if a circuit is opened when an electrician begins work or if a person reenergizes the circuit by mistake. Electrical circuits shut down for repair or maintenance should be locked and tagged out after being deenergized. The circuit that uses capacitors should be discharged first by grounding. Line equipment is normally insulated, but with time the insulation deteriorates owing to many factors such as heat, elevated temperature, moisture and humidity, oxidation of insulators, chemical incompatibility, mechanical damage, high voltage, and photochemical reaction. If the insulation is defective owing to deterioration or damage, a person could be electrocuted.

Equipment failure is another cause of electrical shock. Some examples include leakage in washing machines, electrical irons, water pumps, broken energized power lines, grinding, and drilling machines. The equipment must be grounded with three wire cables.

The shock protection by these sources can be implemented in the following ways: enhanced insulation of wires and equipment, and insulation of a person who is working on a power line. Electrical equipment can be isolated. These should be properly marked by warning signs of high voltage and electrical shock.

Static charge is another hazard for electrical shock. Every moving solid, liquid, or gas carries a charge on it. Whenever there is an excess or deficiency of electrons on moving objects, it causes a potential difference between them. This is capacitive in nature because whenever two objects of different charges come close, they generate an electrical discharge. For example, a person moving on a carpet or a conveyer carrying materials that may generate static electric charge can cause a simple electric shock.

There are ways of controlling static problems. The person working in an oil refinery or in a gas station can be asked to wear cotton clothes instead of nylon or wool. A material that does not generate static electric charge can be coated on pipes and other equipment. Equipment can be sprayed by a conducting material to avoid the charge generation. Electroneutralization can generate high voltage. As a result, a gas ionizes and produces positive and negative charge species that combines opposite charges and neutralizes them. Raising the humidity above 65 percent permits the static charge to load off and dissipate.

Lightning is a massive, natural discharge of static electricity involving very high potential and high current flow. Lightning follows the path of least resistance to earth including high mountains, tall trees, T.V. antennas, light arrestor, and rods. Ground provides the path.

Lightning rods, multiple-point discharge rods, and lightning warnings are now used as protective devices. Lightning rods are placed so that their upper ends are higher than any nearby structure. Grounds are low-resistance paths to provide easy passage of current to earth. Multiple-point discharge dissipates the accumulated charges to a wider area to protect the electrical circuits and all metal equipment in a building or structure from direct passage of lightning. The lightning warning devices can detect lightning in a vast area and can be coupled with protection units. All overhead power lines are equipped with these lightning warning devices.

Keeping sparks and arc away from combustible materials or chemicals can provide protection from electrical hazards. It is also advisable to eliminate all electrical equipment from hazardous areas in which a flammable atmosphere might exist. It can also be achieved by designing inherently safe devices, explosion proof equipment with heating and overheating control, fuses, circuit breakers, reset relays, and other protection units.

2.6.4 Mechanical hazards

Most of the injuries in industrial plants are originally from mechanical causes. These industrial plants have belt-driven rotating equipment, open geared power-presses, power hammers, cutter conveyers, kilns, and incinerators. These different kinds of mechanical equipment are used in industrial plants and each has its own mechanical hazards including cutting, tearing, and breaking.

A person working in a paper plant at a manually fed paper cutter may have chances of cutting skin or body parts. Tearing of skin may occur when a sharp point or edge pierces the skin and flesh. The sharp edges of equipment and poor finishes are sometimes major causes of cutting. The equipment must be designed in such a way that it does not have sharp edges and poor finishes.

Shearing will occur when a sharp edge is in a linear motion in a direction vertical to the line of the edge. Examples include powered paper cutter and metal plates. The effect of shear can cause amputation to a person working at the machines, and can be fatal.

An impactor can crush the muscle tissues or any part of the human anatomy. Sometimes two rotating objects can cause crushing of body parts when they are moving toward each other. Common examples include meshing gears, belts running over pulleys, cables on drums, chains on sprockets, rollers on manual type washing machines, and rolls on rubber mills or paper calendars.

When a part of the body is caught between two hard surfaces it can cause a bone-shattering effect. Sometimes if an attempt is made to bend a rigid bone, a break may occur. Breakage of fragile material occurs when these are dropped or thrown on a hard surface violently.

Normally a guard is installed on a moving part of the machine, which acts as a barrier to prevent the entry of any part of the human body in the hazardous area. It is also possible that a safety device is installed that prevents or interrupts the operation if part of the operator's body is in a hazardous area or requires its withdrawal prior to machine operation. The guard or safety device itself must not constitute a hazard, must be safe, low maintenance, easy-to-use, automatically controlled, or fixed on the machines. There are different types of guards and safety devices available according to the design and demands of machines.

Total enclosure is represented by fixed covers over the pulleys, gears, shafts, and couplings to prevent access to the hazardous area. They can also be coupled with interlock devices for shutting down the machine if a portion or the whole cover is removed.

Moveable barriers or gates can also be provided that open and close easily for loading and unloading of materials. Double control devices that are operated by dual switches far apart cannot be operated by a single hand.

Mechanical feed is provided by a mechanical feeder, in which a processing material is placed over a feeding device. It moves automatically in a processing zone from which the part is ejected. There are certain safety devices such as optical sensors that monitor the light intensity of a reference source. The variation of light intensity owing to the presence of a person or a part of the body in a hazardous area prevents the activation of the machine. This can also be achieved by ultrasonic or piezoelectric detectors that produce high-frequency inaudible waves to detect the presence of any moving object in a hazardous area of the machine.

Electric field transducers can also be used. They generate a capacitive field in a hazard area. Any grounded object in the field can be detected. Operators working in that area are grounded and can be sensed by this method to stop the machine before its activation. These are different guards and safety devices that are normally used to avoid mechanical hazards.

2.6.5 Toxic materials

Many incidents caused by the release of chemicals into the environment have resulted in the loss of life and property. Fear of toxic chemicals has increased because of these incidents. The increased awareness of industrial plant workers and the general public has resulted in minimization of these releases. Highly reactive chemicals are being used more frequently in industries, agriculture, research, and defense. Many of these chemicals are found to be carcinogenic, teratogenic, and a cause of long-lasting injuries.

It is therefore necessary to provide suitable safeguards to prevent or minimize the injuries that can occur to workers in industrial plants and to the general public. There is a need to understand the ways by which these chemicals enter the human body and their physiological effects. Preventive measures should be exercised to avoid this absorption.

A material is considered toxic when a small quantity injures the body of an organism. Almost all materials are injurious to health but at different levels. The oxygen we breathe can be dangerous if taken at 100 percent without dilution. Nitrogen and carbon dioxide can be dangerous although they are present in air and lungs at high concentrations.

The concentration or the toxicity level of the substance is not the only factor of a toxic chemical. The susceptibility of the human body to toxic chemicals and their concentrations varies. Other factors that affect the severity of the injury are concentration, duration of exposure, route, and temperature.

Toxic injuries can occur at the first point of contact between the toxicant and the body, or later, systemic injuries to various organs of the body. The routes of these injuries can be through the skin, respiratory system, or the gastrointestinal tract.

The toxic materials may be solid, liquid, or gas. The solid toxic materials are radioactive substances and metals such as Pd, Cd, As, Cr, Al, and others in various forms. The chemicals are mostly in liquid and gaseous forms. For example, diethyl bromide, chlorofluoro carbons (CFCs), trichlorethane, or trichloromethane are liquids whereas phosgene, chlorine, carbon monoxide, hydrogen cyanide, and isocyanate are gases.

What happens in an industrial plant when a leak of some toxic gases such as isocyanate, ethane, or others occurs? The concentration of these gases in air increases whereas the concentration of oxygen decreases. The worker feels suffocation or asphyxia. The concentration of carbon dioxide increases; as a result, blood carbonic acid level increases, which lowers the concentration of oxygen further. The worker undergoes a condition of hypoxia (hypo: below; oxia: oxygen). The effect of hypoxia includes loss of perception, decrease in brain activity, unconsciousness, and deep breathing. It may lead to irreversible damage to the brain, paralysis, and ultimately death. Some gases alter the oxygen-carrying cells in the blood (hemoglobin). For example, the exposure to carbon monoxide (1 to 1.5 percent) decreases the oxygen-carrying capacity of blood that results in hypoxia. Some chemicals such as nitrates, nitrites, or other oxidizing agents are also harmful to the human body. Other chemicals are irritating and cause serious injuries to the body by inflaming the tissues. It may also cause inflammation of the skin, eyes, and respiratory tracts. Even a small amount of irritant can cause physiological injury to an extensive area of tissue. These may be chemical, gas, liquid, or thin particulate matter. Ammonia, acrolein, hydrazine and hydrofluoric acid, fluorosilicic acid, and asbestos can cause injuries to the upper respiratory tract, whereas chlorine, fluorine, ozone, nitric acid, and nitrogen tetroxide affect the lower portion and the alveoli.

Some chemicals are carcinogenic (cancer producing). For example, bitumen, mineral oil, aromatic compounds, vinyl chloride, benzidene, and biphenyl pyridine are the known carcinogens and their use is eliminated or replaced by noncarcinogenic chemicals. Asbestos is a particulate matter that causes asbestosis and cancer of the lungs, colon, rectum, and stomach. Therefore, OSHA has imposed a ban for zero fiber or particulate matter in the working environment.

All industrial plants are obligated to observe criteria stipulated in OSHA standards that include the exposure to different chemicals and their threshold limit for industrial workers. The preventive measures in an industrial plant depend on the type of processes involved.

Protective equipment must be used for protection from toxic gases and vapors and are required for normal hazardous operations such as working in a spray-painting plant, production and use of toxic chemicals, and fumigant use. Safe respiratory protective equipment is required for all these activities.

There are two types of respiratory protective equipments:

1. *Air purifier*: Contaminated air is purified by chemical or mechanical means. The air containing oxygen, particulate matter, gases, and vapors is first passed through a filter that removes the particles. This air is then passed through a reaction chamber that contains chemicals used for purification. For example, the removal of organic vapors and acidic gases, ammonia, carbon monoxide, and carbon dioxide is done over charcoal, silica gel, hopocalite (MnO_2:CuO [60:40%]), and soda lime, respectively.
2. *Oxygen-breathing apparatus*: The portable equipment that supplies oxygen for respiratory needs is called an oxygen-breathing apparatus. There are many types of equipment available depending on the composition of air quality supplied. They mainly consist of air or oxygen supply, face piece or helmet, and tubing for air and supply gas regulator.

The regulator controls the pressure of gas required by the user. It can supply air on a continuous or pressure demand basis. The source of air is a compressed air or liquid. They may be in closed or open circuit to reuse the air in the former case. These self-contained air breathing units have chemicals capable of generating oxygen. These are the units used for normal operations and for emergencies to protect personnel.

Special protective clothing should be provided to working personnel for protection from toxic chemicals. The clothing is made from materials resistant to acids, bases, toxic chemicals, and even to high temperatures and fire.

In an operational plant there is a need to mark the container containing chemicals with proper labeling. These chemicals and hazards have been categorized into different classes. Different colors were assigned depending on their physical or chemical hazards as shown in Table 2.1.

TABLE 2.1 Classes of Hazard Materials and Their DOT Symbols

Hazard class	Color	Symbols
Class 1: Explosives	Orange	Exploding device
Class 2: Gases	Yellow	Burning "O"
	Red	Flame
	White	Skull and cross bones
	Green	Cylinder
Class 3: Flammable liquids	Red	Flame
Class 4: Flammable solids	Red/white stripes	Flame
	Red/white/field	Flame
	Blue	Flame
Class5: Oxidizers/ organic peroxide	Yellow	Burning "O"
Class 6: Poisons/ etiologic agent	White	Skull and cross bones
	White	Sheaf of wheat with cross
	White	Broken circles
Class 7: Radioactive	Yellow/white field	Trefoil/spinning propeller
Class 8: Corrosive	Black/white field	Melting metal bar and hand
Class 9: Miscellaneous	Black stripes, white field	Black and white stripes

According to this classification an inflammable liquid or solid chemical is given a number designating its class, and a red color that indicates its physical or chemical hazard such as flammability. For toxic, corrosive, explosive radioactive material a container should be marked with different numbers and colors (Fig. 2.4).

Personnel should be informed and trained on the significance of these numbers and colors and how to handle these chemicals to avoid any incident. Clear information should be given on the pressure in a line carrying any chemical, inflammable or toxic, and at what temperature these chemicals should be pumped. Do they radiate or explode on absorbing moisture or oxygen from air? These are the technicalities that should be in the mind of personnel who are working with these chemicals.

2.6.6 Fire and explosion

Fire and explosion are common in many chemical industries. There are chances of fire breaking out in an operational plant. A fuel, an oxidizer, and a source of ignition are required to start a fire. However, fire and explosion take place only when there are appropriate conditions for it.

Many types of fuel and oxidizers are available in any industry. There are three types of fuel. They are mainly solids, liquids, or gases.

These fuels may be required for heating boilers, running engines, and for welding. Also the chemicals that are used as cleaning agents or solvents act as fuels. Lubricants, coatings, paints, industrial chemicals,

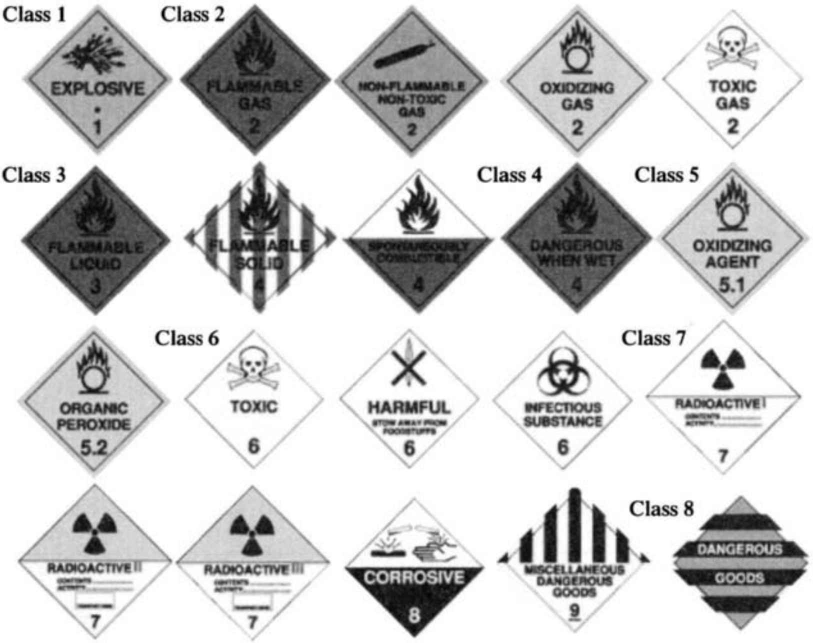

Figure 2.4 Symbols as recommended by the Department of Transportation (DOT).

refrigerants, hydraulic fluids, polymer plastics, and paper wood cartons are potential fuels.

The next element for fire is an oxidizer. The most common oxidizer is oxygen present in the air that helps in oxidizing the fuel. Sometimes a chemical can be self-ignited in the presence of an oxidizer. For example, white phosphorus catches fire as soon as it comes in contact with air. Pure oxygen is a strong oxidizer. A small leak in an oxygen cylinder may cause a fire hazard.

Fluorine is another strong oxidizer. It can react with moisture in air and catch fire. It is normally used diluted with nitrogen. Other oxidizers include chlorine, halogenated compounds, nitrates, nitrites, peroxides, and acids. These oxidizers should be handled with care and their contact with fuel should be avoided.

The source of ignition consists of materials that may initiate a fire on friction. A reaction is initiated in a mixture of fuel and oxidant. As a result of this reaction, heat is evolved in the form of flame or light that produces a fire after reaction with fuel and oxidizer. The igniter may be sunlight, an arc, or an electrical spark.

The common sources of electrical ignition in an industrial plant are the sparks of the electric motors, generators, or electrical short circuits, arcing between contacts of electrical switches or relays, discharges of charged electrical capacitors, or a discharge of static electricity accumulated on underground surfaces.

The sources of other igniters are hot plates, hot moving parts of some instruments, engines, radiators, overheated wiring, boilers, metals heated by friction, metal being welded, or sometimes a cigarette.

Fire can have a tremendous effect on human life, immediate surroundings, and even on the environment. Fire produces carbon monoxide, carbon dioxide, solid carbon particles, and smoke. Heat and high temperature make a fire highly dangerous for the employees of any industry. Death may occur as the concentration of the oxygen in air decreases in case of fire. Therefore, personnel are advised to escape before the fire expands and the temperature rises beyond 65°C.

In any industrial plant, there are devices installed to detect any kind of fire, smoke, soot, or heat. There are fire detection instruments including thermosensitive switches, thermoconductive detectors, radiant energy detectors, gas detectors, or ionization detectors.

Suppression of the increasing fire can be carried out by various methods. The very first method is to cut the supply of fuel to the fire. Fire suppression can also be achieved by blanketing a fire or by covering it with inert solid, foam, thickened water, or covering it with a nonflammable gas such as CO_2. The other available method is the dilution of the fuel, if it is a liquid fuel, by adding noncombustible liquid into it; and if it is a gas, by adding nonflammable gas.

Fire is a chain process. It can be stopped by breaking this chain. Scavengers are used to stop the free radical chain reactions and subsequently fire is extinguished. Halogenated compounds are usually good chain-reaction inhibitors.

When fire is ignited because of fuel and there is no electrical hazard nearby, water is used as a fire suppressant. This is readily available, cheap, simple to use, and effective. Normally firefighters use stream water on fuel and fire. However, water is not recommended for sodium or magnesium metals.

Water can also be used as a diluent and to stop chain reactions. The only limitation is that its effective range is very low. Sometimes thickening agents are added to the water to increase the residence time of water and its effectiveness. The thickening agents such as clays, gums, and sodium and calcium borates are used in forest fires. They act as slurries and adhere to the burning materials. The chlorides of calcium and lithium lower the freezing point to –40°C. The salts of potassium carbonate deposited on burning materials or the gas produced act as fire inhibitors.

Gas extinguishers may be used for enclosed spaces. These are largely meant for small fires or fires where electrical hazards are probable.

Carbon dioxide is widely used as a fire extinguisher. Its main function is blanketing the fire, thus lowering oxygen concentration and subsequently inhibiting the fire. It also acts as a coolant and a combustion inhibitor. When carbon dioxide is sprayed on fire it emerges as snow and lowers the temperature.

Halogenated hydrocarbons act solely by inhibiting chain reactions. The nature of halogens is very important. The least reactive would be the best fire extinguisher. However, the problem with these halogenated compounds is their toxicity, which limits their use.

Foams are also used as fire suppressants. They suppress fire by cooling, blanketing, and sealing the burning fuel from the surrounding atmosphere. They are not suitable for gaseous fuel and fuel that reacts with water.

Solid extinguishers such as sand or clay are also used to cover the oil or grease under a fire. They also suppress fire by blanketing. They are suitable for metal fires. Sodium and potassium bicarbonate are also used as solid extinguishers for liquid fuel. They act as chain reaction inhibitors. At high temperatures, they decompose to give carbon dioxide that itself is an extinguisher that suppresses fire.

The use of certain suppressants under wrong conditions may be hazardous. Water cannot be used on burning cables carrying electricity or magnesium metal.

Fire extinguishers that work automatically are available. They sense temperature, gas, or fumes and start sprinkling the extinguishing materials (CO_2 or others). There are other portable units available that are marked, A, B, or C depending on the class of fires to be extinguished. Mobile extinguishers are too heavy to be carried and therefore are often wheel-mounted. These contain potassium bicarbonate (purple-K), dry chemical, and other light water. The advantage is in their high capacity to suppress fires.

2.6.7 Accelerator and falling objects

Most of the incidents that occur in an industrial plant are because of accelerator fall or falling objects. Data have shown that nonfatal occupational injuries and illnesses involving the days away from work are more than 60 percent of the total accidents. These may be a result of getting struck by an object falling to the same or lower level. These great numbers of accidents have led to federal and state laws for corrective measures, such as provision of safeguards, safety nets, and helmets for workers. It was observed that a good number of workers fell down from heights in the fields of construction, cleaning of chimneys, and towers. Injuries also occurred when workers slipped and fell, while working on the same level. The fall may not be fatal in this case. Workers have been killed when they have struck their heads by falling from upright positions on slippery floors. The most serious damage from all of these falls is broken bones of head (skull), arms, legs, and chest. The ability of the human body to sustain an impact, such as a fall, depends on three major factors: velocity of an initial impact, magnitude of the deceleration, and orientation of the body on impact. At a free fall from a height of 11 ft, the velocity gained by the body is 18 mi/h, enough to kill a man.

During the construction and maintenance of bridges or elevated structures, numerous falls of industrial workers into water occurred. These falls resulted in various kinds of injuries such as spinal injuries, bleeding of lungs, shock, and sometimes death.

The main task is to determine the measures that should be taken to prevent these kinds of accidents. The best way to prevent a fall is by providing safeguards. Workers working at an elevation should be provided a safeguard net and fences. They may be tied with ropes as well. Their mental and physical fitness should be checked regularly to determine whether they can work at elevations and can sustain vertigo (a dizzy, confused state of mind).

A person may fall down on the floor at the same level by slipping while working or walking briskly. A person may fall because of the collapse of a piece of equipment, ladder, structural support, or hoist on which he is working. Preventive measures should be adopted while working at these places.

Workers who are not properly trained should not be allowed to work on elevated sites. A worker should be chosen for work on bridges and elevated structures depending on psychological and physiological states. Workers can be provided with emergency nets, coiled knotted ropes, ladders, fire escapes, and parachutes.

Sometimes very small objects are more damaging than bigger objects. For example, a small object thrown at a higher speed is more dangerous than bigger one. This happens when there is an explosion of gas cylinders, high pressure tanks, or gas pumps. Furthermore, the debris or fragments may travel at a very high speed and can cause bruises, tissue damage, or bone fractures. Different body parts, for example eyes, are more susceptible to an impact. While welding, grinding, tooling, spraying, or coating spray pressure, glasses should be used. These and other acceleratory effects in an industrial plant or construction site can be avoided by taking preventive measures for workers.

2.6.8 Confined space

The danger associated with working in confined spaces is not new. Since the discovery of mines, many fatalities have been reported owing to suffocation, gas poisoning, accumulated gas explosion, and asphyxiation. Workers dealing with wastewater sewage repair, cleaning, inspection, painting, and fumigation face the problems of asphyxiation, drowning, and toxicity from chemical exposure because of working in confined spaces.

A space large enough for an employee to enter and work with restricted activities or movement may have a hazardous atmosphere. The incident occurs because of failure of recognizing the hazards associated with confined spaces. The different kinds of confined spaces for a worker in a plant are tanks, silos, storage bins, vessels, hoppers, pits, and sewer lines. Big fermenters, multieffective evaporators, boilers, and wells are also included in this list.

There is another criterion called permit-required confined space such as an engulfment, entrapment, or any other recognized serious safety or health hazards.

The permit-required confined space that has a hazardous atmosphere includes chemical sludge; sewage; flammable gases or vapors; combustible, low-oxygen concentration; and higher carbon monoxide and carbon dioxide concentrations. Any recognizable environment and condition that can cause death, incapacitation, impairment of ability to rescue, injury, or acute illness is a permit-required confined space. The confined space may have a liquid, or finely divided solid substance that can be aspirated to cause the plugging of the respiratory system, or exert enough force to cause death by strangulation, constriction, or crushing.

Sometimes in a confined space the internal configuration or shape is built to have inwardly converging walls or a floor that slopes downward and tapers to a smaller cross section that could trap an entrant or contribute to asphyxiation. This is designed as a permit-required confined spaced. Examples are fermenter and digester.

The space that contains any other recognizable serious safety or health hazards is also a permit-required confined space. These hazards may be physical, electrical, mechanical, chemical, biological, radiation, temperature extremes, and structural hazards.

The atmospheric hazards are due to the presence and absence of certain gases and the presence of flammable and toxic vapors. There are three types of confined spaces:

Class A: Immediately dangerous to life that contains oxygen: 16 percent or less or greater than 25 percent and flammability of more than 20 percent and the toxicity is very high.

Class B: Dangerous but not immediately life threatening, having oxygen greater than 16 to 19.4 percent and from 21.5 to 25 percent, flammability of 10 to 19 percent and the toxicity is greater than the contamination level.

Class C: Potentially hazardous to life having oxygen 19.5 to 21.4 percent, flammability lesser than 10 percent, and the toxicity is less than the contamination level.

Physical hazards are owing to mechanical, electrical, engulfment, noise, and the size of ingress and egress-opening.

The activation of mechanical and electrical equipment, agitators, blenders, stirrer fans, pumps, and presses can cause injury to workers in confined spaces.

The chemical release into a confined space is life threatening. High-pressure liquid, falling objects, and slippery surfaces in a confined space are all potential hazards. The limited space, inadequate ventilation and light, and excessive noise are also physical hazards that increase the confined space hazards. The chemical waste and useful chemicals are also life threatening.

While working in waste streams, pools, ponds, sludge pits, sewers, or fermenters a worker is exposed to infectious microorganisms. The industrial processes that grow these infectious microorganisms for beneficial purposes can be a threat to workers in a confined space.

There should be a thorough program for confined-space working. The main points of a program are as follows:

Identifying and evaluating with respect to hazards of all confined spaces at the facility

Posting a warning sign at the entrance of all identified spaces

Performing a job safety analysis for each task at confined spaces, for example entry plan, assigned standby persons, communication between workers, rescue procedures, and specified work procedures

Testing and monitoring air quality in the confined space such as oxygen level, toxicity level, flammable materials, air pressure, and air contaminants

Preparing a confined space; for example, by isolation, lockout, tag out, purging, cleaning, and ventilation, and procuring special equipments and tools if required

The use of personnel protective equipment to protect eyes, ears, hands, feet, body, chest, and respiratory protection, harness, and mechanical lift devices

In addition to the above points, training and drill for workers, supervisors, standby personnel, and rescuers at regular intervals are absolutely needed.

2.6.9 Radiation

Since the discovery of radioactivity, some elements are classified as dangerous even if they are used for beneficial purposes. Energy is emitted by any material that travels in the form of particles or electromagnetic waves. Energy emitted by the sun reaching the earth travels in the form of electromagnetic waves and particles. Light comprises a spectrum of wavelengths that consist of high-energy cosmic rays, ultraviolet rays, visible light and low energy, infrared rays, and micro and radio waves.

The radioactive elements consist of alpha particles (helium nuclei), beta particles (positron), neutron, and gamma rays. X-rays are also emitted by elements when high-energy electrons strike a metal. The high energy of X-rays and gamma rays make them more penetrating. Beta rays have less energy than gamma rays and hence less penetration. Alpha, beta, X-rays, and gamma rays are ionizing radiation. These may cause injury by producing ionization of cellular components leading to functional changes in the tissues of the body. The energy of these radiations is great enough to cause ionization of atoms that make up the cells, producing ion pairs, free radicals, and oxidation products. The damage to the cell is mostly irreversible. These radiations have certain hazard limits in causing damage to the cell. Therefore, they are also used for diagnostic, beneficial purposes, and for the treatment of cancer cells. Radioactivity does not lose its potency by absorption or ingestion by living tissues. Thus, the radioactive material from airborne fallout on land or on grass taken up by grazing cattle ultimately passes on to human beings.

X-rays, gamma, and cosmic rays are similar except for the fact that gamma and cosmic rays are natural. They ionize matter by photoelectric effect, Compton effect, and pair production (electron and positron). These radiations are of very high energy and therefore more penetrating. They cause injury to the tissues of the whole body. Therefore, they are more damaging to the living tissues.

There are certain factors that affect the exposure and risk. These are the strengths of the source, type of radiation, and the distance. The energy order with respect to decreasing hazards is cosmic, gamma, X-rays > beta > α-particles.

The sources of ionizing radiation are nuclear power plant, nuclear material processing, and radionuclide generation for nondestructive purposes. Medical and chemical laboratories use these radionuclides—for example, iodine, thallium, and barium—as tracers. The danger of mishandling these materials could cause release of these materials into the environment. Other than medical diagnostic tests for fracture of bones and constriction of blood vessels, these are used for the treatment of cancers.

The industrial use comprises examination of welds; internal structures for the existence of cracks, voids, or contaminants; food preservations, and examination of packages and baggage for illegal articles, especially at airports.

During the last decade various nuclear power plant (NPP) accidents have made the construction and use of NPP more difficult. Among them, the Chernobyl accident was the most severe—causing damage to vegetation, animals, and property, over an area of 1000 square kilometers, and taking 36 lives immediately; but after a decade the death tolls have risen to tens of thousands. Workers engaged in the milling of uranium are also the most exposed to α-particles that can be avoided by protective clothing; however, the presence of radon gas, owing to the decay of uranium, is more dangerous.

After fission of uranium 235, the radionuclides produced in the spent fuel have cesium, strontium, iodine, and other radionuclides of very long half-lives that can be a danger. The other radio wastes include contaminated filters, wiping rags, solvents, protective clothes, hand tools, instruments and instrument parts, vials, needles, test tubes, and animal carcasses.

Precautionary and preventive measures include:

Well-trained personnel should be allowed to work, use, operate, handle, and transport the material

Safety engineers should inspect any facility producing radiation, its protective devices, and worker's protection prior to start

Access to these areas should be restricted and only an authorized person should be allowed

Suitable warning signs should be posted in the ionization equipment area

Emergency drills should be performed regularly

All instruments that use radioactive sources should be kept in a shielded enclosure and made up of lead-containing glasses, sheets, and bricks that attenuate the radiation to a permissible level: radiation going outside the area should be continuously monitored

Every personnel should be given a dosimeter or film to estimate the absorbed radiation and a record should be maintained

Keep the exposure time for personnel as low as possible

The vital parts of the body should be protected by protective clothing, glasses, gloves, masks, and shoes

Drinking, eating, and smoking in that area should be prohibited

Cleanup of any spill should be performed with the help of safety engineers that includes complete prevention of the spread, complete cleaning of the spilled area, and a thorough decontamination of the contaminated personnel

The nonionizing relations are ultraviolet, visible, infrared, and microwave. Ultraviolet radiation is the most dangerous. It is a high-energy radiation that comes from the sun naturally and is generated by human beings by electric arc wielding, Tesla lamps, plasma arc, and lasers for beneficial purposes. The danger of ultraviolet light is that it causes burning of the skin and blindness to the eye. The redness of the skin is often observed in the sun. It is as a result of the penetration of ultraviolet radiation to the dermis. The cornea and conjunctiva of the eyes absorb UV rays and become bloodshot and irritated.

The laser radiates various kinds of radiations from infrared to visible and ultraviolet. These are coherent rays with very high, focused energy. This power can be very dangerous to the human eye or skin if not used properly.

To avoid these radiations, glasses with a face UV blocker and protective coats should be worn. Goggles made of glass containing iron are more absorbing than simple glass, while quartz is nonabsorbing to UV radiation.

Visible radiations are less harming. Simple protection from visible light is beneficial. Infrared radiations are heat radiations. Any heated body radiates heat radiation that gives off thermal energy. These radiations can cause cataract to the eyes, skin burns, increased perspiration, and loss of body salt. The workers at an iron or metal casting plant, hearth, and furnace should be provided with clothing, gloves, and facemasks to protect skin against infrared radiation. Adequate cooling should be provided to personnel working near the infrared sources. It is also recommended to provide adequate salt and water in the form of juices or salt tablets to replenish the salt lost through perspiration.

Microwave radiation is emitted by dryers, ovens, and heaters normally used in the home. The high-power radars used for military purposes, communication equipment, alarm systems, and signal generators are other sources of microwave radiation. The low-power microwave radiation can cause heating and skin redness whereas high-power microwave radiation can cause inductive heating of metals and induced currents that can produce electric spark. Containers with flammable materials may catch fire if they are placed in the microwave fields. Rings, watches, metal bands, keys, and similar objects worn or carried by a person in such a field can be heated until they burn the bearers.

High-power microwave antennae should not be inspected when energized or directed toward inhabited areas. Flammable materials stored in metallic containers should not be left in microwave-induced magnetic fields. A warning device should be provided to microwave equipment to indicate when it is radiating.

Radio frequency (RF) is another kind of radiation that is used in radio, television, satellite, and mobile communications. The frequency radiated by these generators ranges from 3 KHz to 300 GHz.

The increasing use of mobile phones may have resulted in cases of brain cancer. Experiments are under way to assess the damage caused by mobile phones to the brain. Experiments are also in progress to assess the safe range of the broad spectrum of radio waves. The most restrictive limits occur between 30 and 300 MHz where absorption of RF energy by the whole body is most efficient.

2.6.10 Noise and vibrations

Vibrations, sound, and noise are other examples of common industrial hazards. The most common injury because of vibration is sound-induced hearing loss. The vibrations of machines, high-speed pumps, generators, boilers, and conveyers produce unwanted sound *noise*. The adverse effects produced by these sounds are as follows:

Loss of hearing sensitivity

Immediate physical damage (ruptured ear drum)

Interference resulting in the masking of other sounds

Destruction

Annoyance

Other disorders such as tension and mental fatigue

A normal human can hear a sound ranging from 20 to 20,000 Hz. Less than normal ability to hear a voice indicates there has been degradation. Hearing loss is an impairment that interferes with the reception of sound and with the understanding of speech in sentence form. The general loss of hearing sound in the frequency range of 200 to 5000 Hz is compensable under the Worker's Compensation Act. Degradation of hearing can also result from aging, long-term exposure to sounds of even moderately high levels, or a very high-intensity noise. Much of this degradation with age may be owing to continuous exposure to environmental noise of the modern society rather than to simple aging. Hearing losses can occur even at noise levels lower than those permitted by OSHA standards as given in Table 2.2.

OSHA has estimated a safe maximum noise level of 85 dB. The time-weighted average (TWA) is an exposure for an 8-h to a noise level not exceeding 90 dB. If this level exceeds 85 dB, OSHA requires the employer to institute a hearing conservation program (HCP). Therefore, if a company wants to avoid loss claims under worker compensation laws, it must not only meet the prescribed legal standards, but also attempt to reduce noise to the lowest possible level (< 80 dB).

Noise annoys people and causes tension among people. However, the types and levels are difficult to determine. Sometimes the noise of a different sound resonates at a frequency that masks other sounds. The noise level should be checked at all places before operations begin.

Vibration not only causes noise but also other disturbances. A vibrating instrument is difficult to handle for a long time. Vibrations also

TABLE 2.2 Permissible Noise Exposures for Workers as Described by OSHA

Duration/day (h)	Sound level (dB)
8	90
6	92
4	95
3	97
2	100
1.5	102
1	105
0.5	110
0.25	115

SOURCE: *http://www.osha.gov/pls/oshaweb/owadisp.show_document? p_table = FEDERAL_REGISTER&p_id = 17368.*

cause metal fatigue of the instrument that can result in failure of rotating, moving parts, and other stressed mechanical equipment. They may also result in leakage of fluid lines, pressure vessels, containers, damage to part of the equipment, and possible injury to personnel. Vibration can cause what is known as Raynaud's phenomenon that involves paleness of the skin from oxygen deficiency owing to reduction of blood flow caused by injured blood vessels and also nerve spasms. The disease is produced by vibration directly on the fingers or hands. Vibrating tools can also cause arthritis, bursitis, injury to the soft tissues of the hands, and blockage of blood vessels. In addition to hearing loss, nervousness, psychosomatic illness and inability to relax, upset balance, and disruption of sleep are other serious effects of vibration.

The hearing conservation program (HCP) includes recording and categorizing the audiometric testing, monitoring of noise exposure, use of hearing protection devices (HPD), employee's training, and noise control engineering.

Exposure monitoring is another element of HCP. The sound level and exposure time should be measured. It is very important that sound levels measured are typical of those encountered by the worker. Proper survey techniques include sound-pressure-level (SPL) meters that should be vigorously applied at monitored workplaces. They measure the smallest pressure changes initiated by the vibrating source and transmitted through the air.

There are other instruments used for measuring noise including weighted-sound-levels and octave-band analyzers. These instruments measure the noises of different frequencies.

Ear protection can be carried out naturally and by using hearing protection devices. The ear itself has a protective mechanism that helps reduce possible effects of loud noises. The sound waves do not impinge directly on the eardrum because of the curved ear canal. Eardrum muscles are very sensitive to sudden loud noises. They contract in response to these noises by causing the ossicles to stiffen, thereby dampening the vibration transmitted.

Personnel protection devices must be used to protect the ear in an industrial plant. These are earplugs made of rubber or plastic that fit snugly in the ear canal without discomfort and effectively protect the ear. They are also available as a foam cylinder that can be compressed and twisted to be inserted into the ear canal. There are helmets available that have noise attenuating electronic components and communication features. In selecting these helmets, safety engineers must exercise caution and must take steps to ensure that the devices are properly selected and used by the workers without distraction and annoyance.

2.6.11 Ergonomics

The psychological and physiological limitations and capabilities constitute the ergonomics or human factors. It is the most important part of the occupational safety and health program. This is to evaluate personnel capabilities and improve human safety, comfort, and productivity in the workplace. Work-related musculoskeletal disorders (WMSD) are the results of ergonomics and limitations of the human body to a sudden change or continuous working on a physical job, especially where most of the jobs are carried out manually.

Efforts should be made to identify workers' complaints of undue strain, localized fatigue, discomfort, or pain that does not go away after overnight rest. Job testing that requires repetitive and strenuous exertions; frequent, heavy, or overhead lifts; awkward work positions; or the use of vibrating equipment should be identified along with the WMSD risks. The extent of the problem will determine the level of effort required to provide a reasonable prevention effort. Human factors should be an important part of a company's safety and health program. Safety efforts require the involvement and commitment of management and workers. Inputs from personnel in safety and hygiene, health care, human resources, engineering, maintenance, and human factors should be the main points of safety policy.

There are three types of control: engineering control, administrative control, and use of personal protecting instruments. The design or redesign of the job changes in a workstation layout depends on the selection and use of other tools and work procedures to take account of the capabilities and limitations of the workers. Administrative control deals with the change of job, modified rules and procedures, scheduling more

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rest breaks, ample supply of personnel protective equipment, use of various kinds of braces to protect from stress and strain, and the rotation of workers on physically tiring jobs. In addition, the workers should be well-trained to recognize ergonomic risk factors and techniques to reduce stress and strain while working on certain instruments.

Regular health checking of the worker can help in early detection and prompt treatment for stress. Medical care should be provided for any damage to the employee. It is supposed that an employee should follow workplace safety and health rules and work practice procedures and should report early symptoms of WMSD.

2.7 Risk Management Plan

In risk management plan, we will discuss how safety personnel organize a plan to design and modify the process to avoid any incident. The use of protective equipment and its procurement will also be discussed. The need for planning for emergencies is an important task in risk management plan.

2.7.1 The role of safety personnel

Technology is changing with time. In the past, industries often had accidents owing to mechanical and electrical failure. As industry entered new fields, new safety problems subsequently arose. Generally, inventors of these new hazards were only concerned with the utility derived from the new invention rather than with an assurance of safety. New problems arose when the laboratory equipment and processes were transformed into industrial equipment, where the safety problems involved became a concern in the process design for the plant engineers. The hazard and toxicity of chemicals, high temperatures, and pressures were tackled initially by chemists and engineers. It became necessary to have other persons responsible for accident prevention. Efforts were made to prepare trained personnel to take care of the hazards related to a particular process and the precautionary steps that should be taken to avoid them.

The job of safety personnel is much diversified and is of high skill. Safety personnel must be knowledgeable in a wide range of technical, legal, and administrative activities. It is also supposed that a safety professional has in-depth knowledge in all areas of accident prevention and is capable of solving problems that may arise.

As a result of the diverse nature of the industry, their hazards, and organizational structure, management attitudes toward a safety program and government emphasis on accident prevention have created a wide diversity of safety positions, duties, and responsibilities in industrial plants.

Fat and Vegetable Oil Industries

Introduction

Oils and fats are important nutrients in a healthy diet. Structurally, they are esters of glycerol with three fatty acids. As such, they are scientifically called triacylglycerols but are commonly referred to in the food industry as triglycerides. Although the terms 'oils' and 'fats' are often used interchangeably, they are usually used to distinguish triglycerides in the liquid state at ambient temperatures (oils) from those in the solid state (fats).

Oils and fats form an important part of a healthy diet. Structurally they are esters of glycerol with three fatty acids (called either triacylglycerols or triglycerides). It is these fatty acids that give the functionality to fats. Chemically, they can be divided into four main types – saturated, *cis*-monounsaturated, *cis*-polyunsaturated and *trans* fatty acids. In very broad terms, saturated fatty acids and *trans* fatty acids are solid at room temperature while the *cis*-unsaturates are liquid at room temperature. Although no naturally occurring fat is either 100% saturated or 100% unsaturated (but is a mix of the two), fats are often referred to as ‘saturated’ or ‘unsaturated’ because of the predominance of one or other type of fatty acid.

Vegetable oils constitutes an important component of human diet. Major edible vegetable oils in terms of production include from soybean, canola, sunflower and peanut. They are source of edible FAs (saturated, monounsaturated or polyunsaturated), which play an important role in cellular metabolism as a way to store energy and also by providing energy when required. FAs are known to play an important role in cell division and growth. They are an integral component of cell membranes, hormones, neurotransmitters etc. Intake of different fatty acids has a direct influence on human health.

Oil and fat processing methods

One of the earliest oil processing methods was hydrogenation. In the presence of a catalyst (usually nickel) the double bonds in a liquid oil can react with hydrogen in two ways. Either a hydrogen molecule can react with the carbon atoms in an unsaturated bond to convert it into a saturated single bond. This has a higher melting point and so a liquid oil can be converted into a solid fat. The other way it can react is to convert the cis double bond into a trans double bonds. As trans fatty acids are higher melting than the corresponding cis unsaturated acids the liquid oil is again converted into a higher melting fat. Apart from the natural occurrence of low levels of trans fatty acids in some milk and meat fats, trans fatty acids are only produced by the industrial process of hydrogenation (or by gross thermal mistreatment of oils). Hydrogenation, therefore, converts liquid oils into potentially more functional solid fats and changes the fatty acid composition of the starting mix of oils significantly.

There are considerable health and nutritional problems associated with trans fatty acids (see below for details of these) and so the use of hydrogenation as an oil modification technique has now been largely phased out both in the UK and in many other countries throughout the world, either voluntarily or as a result of legislation.

Functionality of fats and oils in food products

Different food products have different requirements as far as the functionality of the fat they contain is concerned. These requirements can often be condensed down to four basic headings:

- melting point and melting profile
- crystallization characteristics
- storage stability (oxidative and hydrolytic stability)
- nutritional requirements.

1. Bakery products

Fats used in bakery products, for example biscuits and pastry, need to have a certain level of solid fat present at the temperature at which the dough is mixed in order to give enough structure to hold a light aerated structure and to stop more liquid triglycerides from separating from the baked end product. Biscuit and pastry doughs are often mixed at about 25°C, which is close to the ambient temperature in many bakeries. At this temperature, the dough fat used needs to, ideally, contain between 25% and 40% solid fat. Higher solid fat levels make the dough difficult to mix; lower solid fat levels risk some of the liquid fat exuding from the final biscuit or pastry making it oily to the touch.

2. Chocolate and confectionery coatings

Chocolate and chocolate like coatings need to be solid at ambient temperatures but then melt quickly at mouth temperature. Cocoa butter does this and is obviously the gold standard as far as this is concerned. Chocolate manufacturers in the EU (European Union, 2000) and a number of other countries across the world (not the USA, though) permit a small amount of non-cocoa vegetable fat (called cocoa butter equivalents) to be used in chocolate. There are various limitations put on this both in terms of the amount that can be used and the types of fat that are used.

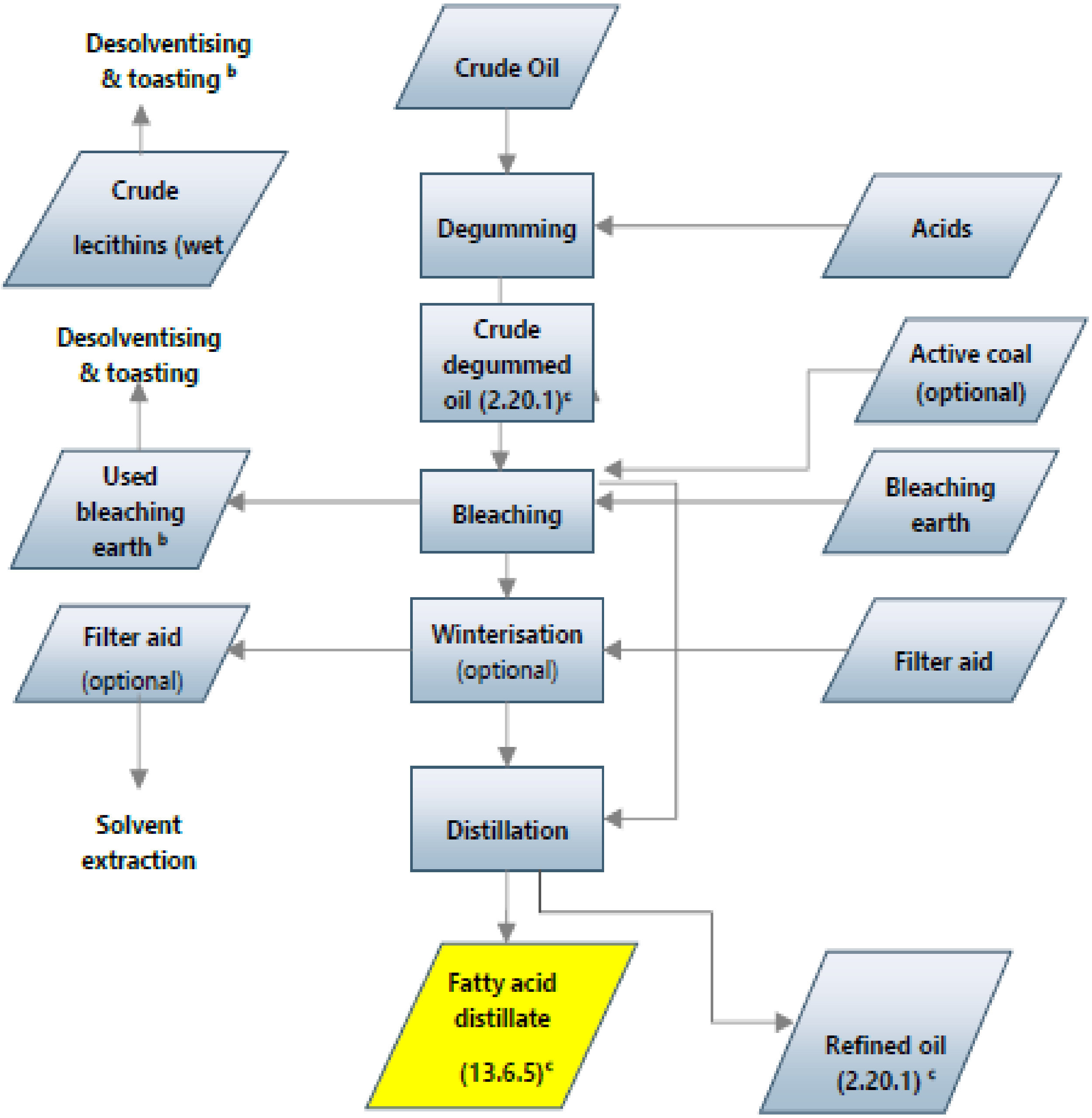
3. Ice cream

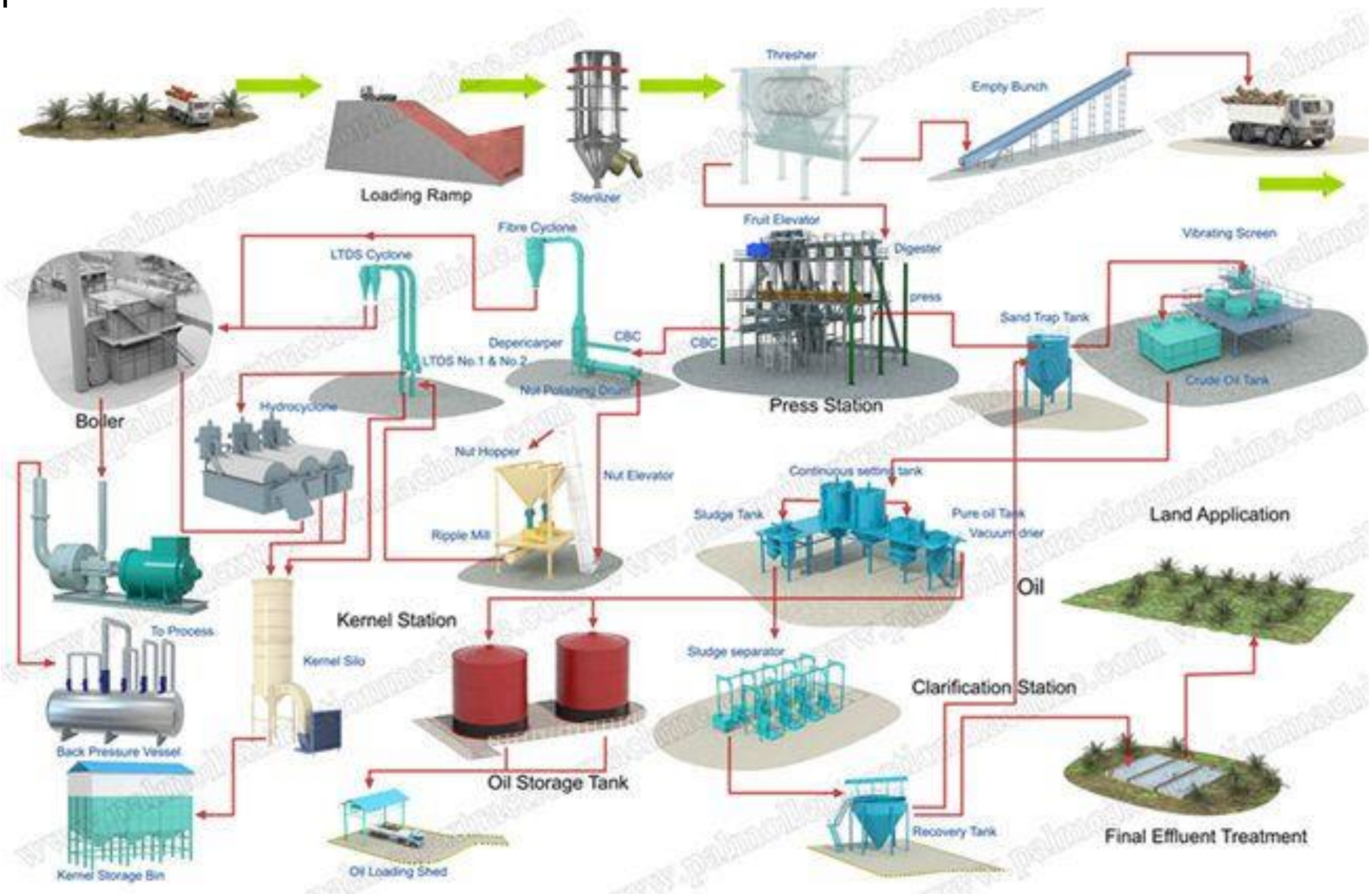
In general, fats for ice cream need to have at least 50% solid fat at 0°C to structure the ice cream but should have a melting point below normal mouth temperature because, during ice cream consumption, the mouth cools. Dairy ice cream must contain only dairy fat, i.e. normally cow's milk fat (unless labelled otherwise). Non-dairy ice cream can be based on vegetable fats. Because of these melting requirements, palm kernel oil or coconut oil are usually used as the base oil in non-dairy ice cream.

4. **Frying**

Frying oils need to have a high degree of oxidative stability because of the high temperature of use. Saturated fatty acids and *trans* fatty acids have a much higher degree of oxidative stability than do *cis* unsaturated fatty acids. As these oils are being used at 180°C for frying, the higher melting points and levels of solid fat in more saturated or *trans*-rich fats is irrelevant

Flow chart physical refining

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Press Station
Boiler
Hydrocyclone
Nut Hopper
Nut Elevator
Ripple Mill
Continuous setting tank
Sludge Tank
Pure oil Tank
Vacuum drier
Land Application
Oil
To Process
Kernel Station
Kernel Silo
Sludge separator
Clarification Station
Back Pressure Vessel
Oil Storage Tank
Kernel Storage Bin
Oil Loading Shed
Recovery Tank
Final Effluent Treatment

FERMENTATION INDUSTRIES

INTRODUCTION

The word fermentation comes from the Latin “fermentare” means to boil. Fermentation stood for the decomposition of foodstuff, generally accompanied by evolution of gas e.g. fermentation of sugars to alcohols and carbon dioxide by yeast. Now a days the term fermentation is applied to changes brought about by microorganisms. Evolutions of gas are not an essential criterion. In daily life many complex chemical reactions are brought about by the agency of living organisms e.g. souring and curdling of milk, putrefaction of meal, production of indigo dye from the compound indicate in the food, curing of tobacco, the development of benzaldehyde or oil of biter almonds from the amygdaline contained in the almond seed, conversion of fruit juice into wines etc. All these processes are called fermentation processes, in which complex organic material is broken down into smaller substances and decomposition it brought about by the action of living organisms, which secretes the enzyme catalyst, suitable to the process.

Fermentation of fruits to alcohol and making of beverage out of fruits and grain have been practiced for centuries. Now man is directing the life process of microorganisms, yeasts, bacterial and moulds to the production of large number of chemicals, like alcohol, acetone, acetic acid, lactic acid citric acid and many antibiotics which are of great synthetic as well as industrial important.

Microorganism

The organism having microscopic dimension is called as micro-organism. In other words the organism cannot be seen by naked eyes but required microscope are micro-organism e.g. pseudomonas, bacillus species, e – coli etc.

Aerobe

An organism that can use oxygen as an electron accepter at the terminus of an electron-transport chain can grow at a level of O_2 equivalent to or higher than that present in an air atmosphere (21 %) and has a strictly respiratory type of metabolism.

Anaerobe

An organism that does not use O_2 to obtain energy that cannot grow under air atmosphere. O_2 is toxic for this class of organism.

Facultative Anaerobe

An organism that can use oxygen but also has anaerobic methods of energy production. It can survive in either environment.

Sterilization

Sterilization is the process of killing of all forms of life including transmissible agents such as fungi, bacteria, viruses, spore forms, etc. present on a surface, contained in a fluid, in medication, or in a compound such as biological culture media. Sterilization can be achieved by applying heat, chemicals, irradiation, high pressure, and filtration or combinations of two or more.

Medium

The substances used to provide nutrients for the growth and multiplication of organisms is called as medium or media.

Culture

It is the population of microorganisms cultivated in a medium.

Inoculation

The artificial introduction of microorganisms or other substances into the body or into the culture medium is called as inoculation. It can also be used to refer to the communication of a disease to a living organism by transferring its causative agent into the organism, the implanting of microorganisms or infectious material into a culture medium such as a brewers vat or a petri-dish, or the placement of microorganisms or viruses at a site where infection is possible

Inoculum

The substance containing microorganism or other material that is introduced in inoculation is called as inoculums.

Incubation

The subjecting of cultures of microorganisms to conditions favourable to their growth is called as incubation e.g. temperature.

Agar

A dried polysaccharide extract of red algae, used as a solidifying agent in microbiological media.

Lyophilisation

The preservation of biological specimens by rapid freezing and rapid dehydration in a high vacuum is called as lyophilisation.

FERMENTATION PROCESS

Prerequisites

The good fermentation process shall have the following prerequisites.

- Selection of microorganism that formed a desired end product. The organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yield

- Economical raw materials for the substrate e.g. starch
- Acceptable yield
- Rapid fermentation
- A product that is readily recovered purified

Nutrients for Microorganisms

Microorganisms may or may not require certain type of complex carbon containing compounds as nutrients as in the case of Human and other animals. All living organisms, microorganisms are the most versatile and diversified in their nutritional requirements. Some microbes can grow with just a few inorganic substances as their sole nutritional requirements, while other microorganisms are like higher organisms in their need for complex organic compounds. But all living organisms share some common nutritional needs, like the need for carbon, nitrogen, and water.

Water is particularly important to microorganisms, besides most of microorganisms can absorb nutrients only when the chemicals are dissolved in water.

Classification of nutrients

Nutrients are frequently classified as

- Essential nutrients
- Non essential nutrients

Essential Nutrients

Essential nutrients which are not synthesized internally either at all, or in sufficient quantities. There so, they must be consumed by an organism from its environment. For humans, these include essential fatty acids, essential amino acids, vitamins, and certain dietary minerals. Oxygen and water are also essential for human survival, but are generally not considered "food" when consumed in isolation. Humans can derive energy from a wide variety of fats, carbohydrates, proteins, and ethanol, and can synthesize other needed amino acids from the essential nutrients.

Non-essential Nutrients

Nonessential nutrients are those nutrients that can be made by the body, they may often also be absorbed from consumed food. The majority of animals ultimately derive their essential nutrients from plants, though some animals may consume mineral-based soils to supplement their diet. Non-essential substances within foods can still have a significant impact on health, whether beneficial or toxic. For example, most dietary fiber is not absorbed by the human digestive tract, but is important in digestion and absorption of otherwise harmful substances.

Chemical elements as nutrients

All the microorganisms need a variety of chemical elements as nutrients. These elements are necessary for both the synthesis and the normal functions of cellular components.

The main nutrient elements for cell growth are

1. Carbon
2. Nitrogen
3. Hydrogen and oxygen
4. Sulfur
5. Phosphorous

1. Carbon

Carbon is one of the most important chemical elements required for microbial growth. Carbon forms the backbone of three major classes of organic nutrients e.g.

carbohydrates, lipids and proteins. Such compounds provide energy for cell growth and serve as building blocks of cellular material.

2. Nitrogen

Elemental nitrogen in the atmosphere cannot be used directly by either plants or animals, and must be converted to a reduced (or 'fixed') state to be useful for higher plants and animals. All organisms also require nitrogen in some form. Nitrogen is an essential building block of amino and nucleic acids, essential to life on the Earth.

3. Hydrogen and oxygen

Hydrogen and oxygen form part of many organic compounds. Water is one of the important compounds of hydrogen and oxygen. Water has many distinct properties from biological point of view that are critical for the proliferation of life. All known forms of life depend on water. Water is vital both as a solvent in which many of the body's solutes dissolve and as an essential part of many metabolic processes within the body.

4. Sulfur

Sulfur is needed for the biosynthesis of amino acids cysteine, cystine and methionine.

5. Phosporous

Phosphorous is essential for the synthesis of nucleic acid and adenosine triphosphate (ATP), a compound that is extremely important for energy storage and transfer.

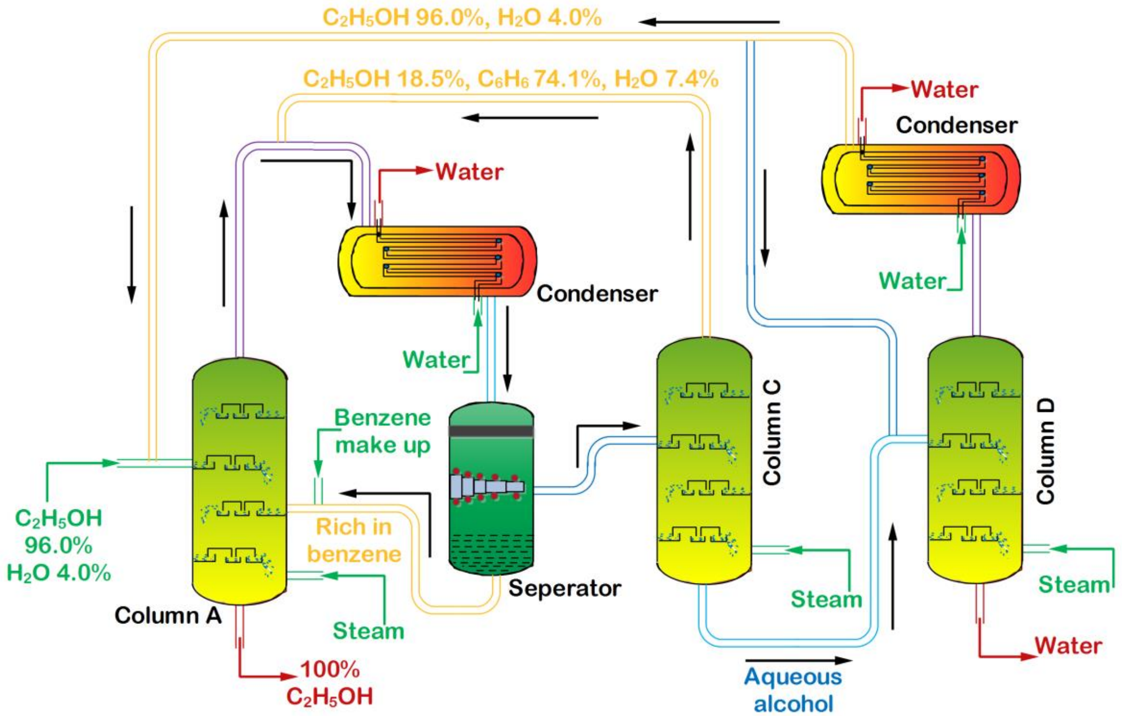


Figure: Manufacture of Absolute alcohol from 96% alcohol

Fertilizers Industries

Introduction

Fertilizer is a key ingredient in feeding a growing global population, which is expected to surpass 9.5 billion people by 2050. Half of all food grown around the world today, for both people and animals, is made possible through the use of fertilizer. As demand continues to grow, farmers around the world will continue to rely on fertilizer to increase production efficiency to produce more food while optimizing inputs. Fertilizers play an essential role in replenishing nutrients in the soil that are used by plants each growing season. Three primary nutrients are necessary for plant growth: nitrogen, phosphorus, and potassium. All must be present in soil in the right amount to grow healthy crops.

NITROGEN IS ESSENTIAL IN THE FORMATION OF PROTEIN, WHICH MAKES UP MUCH OF THE TISSUE PRESENT IN LIVING THINGS. The earth's atmosphere is about 78 percent nitrogen by volume; however, most plants can't get their nitrogen directly from the air and require nitrogen fertilizer. Nitrogen fertilizer is made by capturing nitrogen from the air and combining it with hydrogen derived from natural gas. This production method is called the Haber-Bosch process.

PHOSPHORUS IS INVOLVED IN MANY PROCESSES CRITICAL TO PLANT DEVELOPMENT. KEY AMONG THEM IS PHOTOSYNTHESIS, THE PROCESS THAT PLANTS USE WHEN CONVERTING SUNLIGHT TO ENERGY. The phosphorus in most commercial fertilizers comes from phosphate rock found in fossil remains originally laid down beneath ancient sea beds.Fertilizer manufacturers mine deposits of phosphate rock, which are converted into phosphate fertilizers.

POTASSIUM, ALSO KNOWN AS POTASH, IS ESSENTIAL FOR CARBOHYDRATE AND STARCH SYNTHESIS, AND IT ALSO HELPS PLANTS RESIST WILTING. Up to 98 percent of potassium in the soil is unavailable to plants in its existing form, making potash fertilizer essential for crop production. Potassium, like nitrogen, also helps plants produce protein as they grow. Potassium, like phosphate, is mined from mineral deposits.

Types of Fertilizers

There are our different types of fertilizers that are mentioned below:

1. Inorganic Fertilizers

Inorganic fertilizers are chemical fertilizers that contain nutrient elements for the growth of crops made by chemical means. The inorganic fertilizers are of the following types:

2. Nitrogen Fertilizers

Nitrogen fertilizers contain nitrogen necessary for the development of crops. Nitrogen is the main constituent of chlorophyll that maintains a balance in the process of photosynthesis. It is also a part of amino acids in plants and constitutes protein. Nitrogen fertilizers improve the production and quality of agricultural products.

3. Phosphorus Fertilizer

The main nutrient in a phosphorus fertilizer is phosphorus. The efficiency of fertilizer depends upon effective phosphorus content, methods of fertilizing, properties of soil and crop strains. Phosphorus found in the protoplasm of the cell plays an important role in cell growth and proliferation. The phosphorus fertilizer is beneficial for the growth of roots of the plants.

4. Organic Fertilizers

Organic fertilizers are natural fertilizers obtained from plants and animals. It enriches the soil with carbonic compounds essential for plant growth. Organic fertilizers increase the organic matter content of the soil, promotes the reproduction of microorganisms, and changes the physical and chemical properties of the soil. It is considered to be one of the main nutrients for green food.

Advantages of Fertilizers

The advantages of fertilizers are mentioned below:

- They are easy to transport, store, and apply.

- For supplying a specific nutrient we can select a specific fertilizer due to its nutrient specific nature.
- They are water soluble and can easily dissolve in the soil. Hence, they are easily absorbed by the plants.
- They have a rapid effect on the crops.
- They increase the crop yield and provide enough food to feed the large population.
- They are predictable and reliable.

Disadvantages of Fertilizers

Fertilizers have the following disadvantages:

- They are expensive.
- The ingredients in the fertilizers are toxic to the skin and respiratory system.
- Excessive use of fertilizers damages the plants and reduces soil fertility.
- Leaching occurs and the fertilizers reach the rivers causing eutrophication.
- Long term use reduces the microbial activity and disturbs the pH of the soil.

Uses of Fertilizers

Fertilizers are used for various purposes. The uses of fertilizers are mentioned below:

- They are used to provide additional nutrients to the plants.
- They are added to improve the yield of the crops.
- Nitrogen-rich fertilizers are used for the greening of lawns.
- Organic fertilizers improve the texture and fertility of the soil.
- Gardeners use fertilizers to address certain needs of the plants such as nutritional needs.
- Fertilizers are added to potted plants to replace the lost nutrients.

Impact of Chemical Fertilizers on Natural Resources

1. Effects of Chemical Fertilizers on Water Pollution

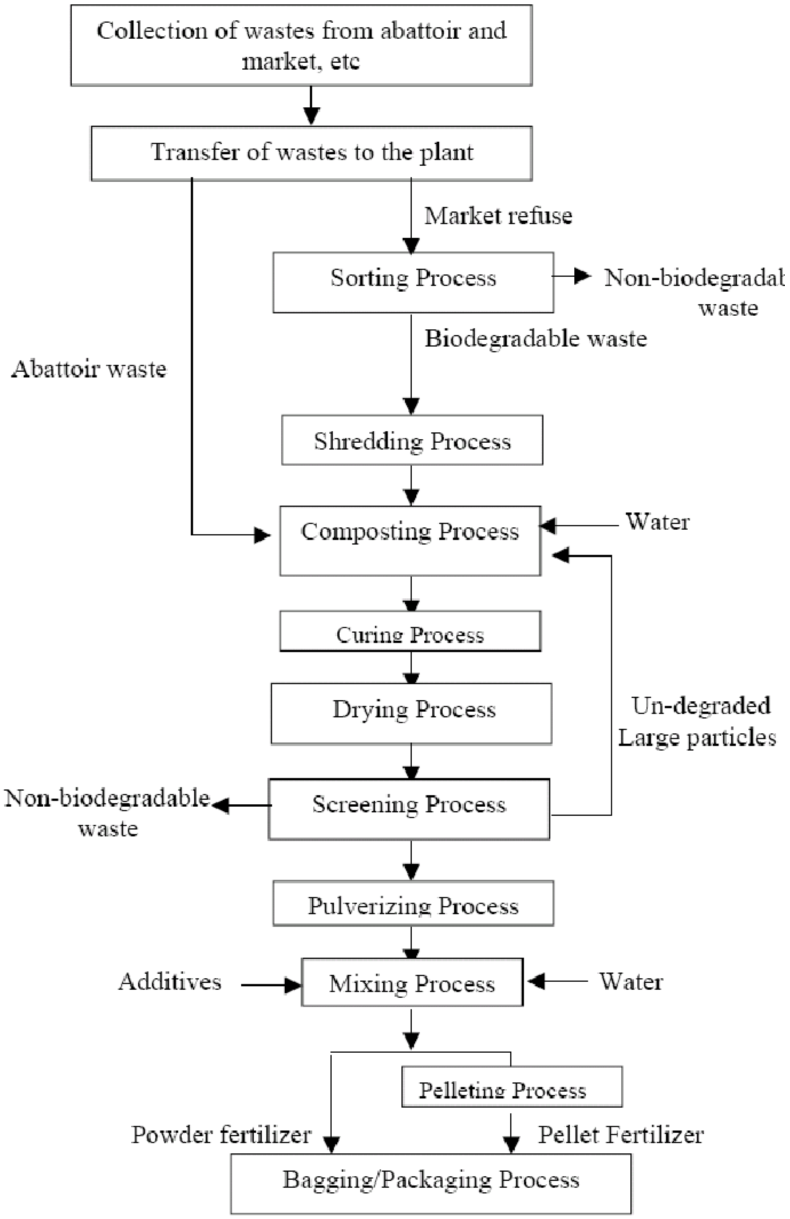
The most important parameters of the pollution of water is nitrate which is the basic component of fertilizer. Nitrate is the most common form of dissolved nitrogen present in groundwater or other water bodies. When nitrate concentration exceeds 50 mg NO_3^-/L in drinking water or high nitrate accumulation can lead to many danger disease.

2. Effects of Chemical Fertilizers on Air Pollution

The greenhouse gases like CO_2, CH_4 and N_2O are produced during the manufacture of nitrogenous fertilizer. The effects can be combined into an equivalent amount of CO_2. Nitrogen fertilizer can be converted by soil bacteria into nitrous oxide, a greenhouse gas. Nitrogen fertilizer whose excess use results in an emission of nitrogen oxides (NO, N_2O, NO_2) is responsible for severe air pollution. Other gases also responsible for the ozone depletion are water vapour, carbon dioxide, methane, hydrogen sulfide and chloro-fluoro hydrocarbons. Nitrous oxide (N_2O) has become the third most important greenhouse gas after carbon dioxide and methane.

3. Effect of Chemical Fertilizer on Soil Pollution

The over-use of chemical fertilizers can lead to soil acidification and soil crust thereby reducing organic matter content, humus content, beneficial organisms, stunting plant growth, can change the soil pH, increase pests, and even contribute to the release of greenhouse gases. The soil acidity diminishes phosphate intake by crops, increases the toxic ion concentration in the soil, and inhibits crop growth.


Collection of wastes from abattoir and market, etc
Transfer of wastes to the plant
Market refuse
Sorting Process
Non-biodegradal waste
Biodegradable waste
Abattoir waste
Shredding Process
Composting Process
Water
Curing Process
Drying Process
Un-degraded Large particles
Non-biodegradable waste
Screening Process
Pulverizing Process
Additives
Mixing Process
Water
Pelleting Process
Powder fertilizer
Pellet Fertilizer
Bagging/Packaging Process

Paper and Pulping Industry

Introduction

The pulp and paper industry is a large and growing portion of the world's economy. Pulp and paper production has increased globally and will continue to increase in the near future. Most of the pulp and paper mills are located near the major waterways and have an access to a large, uninterrupted supply of water. After using the water for pulp and paper production, these mills discharge the used water into the waterways as waste. The pulp and paper industry is faced with mounting environmental, political, and economic pressures to reduce the volume and toxicity of its industrial wastewater.

Comparison of Pulping and Papermaking Data

Although the determinations of basic density, fibre dimensions and chemical characteristics of wood are fairly straightforward and reasonably well standardized so that values obtained in different laboratories are comparable, this is not so when it comes to determination of the papermaking characteristics of pulps. In spite of the standardization work which has been carried out in this field, there still remains considerable discrepancy in strength property values. The reason for this is basically that the strength properties of a test sheet of pulp depend, to a great extent, on the treatments given to the pulp before the actual determination of a certain strength value is carried out, as well as on the atmospheric conditions in the room where the determination is made.

Pulping Processes

Pulping of non-wood plants is of more advantage compared to wood fibre in such that non-wood materials can be pulped with simple chemical systems (caustic soda). The alkali charge required for these materials is normally lower than what is required for wood-based raw material in which the same degree of delignification is achieved thereby reducing the energy required during this process. The pulping strategies which are commonly used for pulp extraction are categorised as mechanical, thermal, semi-chemical or wholly chemical methods. The major aim to be achieved when using chemical pulping is the degradation of lignin and hemicelluloses into small water-soluble molecules which can be washed away from the cellulose fibres without depolymerising the cellulose fibres. Specific end-products are produced from a given nonwood fibrous raw material based on the choice of process such as; technique used, size of mill the chemicals available, and their relative cost. The pulping process applied in pulping of non-wood fibres determines the quality and properties of the total yield of pulp to be obtained. This is a significant factor in considering the type of paper to be produced. Some of these pulping techniques have been in use since the ancient times and are ultimately due for improvement in other to overcome their drawbacks. In addition to pulping techniques.

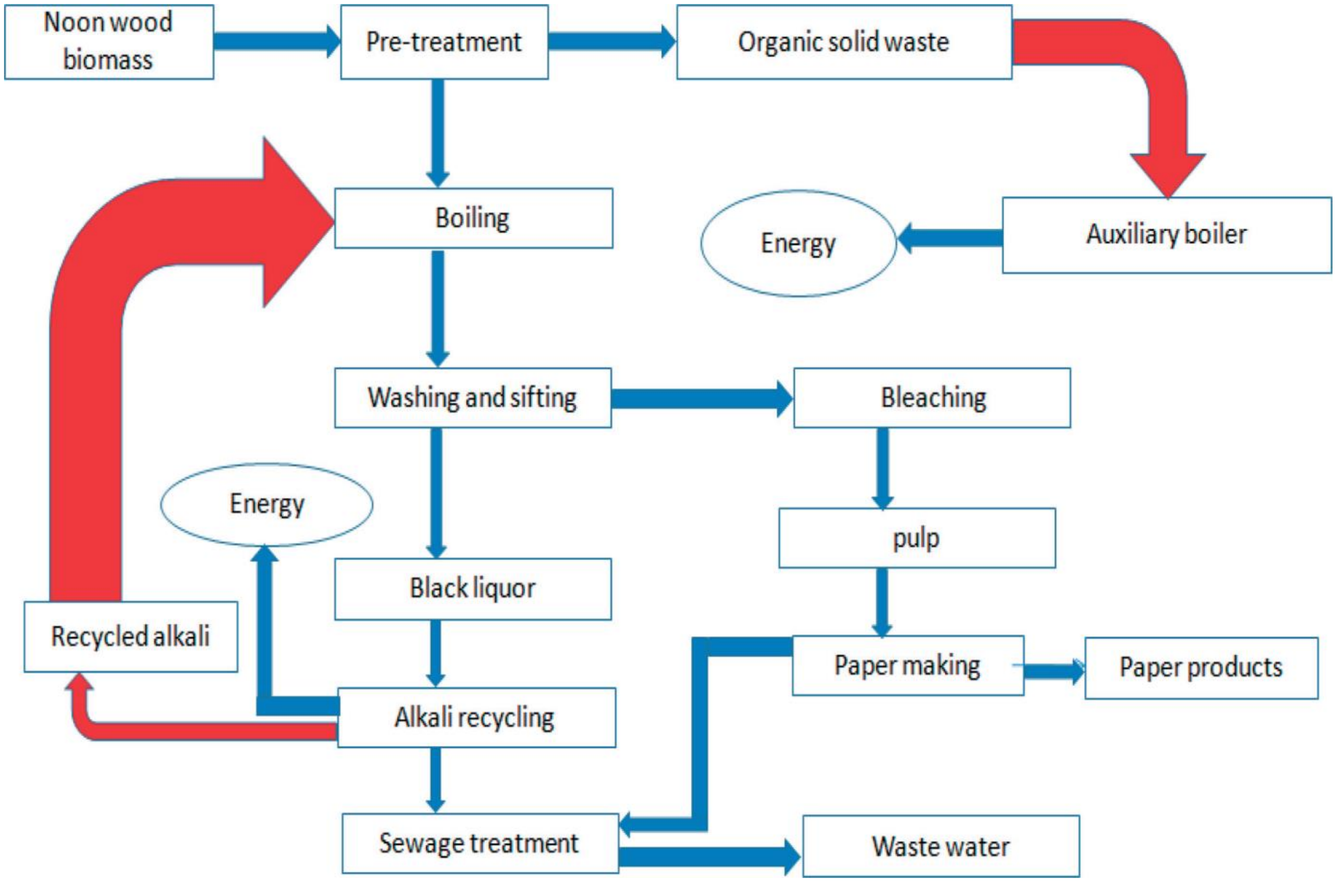
The lime or lime-soda pulping methods are usually used for the production of lower grade unbleached pulps. Most of the pulping techniques are used in pulping non-wood plant stalks and this result in the production of bleachable and high-grade unbleached pulps. The Kraft, soda and the sulphite processes are used majorly in the pulping of leaf and bast fibrous raw materials. Leaf and bast fibres have excellent pulp strength properties which are greater than softwood pulps. Of all the bast fibres, when jute pulped using the soda or Kraft method, the jute fibre strands is reduced to the ultimate fibres, and jute pulps with weaker properties compared to softwood are produced. Jute is an exceptional case of the bast fibres. The use of mild lime or sodium carbonate during pulping process, results in the production of pulp with durable, strong and hard properties. When jute is pulped using this process, long fibres are obtained with increased strength similar or greater than those of softwood pulps.

Pulp, the main raw material for papermaking, is a ligno-cellulosic fibrous material, which is produced from separation of the cellulose fibers in wood, fiber crops and waste paper. The pulp-making process can be divided in timber and debarking, chipping, pulping, cleaning, bleaching, and washing and drying. Timber utilized for pulping is denoted pulpwood.

The purpose of pulping is to break down the structure of the fiber feedstock into its constituent fibers. The main inputs for paper and paperboard are different forms of pulp, which in turn are made from wood or other raw materials containing cellulose fibres. In Europe, wood is the main raw material, although in a few cases cellulose material, such as straw, hemp, grass or cotton.

Pulp and paper mills can either be integrated or separated. An integrated mill produces pulp on site, while in a non-integrated pulp mill market pulp is dried and pressed before being transported to the paper mill. Since pulp is a product by itself, pulp and paper are treated separately throughout this report.

The pulp for papermaking can be produced from virgin fibre or from re-pulping of recycled paper. To produce virgin pulp, wood logs are first debarked and chipped. Then water and heat are added and by mechanical or chemical means the wood is separated into individual fibres.



Process flow diagram for pulp and paper production

Recycled Paper Operations

The use of waste or recycled paper as the raw material for pulp production has increased during the last several decades, and some paper plants depend almost completely on waste paper. In some countries, waste paper is separated from other household waste at the source before it is collected. In other countries separation by grade (e.g., corrugated board, newsprint, high-grade paper, mixed) takes place in special recycling plants.

Recycled paper can be repulped in a relatively mild process which uses water and sometimes NaOH. Small metal pieces and plastics may be separated during and/or after repulping, using a debris rope, cyclones or centrifugation. Filling agents, glues and resins are removed in a cleaning stage by blowing air through the pulp slurry, sometimes with the addition of flocculating agents. The foam contains the unwanted chemicals and is removed. The pulp can be de-inked using a series of washing steps which may or may not include the use of chemicals (i.e., surfactant fatty acid derivatives) to dissolve remaining impurities, and bleaching agents to whiten the pulp. Bleaching has the disadvantage that it may reduce fibre length and therefore lessen final paper quality. The bleaching chemicals used in recycled pulp production are usually similar to those used in brightening operations for mechanical pulps. After the repulping and de-inking operations, sheet production follows in a manner very similar to that using virgin fibre pulp.

Environmental and Public Health Issues

Because the pulp and paper industry is a large consumer of natural resources (i.e., wood, water and energy), it can be a major contributor to water, air and soil pollution problems and has come under a great deal of scrutiny in recent years. This concern appears to be warranted, considering the quantity of water pollutants generated per tonne of pulp (e.g., 55 kg of biological oxygen demand, 70 kg of suspended solids, and up to 8 kg of organochlorine compounds) and the amount of pulp produced globally on an annual basis (approximately 180 million tonnes in 1994). In addition, only about 35% of used paper is recycled, and waste paper is a major contributor to total worldwide solid waste (about 150 million of 500 million tonnes annually). Historically, pollution control was not considered in the design of pulp and paper mills. Many of the processes used in the industry were developed with little regard for minimizing effluent volume and pollutant concentration. Since the 1970s, pollution abatement technologies have become integral components of mill design in Europe, North America and other parts of the world. Figure 71.12 illustrates trends over the period 1980 to 1994 in Canadian pulp and paper mills in response to some of these environmental concerns: increased use of wood waste products and recyclable paper as fibre sources; and decreased oxygen demand and chlorinated organics in wastewater.

Pharmaceutical Industries

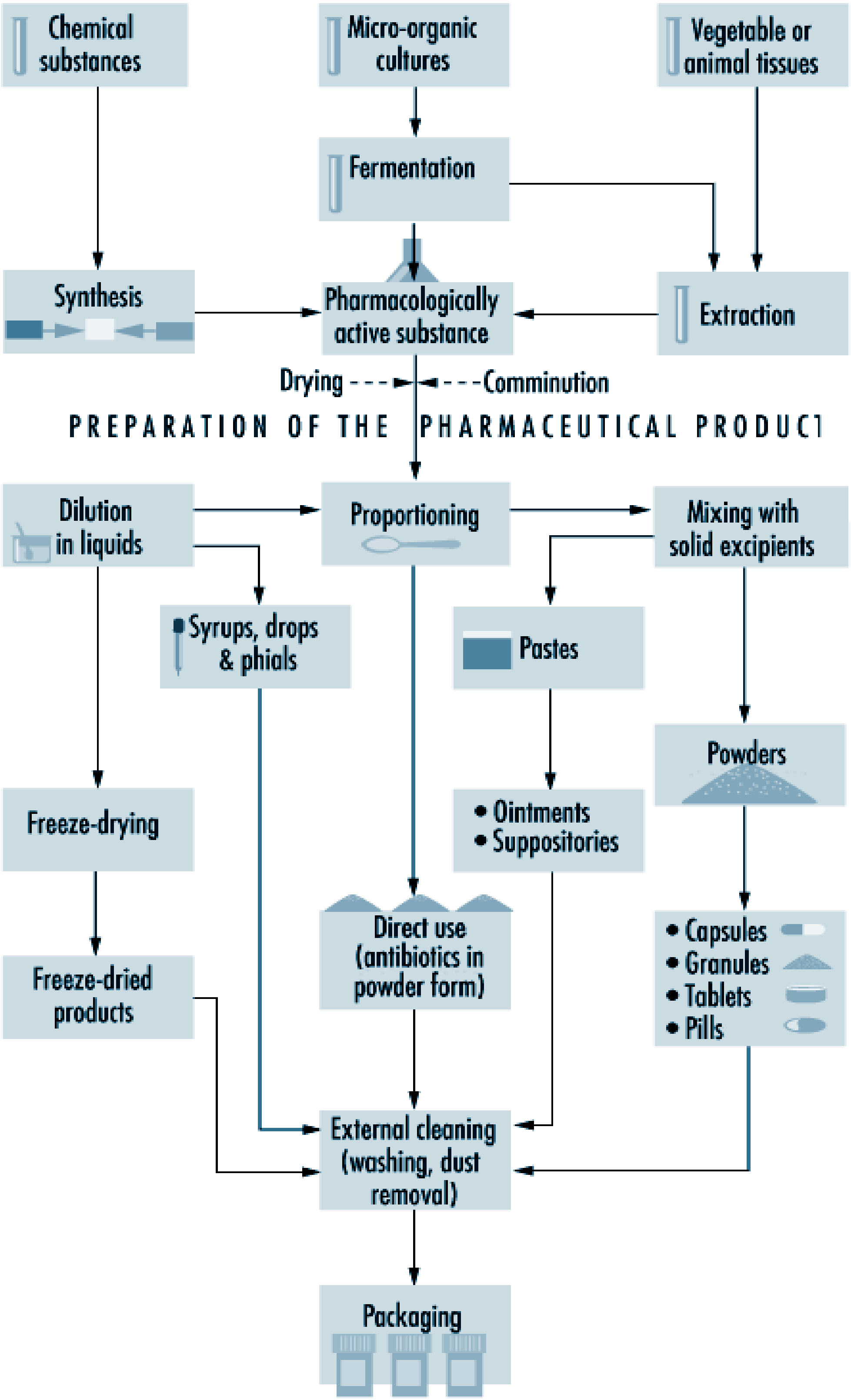
Introduction

The pharmaceutical industry is an important component of health care systems throughout the world; it is comprised of many public and private organizations that discover, develop, manufacture and market medicines for human and animal health. The pharmaceutical industry is based primarily upon the scientific research and development (R&D) of medicines that prevent or treat diseases and disorders. Drug substances exhibit a wide range of pharmacological activity and toxicological properties. Modern scientific and technological advances are accelerating the discovery and development of innovative pharmaceuticals with improved therapeutic activity and reduced side effects. Molecular biologists, medicinal chemists and pharmacists are improving the benefits of drugs through increased potency and specificity. These advances create new concerns for protecting the health and safety of workers within the pharmaceutical industry.

The pharmaceutical industry is largely driven by scientific discovery and development, in conjunction with toxicological and clinical experience. Major differences exist between large organizations which engage in a broad range of drug discovery and development, manufacturing and quality control, marketing and sales and smaller organizations which focus on a specific aspect. Most multinational pharmaceutical companies are involved in all these activities; however, they may specialize in one aspect based upon local market factors. Academic, public and private organizations perform scientific research to discover and develop new drugs. The biotechnology industry is becoming a major contributor to innovative pharmaceutical research. Often, collaborative agreements between research organizations and large pharmaceutical companies are formed to explore the potential of new drug substances.

Pharmaceutical Operations

Pharmaceutical manufacturing operations may be categorized as basic production of bulk drug substances and pharmaceutical manufacturing of dosage form products. Figure 1 illustrates the manufacturing process.


Chemical substances
Micro-organic cultures
Vegetable or animal tissues
Fermentation
Synthesis
Pharmacologically active substance
Extraction
Drying
Comminution
PREPARATION OF THE PHARMACEUTICAL PRODUC
Dilution in liquids
Proportioning
Mixing with solid excipients
Syrups, drops & phials
Pastes
Powders
Freeze-drying
• Ointments
• Suppositories
Freeze-dried products
Direct use (antibiotics in powder form)
• Capsules
• Granules
• Tablets
• Pills
External cleaning (washing, dust removal)
Packaging

Environmental Pollution Prevention

Good engineering and administrative practices minimize the environmental impact of bulk chemical production and pharmaceutical manufacturing operations. Pollution prevention employs modifying processes and equipment, recycling and recovering materials and maintaining good housekeeping and operating practices. These activities enhance the management of environmental issues, as well as worker health and safety.

Process Modifications

Processes may be modified to reformulate products by using materials that are less hazardous or persistent or changing manufacturing operations to reduce air emissions, liquid effluents and solid wastes. Reducing the amount and toxicity of wastes is wise, since it improves the efficiency of manufacturing processes and reduces the costs and impacts of waste disposal. Government drug approval regulations may limit the ability of pharmaceutical manufacturers to change hazardous materials, manufacturing processes, equipment and facilities. Drug manufacturers must anticipate the environmental, health and safety impacts of selecting hazardous materials and designing manufacturing process at an early stage.

It becomes increasingly difficult to make changes during the later stages of drug development and regulatory approval, without considerable loss of time and expense.

It is very desirable to develop manufacturing processes with less hazardous solvents. Ethyl acetate, alcohols and acetone are preferable to highly toxic solvents such as benzene, chloroform and trichloroethylene. Whenever possible, some materials should be avoided due to their physical properties, ecotoxicity or persistence in the environment (e.g., heavy metals, methylene chloride). Substituting aqueous washes for solvents during filtrations in bulk chemical production reduces liquid wastes and vapour emissions. Also, substituting aqueous for solvent-based solutions during tablet coating reduces environmental, health and safety concerns. Pollution prevention is promoted by improving and automating process equipment, as well as performing routine calibration, servicing and preventive maintenance. Optimizing organic synthesis reactions increases product yields, often decreasing the generation of wastes. Incorrect or inefficient temperature, pressure and material control systems cause inefficient chemical reactions, creating additional gaseous, liquid and solid wastes.

The following are examples of process modifications in bulk pharmaceutical production:

- Minimize the quantities of hazardous materials used and select materials whose wastes can be controlled, recovered and recycled, whenever possible.
- Develop and install systems for recycling raw materials (e.g., solvents), intermediates, wastes and utility materials (e.g., cooling water, heat transfer liquids, lubricants, steam condensate).
- Examine reactants, solvents and catalysts to optimize the efficiency of chemical reactions.
- Modify the design and features of processing equipment to minimize pollution and wastes.
- Improve processes to maximize product yields and desired properties, eliminating additional processing (e.g., re-crystallization, drying and milling).
- Consider using multi-purpose equipment (e.g., reactors, filters and dryers) to reduce pollution and wastes during transfers, cleaning and additional process steps.
- Use appropriate instruments, automated control systems and computer programs to maximize the efficiency of processes and reduce pollution and wastes.

Phosphorus Industries

The use of artificial fertilizers, phosphoric acid, and phosphate salts and derivatives has increased greatly, chiefly because of aggressive and intelligent consumption promotion on the part of various manufacturers and federal agencies. However, before full consumption of these products could be achieved, more efficient and less expensive methods of production had to be developed. During recent decades, the various phosphate industries have made rapid strides in cutting the costs both of production and distribution and have thus enabled phosphorus, phosphoric acid, and its salts to be employed in wider fields and newer derivatives to be introduced. Supplementing the development of more efficient phosphorus industries have been the pure chemical studies of phosphorus, in its old and in its new compounds. These phosphates are not simple inorganic chemicals, as was assumed several decades ago, and their study has become a unique and complicated branch of chemistry that may some day be compared with the carbon (organic) or silicon branches of today. The properties of phosphorus chemicals are unique because of the important role of phosphorus in many biochemical processes, the ability of polyphosphates to complex or sequester many metal cations, and versatility in forming various types of organic and inorganic polymers.

HISTORICAL. The use of phosphatic materials as fertilizers was practiced unknowingly long before the isolation and discovery of phosphorus by the German alchemist Brand in 1669. As early as 200 B.C., the Carthaginians recommended and employed bird droppings to increase the yields from their fields. The Incas of Peru prized guano and bird droppings on their islands so highly that it was made a capital offense to kill birds. We are also familiar with the use of fish and bones by American Indians in their crude agricultural methods. Bones and guano continued to be the chief sources of phosphorus and phosphoric acid until after the middle of the nineteenth century, but these supplies were and still are limited. In 1842, a British patent was issued to John B. Lawes for the treatment of bone ash with sulfuric acid. This patent marked the beginning of a large acid phosphate industry which became the basis of our domestic fertilizer industry. Soon afterward various grades of phosphate ores were discovered in England. These were first finely ground and applied directly to the soil. It was soon recognized, however, that treatment of these phosphate minerals with sulfuric acid increased the availability and efficiency of the phosphate for agricultural purposes. At present, acidulation with nitric acid or strong phosphoric acid gives enhanced fertilizer values.

PHOSPHATE ROCK

USES AND ECONOMICS. See Table 1.1 The most important use of phosphate rock is in fertilizers. See Chap. 26 on Agrichemical Industries. Table 1.2 is a compilation of phosphate-rock treatment processes. Tricalcium phosphate in raw and/or steamed and degreased bones and in basic slag is also used after grinding as a direct phosphate fertilizer. A small percentage of the former is sometimes treated with sulfuric acid for superphosphate or as a source material for phosphate chemicals. Large tonnages of phosphate rock are converted to phosphorus or phosphoric acid and their derivatives.

Domestic phosphate rocks are essentially fluorapatite admixed with various proportions of other compounds of calcium, fluorine, iron, aluminum, and silicon.

The formula of fluorapatite is $CaF_2 \cdot 3Ca_3(PO_4)_2$, equivalent to $Ca_{10}F_2(PO_4)_6$. This compound is extremely insoluble. The various means for making the P_2O_5 content more soluble, not necessarily in water, but in plant juices (as measured by "citrate solubility"), are manufacture of various superphosphates and the defluorination of fluorapatite by calcination at incipient fusion temperatures of 1400 to 1500°C with silica or phosphoric acid.

The production of phosphate rock is concentrated in Florida with 87 percent of the total; the western states of Idaho, Montana, and Utah contribute 10 percent, and Tennessee 3 percent. In 1980, 54 × 10^6 t with a value of $1200 million were produced.[1] Table 16.3 shows the various uses of the rock.

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[1] t = 1000 kg.

Table 1.1 Phosphate Rock Statistics (thousand metric tons and thousand dollars unless otherwise specified)

	1977	1978	1979	1980	1981
United States:					
Mine production	166,893	173,429	185,757	209,883	183,733
Marketable production	47,256	50,037	51,611	54,415	53,624
Value	$821,657	$928,820	$1,045,655	$1,256,947	$1,437,986
Average per metric ton	$17.39	$18.56	$20.26	$23.10	$26.82
Sold or used by producers	47,437	48,774	53,063	54,581	45,526
Value	$829,084	$901,378	$1,063,517	$1,243,297	$1,212,433
Average per metric ton	$17.48	$18.48	$20.04	$22.78	$26.63
Exports[a]	13,230	12,870	14,358	14,276	10,395
P_2O_5 content	4,251	4,118	4,611	4,554	3,300
Value	$288,603	$297,357	$356,481	$431,419	$373,192
Average per metric ton	$21.81	$23.10	$24.83	$30.22	$35.90
Imports for consumption[b]	158	908	886	486	13
Customs value	$6,079	$24,379	$21,595	$12,556	$420
Average per metric ton	$38.47	$26.85	$24.37	$26.45	$32.31
Consumption[c]	34,365	36,812	39,591	40,791	35,144
World:					
Production	[d]119,310	[d]128,620	[d]132,913	[e]138,333	[f]135,630

[a] Exports reported to the Bureau of Mines by companies.

[b] Bureau of the Census data.

[c] Measured by sold or used plus imports minus exports.

[d] Estimated. [e] Preliminary. [f] Revised.

Table 1.2 Phosphate-Rock Processing, Products, and By-Products

Process	Raw Materials and Reagents	Main Products and Derivatives	By-products
Acidulation	Phosphate rock, sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, ammonia, potassium chloride	Superphosphate, phosphoric acid (wet process), triple superphosphate, monoammonium phosphate, diammonium phosphate, monopotassium phosphate	Fluorine compounds, vanadium, uranium (limited)
Electric-furnace reduction	Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water	Phosphorus, phosphoric acid, triple superphosphate, various Na, K, NH_4, Ca salts; phosphorus pentoxide and halides	Fluorine compounds, carbon monoxide, slag (for railroad ballast aggregate, fillers, etc.), ferrophosphorus, vanadium[*]
Calcium metaphosphate	Phosphate rock, phosphorus, air or oxygen, fuel	Calcium metaphosphate	Fluorine compounds
Calcination or defluorination	Phosphate rock, silica, water or steam, fuel	Defluorinated phosphate	Fluorine compounds

[*] Vanadium is present in appreciable quantities only in the western phosphates.

Table 1.3 Phosphate Rock Sold or Used by Producers in the United States, by Use (thousand metric tons)

Use	1980 Rock	1980 P_2O_5 Content	1981 Rock	1981 P_2O_5 Content
Domestic[*]				
Wet-process phosphoric acid	33,884	10,444	29,085	8,956
Normal superphosphate	333	107	184	60
Triple superphosphate	1,348	436	1,198	378
Defluorinated rock	430	145	492	166
Direct applications	37	8	27	6
Elemental phosphorus	4,083	1,067	4,055	1,049
Ferrophosphorus	190	49	89	22
Total[†]	40,305	12,256	35,131	10,638
Exports[‡]	14,276	4,554	10,395	3,300
Grand total[†]	54,581	16,810	45,526	13,939

[*] Includes rock converted to products and exported.

[†] Data may not add to totals shown because of independent rounding.

[‡] Exports reported to the Bureau of Mines by companies.

SOURCE: *Minerals Yearbook 1981*, U.S. Dept. of Interior, 1982, p. 654.

Phosphate rock, when very finely pulverized, has limited direct use as a fertilizer, chiefly because of the relatively slow availability of the P_2O_5. However, it is mainly used as a raw material for the manufacture of phosphoric acid, superphosphate, phosphorus, and phosphorus compounds.

PROCESSING.[1] In Florida, both hard and pebble rock phosphate are mined. Hard rock phosphate occurs as nodules and boulders in irregular pockets, but its exploitation is limited. The more extensive and cheaply mined pebble deposits occur with an average overburden of 6 m, and their phosphatic value is too low for economical processing. The pebble deposits themselves, called the *matrix*, are from 3 to 9 m thick. This matrix is composed of clay slimes, silica sand, and phosphate pebble. Pebble sizes range from 1 to 27 mm. The overburden is removed and dumped into a previously mined-out cut. Electrically operated draglines remove the matrix and drop it into an excavated area. Hydraulic guns break down the mud in the matrix and wash it into the pump suction, where it is transported through pipes by large sand pumps to the beneficiation plant (Fig. 1.1).

In Tennessee four types of phosphate rock are found, nodular, blue, white, and brown. Only the latter is mined at present, using open-pit, dry methods. The overburden varies greatly and has an average depth of from 1.8 to 2.4 m. Although originally deposited in horizontal strata, in the large western fields layers of phosphate rock have been severely folded, faulted, and elevated by crustal deformations and resemble fissure veins. The rock may contain approximately 75% bone phosphate of lime[2] but, because of admixture with wall material, it usually averages nearer 70% BPL (Table 1.4). Because of its rather soft structure, the rock has a moisture content of 4 to 6%. It is generally mined by underground methods. Western phosphate rock contains anywhere from 50 to 200 g of uranium per metric ton of rock. The complicated and costly recovery process now in use extracts uranium from phosphate rock via wet-process phosphoric acid, and the uranium goes into solution upon treatment with sulfuric acid. After filtration, the bulk of the uranium is found in the acid filtrate. Some is recovered, presumably by an ion-exchange technique. Fluorine and vanadium are also valuable by-products from phosphate rock.

In the Florida pebble district, initially only coarse phosphate rock was recovered, which had a high BPL, whereas the fines, with a much lower BPL, representing about equal tonnage, were wasted. In the 1920s, experimental work was started to develop a froth-flotation process which would increase the BPL of the fines or raw matrix to at least 66 or 68% from about 40% or less. This procedure is frequently spoken of as *beneficiation*, and one of the successful processes currently employed is illustrated in Fig. 16.1. Such upgrading operations are of far-reaching and increasing importance, as easily mined or better-grade deposits of phosphate rock, and other minerals, are becoming exhausted. These operations not only produce a higher grade of product, but allow larger amounts to be recovered, beneficiated, and used, even in the case of such a low-priced product as phosphate rock.

The matrix from the Florida phosphate pebble deposits is received at the beneficiation plant as a slurry. There it is washed to remove clays and fine particles. The +16 mesh pebble product is drained and sent to storage bins as a marketable product. The −16 mesh material is deslimed in hydrocyclones to remove the −150 mesh material, which is predominately

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[1a] Slack (ed.), *Phosphoric Acid*, Dekker, 1968; ECT, 2d ed., Vol. 15, 1968, p. 232; Crerar, H_3PO_4 Route Cuts Costs, *Chem. Eng.* **80** (10) 62 (1973).

Table 1.4 Phosphate Rock Sold or Used by Producers in the United States, by Grade and State in 1981 (thousand metric tons and thousand dollars)

	Florida and North Carolina			Tennessee		
Grade (% BPL* content)	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	79	17	1,274	698	170	5,732
60 to 66	5,553	1,585	171,443	681	187	11,669
66 to 70	25,727	7,962	639,586	—	—	—
70 to 72	2,984	967	90,303	—	—	—
72 to 74	2,761	929	102,219	—	—	—
Plus 74	1,371	477	60,015	—	—	—
Total†	38,475	11,938	1,064,939	1379	357	17,401

	Western States			Total United States		
	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	1783	445	16,999	2,560	632	24,005
60 to 66	907	250	14,243	7,140	2,022	197,354
66 to 70	1614	506	46,353	27,341	8,468	555,939
70 to 72	1368	443	52,599	4,353	1,410	142,902
72 to 74	—	—	—	2,761	929	102,219
Plus 74	—	—	—	1,371	477	60,015
Total†	5672	1644	130,194	45,526	13,939	1,212,433

*1.0% BPL (bone phosphate of lime or tricalcium phosphate) = 0.458% P_2O_5.
†Data may not add to totals shown because of independent rounding.
SOURCE: *Minerals Yearbook, 1981*, U.S. Dept. of Interior, 1982, p. 654.

The waste contains only a small percentage of phosphate ore and is run to a tailing area. Figure 1.2 shows a materials balance flowsheet for the mining and beneficiation of phosphate rock; on average about 4.7 t of product are made per work hour.

SLIME WASTE.[3] The slime wastes from the desliming hydrocyclones occupy about 32 times the initial volume of the rock because of the process water added to separate the matrix from the slime. This volume of waste material plus the tailings from the matrix concentration procedures are impounded by earthen dams. These impounded waste areas (often as large as 320 ha) serve to act as holding tanks to dewater the waste, as reservoirs to minimize water discharge from the mining area, to capture and hold rainwater, and to ultimately densify and store the waste clay. It requires many years to fulfill the design storage level of 25% solids inside the dam.

The phosphate industry currently disposes of 60 percent of these wastes below ground level and is reclaiming mined out land. The holding ponds are not environmentally esthetic and there has been a demand that all these wastes be disposed of below ground level. Because the volume of waste products from mining and beneficiation of phosphate rock exceeds the mined-out volume, this is extremely difficult. Over the past 20 years millions of dollars in

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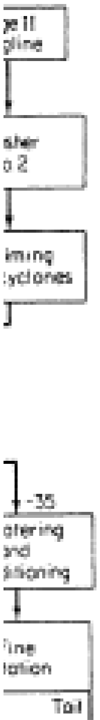
[3] Lawver, The Clay Waste Problem (private communication from International Minerals and Chemical Corp.).



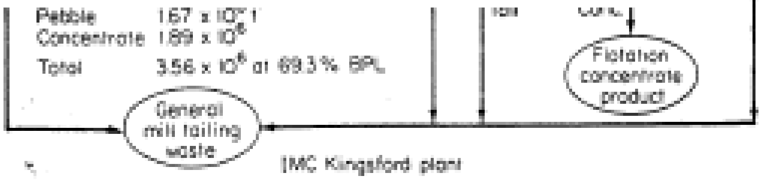


Fig. 1.1. Florida phosphate rock beneficiation flowsheet. *(International Minerals and Chemical Corp.)*

clays. The −16 to 150 mesh feed is sized on inclined stationary screens. The −16 to 24 mesh fraction is treated as shown in Fig. 16.1 to produce the spiral concentrate product. This is a skin flotation operation using Humphrey spirals.

The froth flotation circuit is separated into fine and coarse floats at 35 mesh because this allows for greater overall recovery of the coarser fractions. Flotation reagents such as saponified fatty acids (soap skimmings) are added. The coarse concentrates are further treated with another flotation step using an amine flotation agent. The final concentrate has a 72 to 78% BPL range.

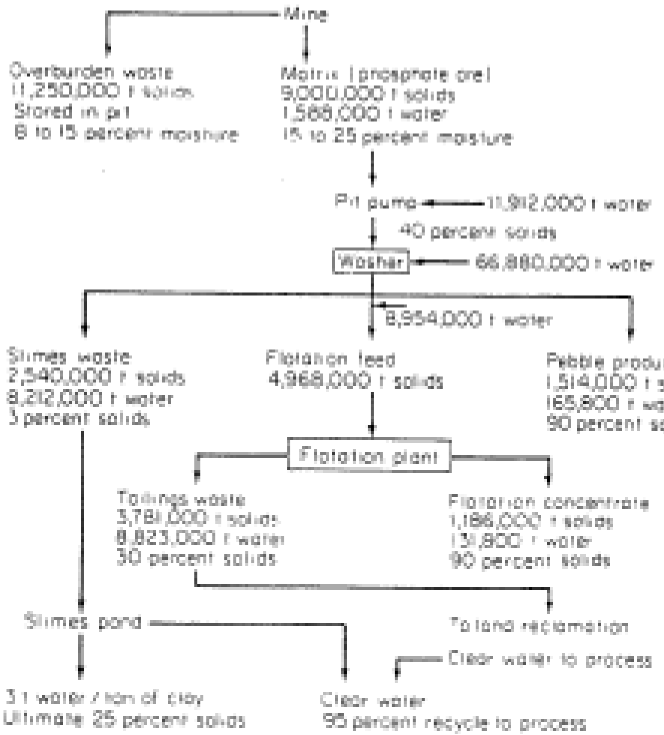


Fig. 1.2 Material balance flowsheet for Florida phosphate rock. Material flow in metric tons per year. *(International Minerals and Chemical Corp.)*

research have been spent in an effort to improve the current waste handling methods. To date no proven large-scale system has been developed that is better, either environmentally or economically.

SUPERPHOSPHATES[4]

The acidulation of phosphate rock to produce superphosphate has been the most important method of making phosphate available for fertilizer purposes for nearly a century. See Chap. 26 on agrichemicals. The reactions are

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow \underset{\text{Monocalcium phosphate}}{CaH_4(PO_4)_2} + \underset{\text{Gypsum}}{2(CaSO_4 \cdot 2H_2O)}$$

$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF\uparrow$$

$$4HF + SiO_2 \rightarrow SiF_4\uparrow + 2H_2O$$

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

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[4] ECT, 3d ed., vol. 10, pp. 71–76, 1980.

The following is a more probable expression of the main reaction:

$$\underset{\substack{\text{Phosphate rock or}\\ \text{fluorapatite}}}{CaF_2 \cdot 3Ca_3(PO_4)_2} + \underset{53\text{–}57°\text{Bé}}{7H_2SO_4} + 3H_2O \rightarrow \underset{\substack{\text{Monocalcium}\\ \text{phosphate}}}{3CaH_4(PO_4)_2 \cdot H_2O} + 2HF\uparrow + \underset{\text{Anhydrite}}{7CaSO_4}$$

The hydrofluoric acid reacts as shown above, forming fluosilicic acid, but with incomplete removal of fluorine. An excess of sulfuric acid is consumed by such impurities in the phosphate rock as $CaCO_3$, Fe_2O_3, Al_2O_3, and CaF_2. The product increases in weight over the 70 to 75 BPL phosphate rock used, as much as 70 percent resulting in a superphosphate with 16 to 20% available P_2O_5. The manufacture of superphosphate involves four steps: (1) preparation of phosphate rock, (2) mixing with acid, (3) curing and drying of the original slurry by completion of the reactions, and (4) excavation, milling, and bagging of the finished product. Although newer plants use continuous processes, some plants still conduct these operations stepwise. All plants first pulverize the rock. With modern pulverizing and air-separation equipment, most rock is ground to an average fineness of 70 to 80 percent through a 200-mesh screen, with the following benefits: (1) the reaction rate is faster; (2) more efficient use is made of the sulfuric acid and consequently less acid is needed; and (3) a higher grade of product in better condition is obtained.

NORMAL SUPERPHOSPHATE.[5] The continuous process is depicted by Fig. 1.3, where ground phosphate rock (90 percent minus 100 mesh) is fed by a weigh feeder into a double-conical mixer (TVA), where it is thoroughly mixed with metered quantities of sulfuric acid. The sulfuric acid is diluted with water in the cone to a concentration of 51°Bé, the heat of dilution serves to heat the sulfuric acid to proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The rate of water addition and acid concentration may be varied to control product moisture. The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock. The fresh superphosphate drops onto the den conveyor, which has a very low travel speed to allow about 1 h for solidifying before reaching the disintegrator. The disintegrator slices the solid mass of crude product so that it may be conveyed to pile storage for "curing," or completion of the chemical reaction, which takes 4 to 6 weeks to reach a P_2O_5 availability acceptable for plant food. The continuous den is enclosed so that fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere. The scrubber water is discharged to a limestone bed to neutralize the acid.

Nitric and mixed acid acidulation of phosphate rock.[6] Europe probably first used nitric and mixed acid acidulation of phosphate rock. The substitution of nitric for sulfuric acid is desirable, since nitrogen has an essential value as plant food and can be resold at its purchase price. Simple acidulation of phosphate rock with nitric acid produces a hygroscopic superphosphate, since it contains calcium nitrate. The TVA and others have studied and recommended commercial processes. In one, the phosphate rock is extracted by mixed nitric and

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[5] Young and Davis, *The Role of Phosphorus in Agriculture*, chap. 7, ASA-CSSA-SSSA, Madison, Wisc., 1980.

[6] Davis, Meline and Graham, TVA Mixed Acid Nitric Phosphate Process, *Chem. Eng. Prog.*, **64** (5) 75 (1968); Jorquera, Nitric vs. Sulfuric Acidulation of Phosphatic Rock, *Chem. Eng. Prog.*, 64 (5) 83 (1968).

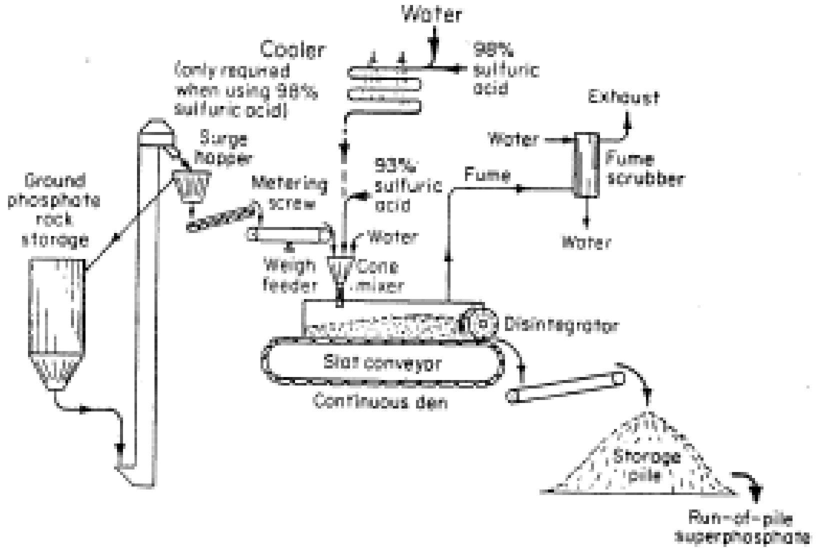

Fig. 1.3. Flowchart for the manufacture of superphosphate. *(Tennessee Valley Authority.)*

sulfuric acids, followed by ammoniation, drying, and the addition of potassium chloride (optional). Another features mixed nitric and phosphoric acidulation, followed by the conventional steps, and others use nitric acid alone for acidulation. These processes, as well as conditioning against moisture absorption as practiced for ammonium nitrate, have led to an extension of the acidulation with nitric acid. Nitrophosphate is also gaining in Europe. Phosphate rock is decomposed with nitric acid plus a small amount of phosphoric acid. The resulting slurry is ammoniated and carbonated and, if desired, combined with potassium salts and spray-dried to yield a uniform pelletized product.

TRIPLE SUPERPHOSPHATE. This material is a much more concentrated fertilizer than ordinary superphosphate, containing from 45 to 46% of available P_2O_5, or nearly three times the amount in regular superphosphate. Triple superphosphate is made by the action of phosphoric acid on phosphate rock; no diluent calcium sulfate is formed.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF\uparrow$$

The TVA continuous granular triple superphosphate production process is illust
Fig. 1.4. Pulverized phosphate rock is mixed with phosphoric acid in a two-st
The resultant slurry is sprayed into the granulator. The granulator contai
from the process. The product from the granulator is dried, screened,
and cooled again. The final product is conveyed to bulk storage whe
4 to 6 weeks during which time a further reaction of acid and roc
the availability of P_2O_5 as plant food. The exhaust gases from the g
scrubbed with water to remove silicofluorides.

Nongranular superphosphate is also available and is prepared using a cone-mixe
veyor belt similar to that used to prepare normal (ordinary) superphosphate. As the
is only 14 to 20 min as compared with 40 to 50 min for normal superphosphate, a si
cupped conveyor belt can be used instead of the slat-type den.

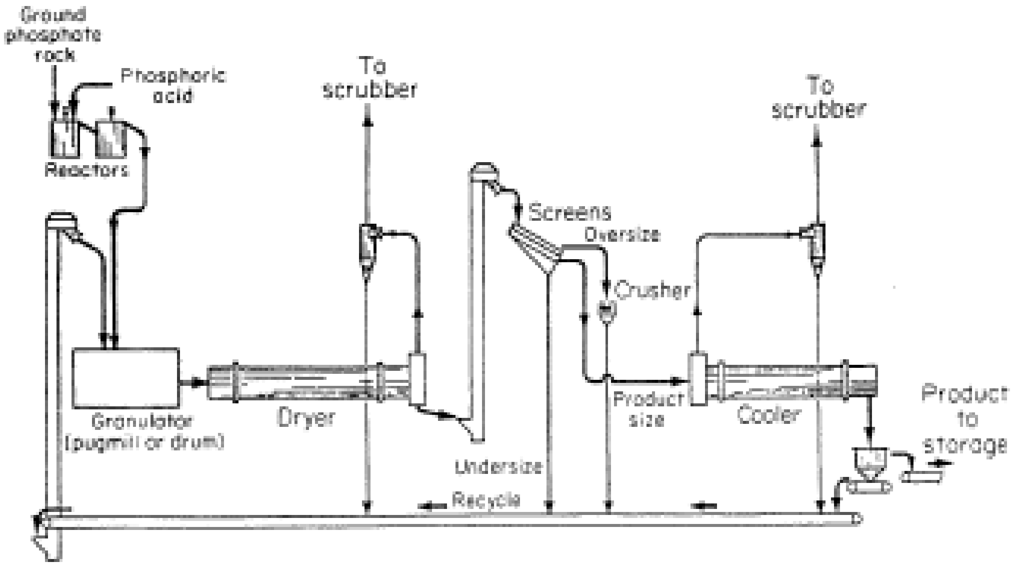

Fig. 1.4. Flowchart illustrating a triple superphosphate process. *(Tennessee Valley Authority.)*

WET-PROCESS PHOSPHORIC ACID

USES AND ECONOMICS. Rapid expansion in the manufacture of wet-process phosphoric acid has resulted from the increased demand for high-analysis fertilizer, triple superphosphate, and ammonium and dicalcium phosphates.

Much earlier, most of the orthophosphoric acid produced was prepared by the action of dilute sulfuric acid, 50°Bé, on ground phosphate rock or bones. This method was supplanted by the Dorr[7] strong-acid process, which produced a strong and economical acid. The equipment must be lined with lead, stainless steel, Hastelloy C, or acid-proof brick, and sufficient time provided in the various agitators for the reaction to go to completion. The temperature in the digester must be kept low enough to ensure the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), and not anhydrite. If the latter is formed, it subsequently hydrates and causes plugging of pipes. Acid made by this process is used almost entirely in fertilizer production, where impurities are unimportant, or after some purification for various sodium phosphates. Pure acid is obtained from elemental phosphorus by the electric-furnace process.

New methods are being developed to purify wet-process acid by solvent extraction using a mixture of di-isopropyl ether and tributyl phosphate as solvent.[8] This process produces pure enough acid to be used for pharmaceuticals and cattle feed.

The major end uses of phosphoric acid are fertilizer, 85 percent; detergent materials, 5 percent; animal feed, 5 percent; and food, beverages, and dentifrices, 5 percent. Excluding fertilizers, the main outlet for phosphorus derivatives has been in soap and detergent manufacture as various sodium phosphates. Because of their ability to precipitate or sequester lime and magnesia, to emulsify or disperse solids in the detergent solution, and to augment the

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[7] See CPI 2, p. 353 for flowchart.

[8] Davister and Peterbroeck, The Prayon Process For Wet Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).

inherent detergent properties of soap and synthetic surfactive agents, these salts have been much used as *soap builders* or *detergent synergists*. Recent concerns about water pollution and algae growth due to the phosphorus content of wastewater have greatly decreased the amount of phosphates in detergents

P_2O_5 production in 1982 was a little over 9×10^6 t of which 8.5×10^6 t was wet-process acid and the remainder "furnace" acid.[9] Exports accounted for almost 10^6 t.

MANUFACTURE. The chief process[10] for producing wet-process phosphoric acid is by the use of sulfuric acid as shown in Figs. 16.5 and 16.6. The essential reactions are:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2HF\uparrow + 6H_3PO_4$$

or, more simply expressed,

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + \underset{\text{Gypsum}}{3CaSO_4 \cdot 2H_2O}$$

Raw phosphate rock, or occasionally calcined rock if a clear, green acid is desired, is digested with sulfuric acid. The retention time ranges from 1.5 to 12 h, and conditions are controlled to produce gypsum crystals that are readily filterable. The reaction is cooled using a vacuum (flash) cooler. The reaction mixture is filtered using a Bird-Prayon tilting-pan filter shown in Fig. 1.6. This process produces 28 to 32% acid which then must be concentrated for most uses.

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[9] Key Chemicals, Phosphoric Acid, *Chem. Eng. News*, 60 (4) 20 (1982).

[10] Fertilizer Needs Spur Wet-Process Phosphoric, *Chem. Eng. News* 45 (12) 54 (1967).

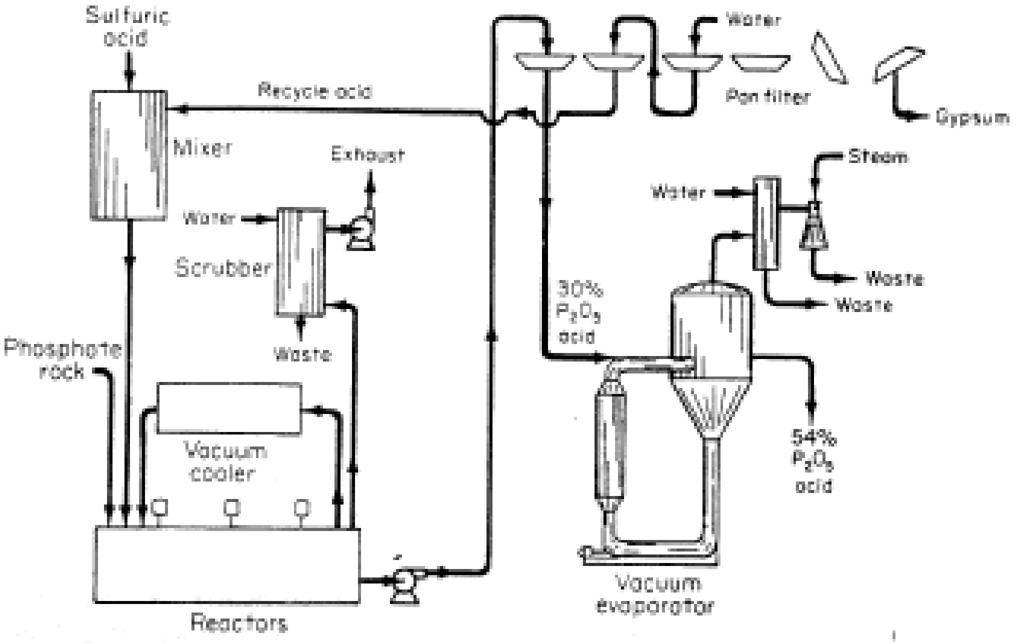

Fig. 1.5. Wet-process phosphoric acid manufacture, using Bird-Prayon tilting-pan washing filters. The overall efficiency is 94 to 98 percent producing an acid of 30 to 32% P_2O_5 concentration.

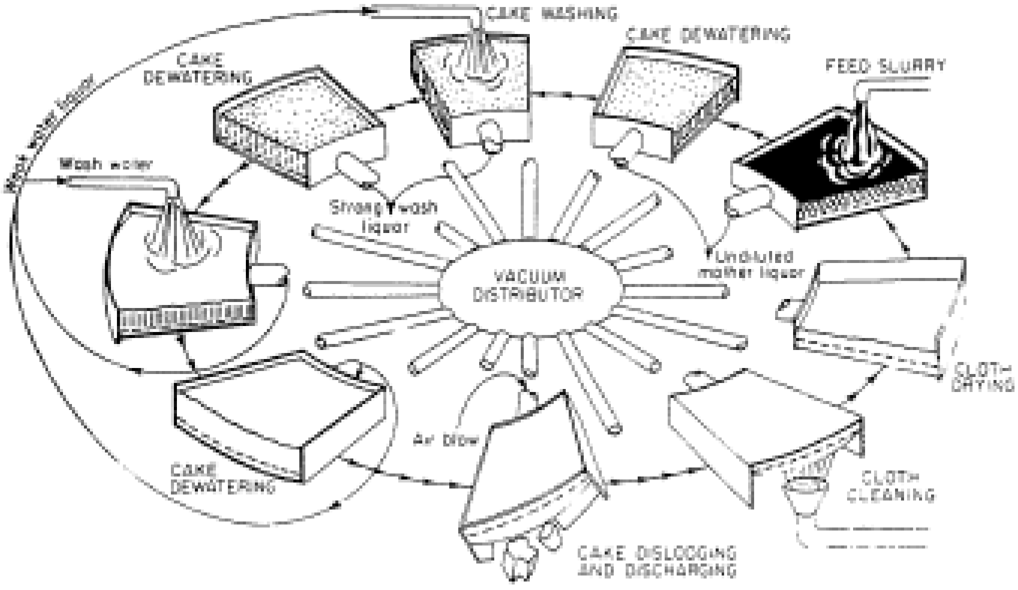

Fig. 1.6. The Bird-Prayon tilting-pan filter for phosphoric acid manufacture. The feed continuously enters the pans, which are connected to the vacuum source. The circular frame supporting the pans rotates so that each pan is moved successively under the desired number of washes. After the final wash liquor has completely drained off, the vacuum is released and the pan is inverted a full 180°. The cake drops off, its removal being ensured by a reverse blast of air through the filter medium, which is then scoured fresh and clean by a high-pressure shower while the pan is still inverted. The filter-medium and drainage area are then purged by vacuum, and the pan returned to the feed position. *(Bird Machine Co.)*

Another process is the Swenson isothermal phosphoric acid reactor which uses a single vessel vacuum crystallizer. The advantages claimed for this process are: reduced capital cost, utilities consumption, and maintenance costs and high operating efficiency with improved P_2O_5 recovery.[11] Recently the idea of producing the calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) instead of the usual dihydrate has been tried.[12] Its disadvantage is that the hemihydrate is unstable and could freeze in the pipes, but the big advantage is that it produces 42 to 50% acid directly without a costly evaporation step as is necessary when the dihydrate is produced. Merchant grade acid is 54%.

Almost all U.S. producers are using the dihydrate process. In 1981 there was only one producer using the hemihydrate process, but as energy costs continue to rise it is expected that more plants will use the hemihydrate process. The potential energy saving is 2.3 to 3.5 GJ/t.

The Haifa process is another method of producing wet-process acid. It uses (1) hydrochloric acid to acidulate (in slight excess to prevent formation of monocalcium phosphate); (2) an organic solvent (C_3 or C_4 alcohols) to extract the phosphoric acid; (3) water to strip out the phosphoric acid (with a small amount of solvent and hydrochloric acid); concentration to

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[11] Olivier, Wet Process Acid Production, *Chem. Eng. Prog.* 74 (11) 55 (1978); ECT, 3d ed., vol. 17, 1982, pp. 426–539.

[12] An Energy Saving Route to Phosphoric Acid, *Chem Week* 128 (2) 45 (1981); Davis, Cogeneration's Place in a Modern Facility, *Chem. Eng. Prog.* 78 (3) 46 (1982); Parkinson, Phosphoric Acid Process Proven for Large-Capacity Plants, *Chem. Eng.* 89 (18) 66 (1982).

remove the small amounts of solvent and hydrochloric acid and to yield a high-grade product. This process was developed in Israel and has been applied in Japan and the United States.[13] The recent dramatic increase in the price of sulfur (from $70 to $140 per metric ton between 1979 and 1981) has renewed interest in the nitric acid process, both for phosphoric acid and superphosphate.

PURIFICATION.[14] Crude wet-process acid is often black and contains dissolved metals and fluorine, and dissolved and colloidal organic compounds. Suspended solid impurities are usually removed by settling. Solvent extraction or solvent precipitation is used to remove the dissolved impurities. Solvent extraction uses a partially miscible solvent, such as *n*-butanol, isobutanol, or *n*-heptanol. The phosphoric acid is extracted, and the impurities are left behind. Back-extraction with water recovers the purified phosphoric acid. Solvent precipitation uses a completely miscible solvent plus alkalis or ammonia to precipitate the impurities as phosphate salts. After filtration, the solvent is separated by distillation and recycled

URANIUM RECOVERY.[15] Uranium is present in all U.S. phosphate rocks. Florida rock contains the most, and rock from western states contains the least. It is present as a trace constituent, but because of its high value, it is becoming important to recover it. The methods usually used are solvent extraction of wet-process acid with octyl pyrophosphoric acid (OPPA) in kerosene, extraction with a mixture of tri-N-octyl phosphine oxide and di-2-ethyl-hexyl phosphoric acid (TOPO-D_2EHPA) or use of TOPO-D_2EHPA combined with octylphenyl phosphoric acid (OPAP). The energy value of the uranium extracted, which is converted to yellow cake, U_3O_8, is ten times greater than the energy required to produce it. This could make the phosphate industry a net producer of energy.

In 1981 1.8×10^6 kg of yellow cake was recovered in the United States. This constituted about 10 to 15 percent of the U.S. demand. More than half the demand is potentially recoverable as a result of phosphoric acid production.

ELECTRIC-FURNACE PHOSPHORUS AND PHOSPHORIC ACID

This element was first produced on a small commercial scale by treating calcined bone with sulfuric acid, filtering off the phosphoric acid, and evaporating it to sp gr 1.45. This was mixed with charcoal or coke, again heated, the water evaporated off, then calcined at white heat in retorts. The phosphorus was thus distilled off, collected under water, and purified by redistillation. The production of phosphorus today still depends on volatilization of the element from its compounds under reducing conditions. During the past decades, the method has

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[13] ECT, 3d ed., vol. 10, 1980, p. 69.

[14] McCullough, Phosphoric Acid Purification, *Chem. Eng.* 83 (26) 101 (1976); Bergdorf and Fischer, Extractive Phosphoric Acid Purification, *Chem. Eng. Prog.* 74 (11) 41 (1978); Davister and Peeterbroeck, The Prayon Process For Wet-Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).

[15] Kouloheris, Uranium from Phosphoric Acid, *Chem. Eng.* 87 (16) 82 (1980); Berry, Recovery of Uranium from Phosphoric Acid, *Chem. Eng. Prog.* 77 (2) 76 (1981). Both articles have excellent flow sheets.

changed chiefly in details and size of production. Elementary phosphorus is manufactured on a large scale as a heavy chemical and shipped in tank cars from the point of initial manufacture, where raw materials are cheap, to distant plants for conversion to phosphoric acid, phosphates, and other compounds.

REACTIONS. Phosphorus is produced by the electric-furnace method (Fig. 1.7). The following reaction is considered to take place, the raw materials being phosphate rock, silica, and coke:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 9SiO_2 + 15C \rightarrow CaF_2 + 6P + 15CO$$

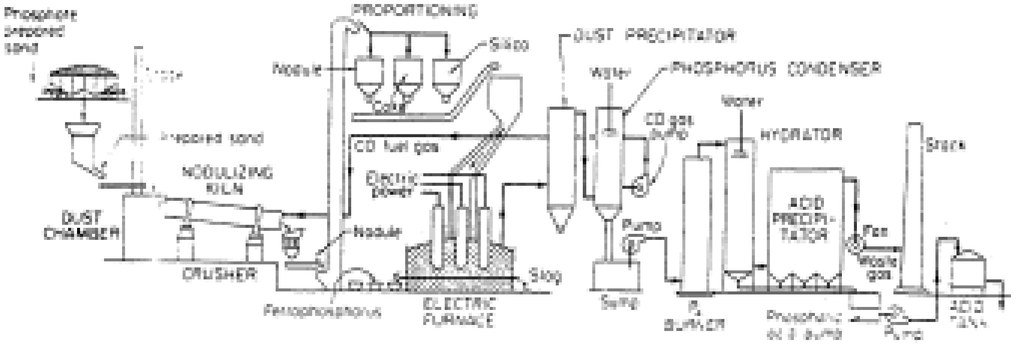
or, more simply expressed,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \qquad \Delta H = -3055 \text{ kJ}$$

The silica is an essential raw material which serves as an acid and a flux. About 20 percent of the fluorine present in the phosphate rock is converted to SiF_4 and volatilized. In the presence of water vapor this reacts to give SiO_2 and H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The fluorine is not recovered by manufacturers of phosphorus, but the CO is employed as a fuel in preparing the furnace charge. The slag tapped from the furnace is sold as ballast, or aggregate or fill. Ferrophosphorus is tapped as necessary, its quantity being dependent on the amount of iron originally in the burden or added to it. The phosphorus is employed usually as an intermediate product, being shipped to consumption centers and there burned or oxi-



In order to produce 1 t of 85% H_3PO_4, the following materials and utilities are needed:

Phosphate rock (35.6% P_2O_5)	1000 kg	Iron	(depends on ferrophosphorus requirements)
Silica rock	320 kg	Electricity	13,840 MJ
Coke	377 kg	Direct labor (est.)	0.5–1 work-h

Fig. 1.7. Phosphorus production flowchart. In most cases, the hot phosphorus is pumped into an insulated tank car and shipped to the oxidizing plant where it is made into phosphoric acid and various phosphates.

dized to P_2O_5, which is dissolved in water to form acids or other compounds:

$$\text{Phosphorus pentoxide: } 4P + 5O_2 \rightarrow 2P_2O_5 \qquad \Delta H = -3015 \text{ kJ}$$
$$\text{Orthophosphoric acid: } P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \qquad \Delta H = -188 \text{ kJ}$$

The foregoing reactions for ordinary or orthophosphoric acid are commercialized in the following sequences as exemplified by Figs. 1.5 and 1.6 for wet-process acid in comparison with Fig. 1.7 for phosphorus and furnace acid made therefrom.

Wet-Process Phosphoric Acid	Electric-Furnace Phosphorus and Acid
Phosphate rock is finely ground and prepulped in the mixing tank with cooled recycled H_3PO_4 from the slurry cooler.	Phosphate rock ground and sized.
Overflow from the mix tank is reacted with H_2SO_4 and recycled H_3PO_4 in an agitated digester system, forming gypsum crystals and H_3PO_4.	Rock and sand mixed with coke, sintered, and introduced into electric furnace.
Bulk of slurry is recycled through slurry cooler.	Mix heated and reduced at an elevated temperature.
Rest of slurry is conducted through the filter feed tank to the cells of the rotary Bird-Prayon tilting-pan filtration unit.	Slag and ferrophosphorus run off separately.
In the progressive and tilting pans of this filter, the H_3PO_4 is separated from the gypsum, using three-stage countercurrent washing	Phosphorus vapor and CO drawn off, phosphorus condensed.
Gypsum is automatically dumped.	Phosphorus transported in tank cars to consuming centers.
Off-gases are scrubbed to remove fluorine before venting.	Phosphorus melted and sprayed into stainless-steel oxidation tower.
H_3PO_4 can be used directly (28–32% P_2O_5) or concentrated	Phosphorus oxidized to P_2O_5.
	P_2O_5 cooled and hydrated in stainless-steel hydrator or tower against water or dilute H_3PO_4.
	H_3PO_4 mist-precipitated in electrostatic precipitator or a Brink Mist Eliminator.
	H_3PO_4 filtered and purified.

The electric-furnace[16] process was first employed commercially in 1920. This process permits the use of lower-grade rock than the wet-process phosphoric acid process, since the slag carries off impurities. Indeed, lower grades are frequently preferred because of the better CaO/SiO_2 balance for slag formation. The principal requirement is cheap electricity.

The phosphate rock must be charged in lump form or as +8-mesh (Fig. 1.1). Fine material tends to block the exit of the phosphorous vapors and to cause bridging and uneven descent of the furnace charge, resulting in puffs and the carrying over of excessive quantities of dust. Phosphate lumps may be prepared in the following ways: (1) pelletizing by tumbling or extrusion, (2) agglomeration by nodulizing at high temperatures, (3) sintering a mixture of phosphate fines and coke, and (4) briqueting, with the addition of a suitable binder. After agglomeration, coke breeze and siliceous flux (gravel) are added, and the materials are charged to the electric furnace. Iron slugs are added to the charge if more ferrophosphorus is desired. A flowchart with the quantities required is shown in Fig. 16.7. The bottom of the furnace is composed of carbon blocks, and this lining extends up the wall to a point well

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[16] Curtis, The Manufacture of Phosphoric Acid by the Electric Furnace Method, *Trans. AIChE* 31 278 (1935); Mantell, *Electrochemical Engineering*, 4th ed., McGraw-Hill, New York, 1960, pp. 523–532 (data and diagram); Highett and Striplin, Elemental Phosphorus in Fertilizer Manufacture, *Chem. Eng. Prog.* 63 (5) 85 (1967); Bryant, Holloway and Silber, Phosphorus Plant Design, *Ind. Eng. Chem.* 62 (4) 8 (1970).

above the slag pool. From this point, a high-grade firebrick lining is used. A domelike steel top with a cast refractory lining caps the furnace. Openings for the electrodes and for introducing raw materials are included here. The electrodes are threaded so as to facilitate replacement as the carbon is consumed. The gases and phosphorus vapor are removed at one end of the furnace. The calcium-rich slag from the furnace is usually tapped periodically and crushed for use in the manufacture of glass, for the liming of soil, and as a roadbed ballast. The ferrophosphorus is tapped separately, or it runs out with the slag when it is separated and sold as a phosphorus additive for steel. In this process 80 percent of the fluorine stays with the slag. The small portion that leaves with the gas is absorbed in the water used in condensing the phosphorus.

Pure, strong phosphoric acid is manufactured from elemental phosphorus by oxidation and hydration. See Fig. 1.7 and preceding reactions and sequences for manufacture. The oxidation tower, or chamber, is constructed of acid-resistant brick or stainless steel.[17] Phosphoric acid runs down the walls and absorbs about 75 percent of the P_2O_5 and also heat. This acid is *cooled*, some drawn off, and some recirculated. The remaining 25 percent is passed as a mist to a Cottrell or Brink mist eliminator for collection. Some modern plants produce superphosphoric acid, 76% P_2O_5, equivalent to 105% orthophosphoric acid, with which higher-percentage plant foods can be made, e.g., ammonium polyphosphate, 54% superphosphate, and 10-34-0 liquid fertilizer. Other processing plants produce 75 to 85% orthophosphoric acid, depending on the process for which it is to be used.

Phosphoric acid of high P_2O_5 content consists of mixtures of various phosphates with a certain distribution of chain lengths. Individual molecular species are difficult to prepare. Pyrophosphoric acid ($H_4P_2O_7$) can be obtained only through a slow crystallization process, and above its melting point it rapidly reverts to a distribution of various chain phosphates. If P_2O_5 is carefully dissolved in cool water, most of the phosphate will be in the form of tetrametaphosphate rings.

PHOSPHATES

SODIUM PHOSPHATES. The various sodium phosphates represent the largest tonnage of chemicals based on pure phosphoric acid obtained mostly from elemental phosphorus. Phosphates are phosphorus compounds in which the anions have each atom of phosphorus surrounded by four oxygen atoms placed at the corners of a tetrahedron. Chains, rings, and branched polymers result from the sharing of oxygen atoms by tetrahedra. *Orthophosphates* are based on the simple PO_4 tetrahedron as a monomeric unit and include monosodium phosphate (MSP) (NaH_2PO_4); disodium phosphate (DSP) (Na_2HPO_4); and trisodium phosphate (TSP) ($Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$). The first two sodium salts are made from phosphoric acid and soda ash reacted in the proper molecular proportions; the solution is purified if necessary, evaporated, dried, and milled. TSP is also made from phosphoric acid and soda ash, but caustic soda is necessary to substitute the third hydrogen of the phosphoric acid. These salts are employed in water treatment, baking powder (MSP), fireproofing, detergents, cleaners, and photography (TSP). *Condensed or molecularly dehydrated* phosphoric acids and salts

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[17] Brink, New Fiber Mist Eliminator, *Chem. Eng.* 66 183 (1959); Brink, in chap. 15B, *Gas Purification Processes for Air Pollution Control*, Nonhebel (ed.), Newnes-Butterworths, London, 1972; see Perry, pp. 18-82 to 18-93, for mist collection equipment.

have a H_2O/P_2O_5 molar ratio of less than 3 and greater than 1 and have the single chain unit P-O-P. The best known are the *polyphosphates:* pyrophosphates ($M_4P_2O_7$) and tripolyphosphates ($M_5P_3O_{10}$). When any of the condensed phosphoric acids are dissolved in water, hydrolysis to orthophosphoric acid takes place. Their salts are represented by the widely used sodium tripolyphosphate and tetrasodium and tetrapotassium pyrophosphates.

To produce sodium tripolyphosphate (Fig. 1.8), a definite temperature control is necessary. When MSP and DSP in correct proportions, or equivalent mixtures of other phosphates, are heated for a substantial time between 300 and 500°C and slowly cooled, the product is practically all in the form of the tripolyphosphate.

Figure 16.8 depicts the following coordinated sequences commercializing the reaction:

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O$$

Soda ash and ±75% phosphoric acid are reacted in the mix tank.

The orthophosphates are dried either in a rotary or spray dryer.

The sodium tripolyphosphate is molecularly dehydrated in a gas-fired calciner.

The tripolyphosphate is annealed, chilled, and stabilized in a continuous rotary tempering unit.

The product is milled, stored, and bagged.

Certain equipment modifications have been used, such as addition of an adjustment mixer following the reactor mix tank and a spray tower for drying of the orthophosphate, together with a long, continuous rotary to carry out the dehydrating (calcining), annealing, stabilizing, and cooling in one unit.

PYROPHOSPHATES. Tetrasodium pyrophosphate (TSPP) ($Na_4P_2O_7$), is used as a water softener and as a soap and detergent builder. It is manufactured by reacting phosphoric acid and

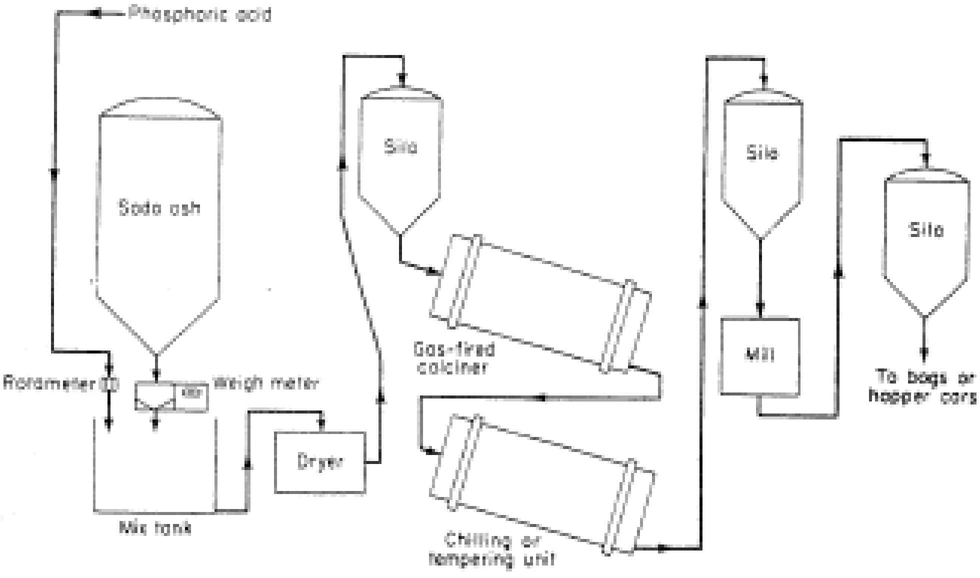


Fig. 1.8. Diagram of a plant for the manufacture of crystalline sodium polyphosphate. *(Thomas L. Hart and John R. VanWazen.)*

soda ash to yield a DSP solution, which may be dried to give anhydrous Na_2HPO_4 or crystallized to give $Na_2HPO_4 \cdot 2H_2O$ or $Na_2HPO_4 \cdot 7H_2O$. These compounds are calcined at a high temperature in an oil- or gas-fired rotary kiln to yield TSPP in a plant such as that shown in Fig. 1.8. The reactions may be written:

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$
$$2Na_2HPO_4 \cdot 2H_2O \rightarrow Na_4P_2O_7 + 5H_2O$$

A nonhygroscopic sodium acid pyrophosphate is used extensively as a chemical leavening agent in making doughnuts, cakes, and packaged biscuit doughs. It is manufactured by partially dehydrating monosodium acid orthophosphate at a temperature of 160°C over the course of 6 to 12 h.

$$2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$$

CALCIUM PHOSPHATES. Monobasic calcium phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] is manufactured by crystallization, after evaporation and some cooling of a hot solution of lime and strong furnace phosphoric acid. The crystals are centrifuged, and the highly acidic mother liquor returned for reuse. This acid salt is also made by spray-drying a slurry of the reaction product of lime and phosphoric acid. This product is used for baking powder.

Dibasic Calcium Phosphate. Dibasic calcium phosphate, which is used as a polishing agent in dentrifrices, is manufactured from furnace-grade phosphoric acid and lime.

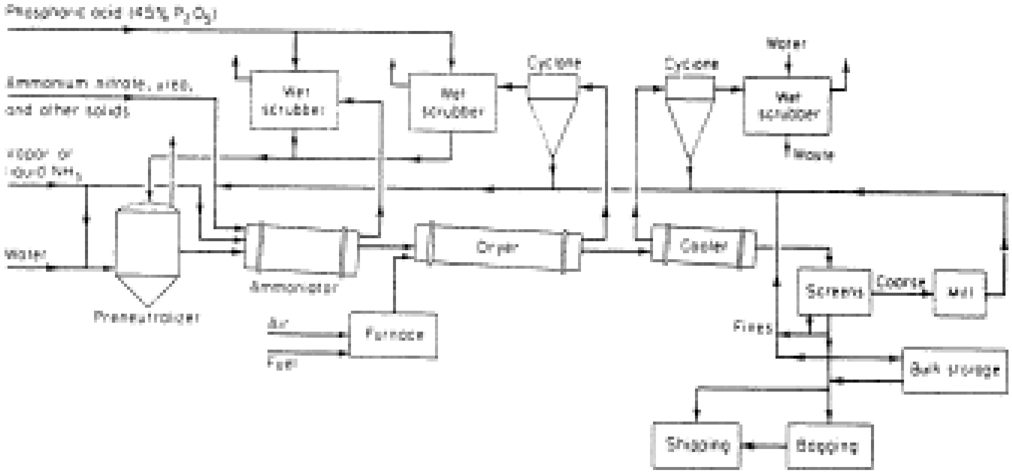
Calcium Metaphosphate. In 1937, the TVA developed a concentrated fertilizer, $Ca(PO_3)_2$, from phosphate rock by the following reaction:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 6P_2O_5 + 2HPO_3 \rightarrow 10Ca(PO_3)_2 + 2HF\uparrow$$

In this process the P_2O_5 contacts the lump rock in a vertical shaft. About 20,000 t of phosphorus equivalent has been manufactured per year. This calcium metaphosphate may be regarded as a dehydrated triple superphosphate made directly from phosphate rock. The calcium metaphosphate is quite insoluble, and it must hydrolyze to become effective:

$$xCa(PO_3)_2 + xH_2O \rightarrow xCa(H_2PO_4)_2$$

GRANULAR HIGH-ANALYSIS FERTILIZER. This is basically a commercial adaptation of the TVA process (Fig. 1.9), designed for the manufacture of diammonium phosphate fertilizer (DAP), either 21-54-0, using furnace phosphoric acid, or 18-46-0, with wet-process phosphoric acid or for any of many grades of granular fertilizer (cf. Chap. 26). The last-mentioned requires the addition of facilities for metering solid raw materials and sulfuric acid to the ammoniator. Vapor or liquid anhydrous ammonia and phosphoric acid (40 to 45% P_2O_5) are metered continuously to an agitated atmospheric tank (preneutralizer) in proportions to maintain a ratio of 1.3 to 1.5 mol of ammonia per mole of phosphoric acid. This ratio is the optimum for maintaining fluidity of the slurry with a minimum quantity of water and a reasonable ammonia loss in the exit vapor from the preneutralizer. In the preneutralizer the heat of reaction elevates the temperature of the mass, evaporating approximately 100 kg of water per metric ton of product. The slurry formed in the preneutralizer flows into a TVA-type ammoniator-granulator at about 120°C, where it is distributed evenly over the bed of



In order to produce 1 t, grade 18-46-0 DAP, the following materials and utilities are needed:

Ammonia	220 kg	Fuel	525 MJ
Phosphoric acid	465 kg	Direct labor	0.5 work-h
Electricity	200 MJ,		

Fig. 1.9. Flowchart for the manufacture of diammonium phosphate (DAP) or high analysis fertilizer. *(Austin Co.)*

solid material and, for most grades, reacts with additional ammonia fed through a distributor pipe below the surface of the bed to complete the reaction with a molar ratio of 2.0 (diammonium phosphate).[18] Dried recycle material from product screening is used to control the moisture, and additional solid raw materials are metered into the ammoniator, depending on the grade of fertilizer in production. The ammoniator combines the functions of chemical reaction, mixing, and formation of the proper size and shape of granular particles. The moist granules leaving the ammoniator fall into an oil- or gas-fired cocurrent rotary dryer, where the moisture content of the material is reduced to about 1%. The dry product is then cooled by a countercurrent flow of air in a rotary cooler and screened, the coarse material being milled and returned to the ammoniator-granulator. In some plants the cooler is eliminated, and hot screening is used. The fines and, if necessary, some of the product are recycled to the ammoniator to control granule formation and size. The product is conveyed to bulk storage or bagged. The exhaust gases from the dryer and cooler pass through cyclones or a wet scrubber for dust recovery. Exhaust gases from the ammoniator are scrubbed with the incoming phosphoric acid, and in some plants the phosphoric acid stream is split, a portion being used to scrub the vapor from the rotary dryer to minimize ammonia loss.

BAKING POWDERS

The baking-powder industry is an important but indirect consumer of phosphate rock
use of leavening agents to produce aeration and lightness in breads and cakes has been [1]
since the time of the Egyptians and was handed down by the Greeks and Romans. Le

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[18] Chopey, DAP: New Plant Ushers in Process Refinements, *Chem. Eng.* 69 (6) 148 (1962); Pipe Reactor Making Diammonium Phosphate, *Chem. Eng.* 85 (41) 81 (1978).

and unleavened bread are both mentioned in the Bible. Some form of yeast or ferment acting on the carbohydrates in flour, giving CO_2 and an alcohol, was the first leavening agent used. Later, baking soda (sodium bicarbonate) was widely employed but, because it often imparted an unpleasant taste or even a yellowish color due to the alkalinity of the Na_2CO_3 formed, the search for better reagents continued. Baking powders consist of a dry mixture of sodium bicarbonate with one or more chemicals capable of completely decomposing it. The principal "baking acids" used are monocalcium phosphate monohydrate, anhydrous monocalcium phosphate, sodium acid pyrophosphate, sodium aluminum sulfate, tartaric acid, and acid tartrates. Monocalcium phosphates are consumed more than all the others, an estimate being more than 30 × 10^6 kg annually in the United States. A filler or drying agent, such as starch or flour, is usually added to the active ingredients to give a better distribution throughout the dough and to act as a diluent or to prevent the reaction until water and heat are applied. The following equations represent the actions of different baking powders:

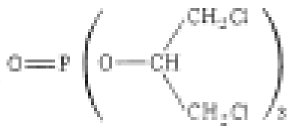
$$Na_2Al_2(SO_4)_4 + 6NaHCO_3 \rightarrow 6CO_2 + 4Na_2SO_4 + 2Al(OH)_3$$
$$3CaH_4(PO_4)_2H_2O + 8NaHCO_3 \rightarrow 8CO_2 + Ca_3(PO_4)_2 + 4Na_2HPO_4 + 11H_2O$$
$$KH_2PO_4 + NaHCO_3 \rightarrow CO_2 + KNaHPO_4 + H_2O$$
$$NaH_2PO_4 + NaHCO_3 \rightarrow CO_2 + Na_2HPO_4 + H_2O$$
$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow 2CO_2 + 2Na_2HPO_4 + H_2O$$
$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + CO_2 + H_2O$$

Baking powders must yield not less than 12% available CO_2, and most powders contain from 26 to 29% $NaHCO_3$ and enough of the acid ingredients to decompose the bicarbonate and yield from 14 to 15% CO_2. The rest, 20 to 40%, consists of corn starch or flour.

FIRE RETARDANT CHEMICALS

In recent years, there has been a great increase in the use of fire retardants both in flameproofing various textiles, polymeric foams, and for combating forest fires.[19] In 1971 the federal government required the use of flame retardant–treated textiles for the production of children's sleepware, carpets, rugs, mattresses, and mattress pads.[20] A flame retardant enables material to resist burning when exposed to a relatively low-energy ignition source such as a cigarette, match, candle, or stove burner.

After 1971 most of the polyester sleepware for children was made from fabrics treated with tris(2,3 dibromopropyl) phosphate, commonly known as Tris, and tris (dichloroisopropyl) phosphate, Fyrol FR-2.



$$O{=}P\left(O{-}CH(CH_2Cl)_2\right)_3$$

Fyrol FR-2

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[19] Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970.

[20] Flammability, *Chem. Eng. News* 56 (17) 22 (1978).

Diethyl N,N-bis (hydroxy) ethylaminomethyl phosphonate (Fyrol 6) is used for the flameproofing of rigid polyurethane foams. For flexible polyurethane foams, Phosgard 2XC20, 2,2-bis (chloromethyl)-1,3 propanediol-[bis(chloroethyl)] phosphate, and Fyrol FR-2 offer excellent flame retardation.

The Consumers Product Safety Commission, acting under the Federal Hazardous Substances Act, banned the use of Tris for children's sleepware in 1977 because some tests had shown that Tris was mutagenic to bacteria, caused kidney cancer in mice and rats, and possibly was carcinogenic to humans. The use of Fyrol FR-2 for this purpose was also adversely affected although this compound had not been shown to be harmful. Large quantities of both compounds are still used for carpets and mattresses.

For combating forest and brush fires, mixtures based on $(NH_4)_2HPO_4$ or $(NH_4)_2SO_4$, thickening agents, coloring matter, and corrosion inhibitors are most commonly used. It is believed that the phosphorus compounds act as catalysts to produce noncombustible gas and char. Furthermore, phosphorus compounds which can yield phosphoric acid from thermal degradation are effective in suppressing glow reactions.[11]

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[11] Lowden et al., *Chemicals for Forest Fire Fighting*, National Fire Protection Association, Boston, Mass. 1963; *User Guide, Phoscheck Fire Retardant*, Monsanto Co., St. Louis, Mo., 1968.

Chapter 5

Soaps and Detergents

Bassam El Ali

5.1 Soap

5.1.1 Introduction

According to an ancient Roman legend, soap got its name from Mount Sapo, where animals were sacrificed. Rain washed a mixture of melted animal fat or tallow and wood ashes down into the clay soil along the

Tiber River. It was found that this clay mixture cleaned the washed clothes with much less effort [1–6].

The term soap is a class name for the sodium and potassium salts of fatty acids. These fatty acids were found in animal fats and in plant oils such as coconut oil, palm oil, olive oil, castor oil, or cottonseed oil [1–6].

5.1.2 History

Records show that ancient Egyptians bathed regularly. The Ebers Papyrus, a medical document, describes the combining of animal and vegetable oils with alkaline salts to form a soap-like material used for treating skin diseases, as well as for washing.

The early Greeks bathed for aesthetic reasons and apparently did not use soap. Instead, they cleaned their bodies with blocks of clay, sand, pumice, and ashes, then anointed themselves with oil, and scraped off the oil and dirt with a metal instrument known as a strigil. They also used oil with ashes. Clothes were washed without soap in streams.

The roman civilization showed a more positive progression in cleanliness than did the early Greeks. As Roman civilization advanced, so did bathing. The first of the famous Roman baths was supplied with water from their aqueducts. The baths were luxurious, and bathing became very popular [1–6].

In Europe, by the 7th century, soap making was an established craft. Soap-maker guilds guarded their trade secrets closely. Vegetable and animal oils were used with ashes of plants along with fragrance. Gradually more varieties of soap became available for shaving and shampooing, as well as bathing and laundering.

Italy, Spain, and France were early centers of soap manufacturing, because of their ready supply of raw materials such as oil from olive trees. The English began making soap during the 12th century. The soap business was so good that in 1622, King James I granted a monopoly to a soap maker for US$100,000 a year. Well into the 19th century, soap was heavily taxed as a luxury item in several countries. When the high tax was removed, soap became available to ordinary people and cleanliness standards improved.

A major step toward large-scale commercial soap making occurred in 1791 when a French chemist, Nicholas Leblanc, patented a process for making soda ash, or sodium carbonate, from common salt. Soda ash in the alkali obtained from ashes combines with fat to form soap. The Leblanc process yielded quantities of good quality, inexpensive soda ash.

Some soap manufacture took place in Venice and Sauona in the 15th century and in Marseilles in the 17th century. By the 18th century, manufacture was widespread throughout Europe and North America and by the 19th century the making of soap had become a major industry [1–6].

TABLE 5.1 Fatty Acid Distribution [1, 6]

Fatty Acid	Coconut	Stripped coconut	Palm kernel	Palm	Tallow
Caprylic ($C_8H_{16}O_2$)	7	1	4		
Capric ($C_{10}H_{20}O_2$)	6	1	5		
Lauric ($C_{12}H_{24}O_2$)	48	55	50		
Myristic ($C_{14}H_{28}O_2$)	19	22	15	2	2.5
Palmitic ($C_{16}H_{32}O_2$)	9	11	7	42	27
Stearic ($C_{18}H_{36}O_2$)	2	2	2	5	20
Oleic ($C_{18}H_{32}O_2$)	8	7	15	41	42
Linoleic ($C_{18}H_{32}O_2$)	1	1	1	10	5
C_{20} or C_{22} isomers			1		2.5

5.1.3 Raw materials [1–6]

Soaps are manufactured from a renewable source. The triglycerides (or triesters of fatty acids) are the raw material for the production of soap. The triglycerides occur widely in plants and animals.

Tallow and coconut oil are the principal fatty materials in soap making in the United States. The palm oils, palm kernel oil, and their derivatives are used in soap manufacture in many other parts of the world. Greases, obtained from hogs and smaller domestic animals, are the second most important source of glycerides of fatty acids. Coconut oil has long been important in soap making. The soap from coconut oil is firm and lathers well. It contains a large amount of the desired glycerides of lauric and myristic acids (Table 5.1) [1–6].

The soap maker represents one of the larger consumers of chemicals, especially caustic soda, salt, soda ash, caustic potash, sodium silicate, sodium bicarbonate, and trisodium phosphate. Builders are inorganic chemicals added to soap. In particular, tetrasodium pyrophosphate and sodium tripolyphosphate were usually effective soap builders [1–6].

5.1.4 Chemistry of soaps

Soaps are water-soluble sodium or potassium salts of fatty acids containing 8 to 22 carbon atoms. The fatty acids are generally a mixture of saturated and unsaturated moieties.

Saturated soap: $CH_3(CH_2)_nCOOM$

Mono-unsaturated soap: $CH_3(CH_2)_nCH_2CH{=}CHCH_2(CH_2)_m{-}COOM$

Poly-unsaturated soap: $CH_3(CH_2CH{=}CH)_xCH_2(CH_2)_y{-}COOM$

[$M{=}Na, K, R_4N^+$]

The basic chemical reaction in the making of soap is saponification:

$$\underset{\textbf{Sodium hydroxide}}{3NaOH} + \underset{\textbf{Glyceryl stearate}}{C_{17}H_{35}COO_3C_3H_5} \longrightarrow \underset{\textbf{Sodium stearate}}{3C_{17}H_{35}COONa} + \underset{\textbf{Glycerin}}{C_3H_5(OH)_3}$$

The other method for making soap comprises fat splitting followed by the neutralization process with sodium hydroxide.

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \xrightarrow[\text{splitting}]{\text{Fat}} \underset{\textbf{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\textbf{Glycerin}}{C_3H_5(OH)_3}$$

$$\underset{\textbf{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\textbf{Sodium hydroxide}}{NaOH} \xrightarrow{\text{Neutralization}} C_{17}H_{35}COONa + H_2O$$

Sodium hydroxide, potassium hydroxide, sodium carbonate, and triethanolamine are the most commonly used alkaline moieties in both the processes.

Recently, soap manufacture by the saponification of fatty methyl esters has been developed in Japan and Italy. The methanolysis of triglycerides takes place in the presence of enzymes (lipase) as catalysts to produce fatty methyl ester and glycerin. The fatty methyl ester undergoes the saponification and forms the final product [1–6].

$$(C_{17}H_{35}COO)_3C_3H_5 + 3CH_3OH \xrightarrow{\text{Catalyst}} \underset{\textbf{Methylstearate}}{3C_{17}H_{35}COOCH_3} + \underset{\textbf{Glycerin}}{C_3H_5(OH)_3}$$

$$\underset{\textbf{Methyl stearate}}{C_{17}H_{35}COOCH_3} + \underset{\textbf{Sodium hydroxide}}{NaOH} \xrightarrow{\text{Saponification}} \underset{\textbf{Sodium stearate}}{C_{17}H_{35}COONa} + CH_3OH$$

5.1.5 Classification of soaps

The two main classes of soaps are toilet soap and industrial soap. Toilet soap is usually made from mixtures of tallow and coconut in the ratios 80–90:10–20. The bar soap includes regular and super fatted toilet soaps, deodorant and antimicrobial soaps, floating soaps, and hard water soaps. The super fatted soaps are also made from a mixture of tallow and coconut oil in ratios 50–60:40–50. All soaps practically contain 10 to 30 percent water and also contain perfume that serves to improve the original soap odor. Toilet soaps usually contain only 10 to 15 percent moisture; they have little added material, except for perfume and a fraction of a percent of titanium dioxide used as a whitening agent. Shaving soaps, in contrast, contain a considerable amount of potassium soap and an excess of stearic acid; the combination gives a slower drying lather [1, 2, 5].

Milled toilet soap is another type of bar soap. Because of the milling operation, the soap lathers better and generally has an improved performance, especially in cool water.

Laundry soap bars are precursors of the chip and the powder forms. They are generally made from tallow or a combination of tallow and coconut oil. Borax and builders, such as sodium silicate and sodium carbonate, are included to improve performance and help soften water [1, 2, 5].

5.1.6 Manufacturing of soaps

Before the 1950s, soap was manufactured in the saponification process. Soap was prepared in large kettles in which fats, oils, and caustic soda were mixed and heated. After cooling, salt was added to the mixture forming two layers: soap and water. The soap was pumped from the top layer to a closed mixing tank where builders, perfumes, and other ingredients were added. Finally, the soap was rolled into flakes, cast, or milled into bars, or spray-dried into soap powder [1, 2].

After the 1940s, an important modern process for producing soap is based on the direct hydrolysis of fats by water at high temperatures. The chart of the continuous process is shown in Fig. 5.1. The process involves splitting (or hydrolysis) where fatty acids are neutralized to soap [1, 2, 5].

The saponification of triglycerides with an alkali is a bimolecular nucleophilic substitution (SN2). The rate of the reaction depends on the increase of the reaction temperature and on the high mixing during the processing. In the saponification of triglycerides with an *alkali*, the two reactants are immiscible. The formation of soap as a product affects the emulsification of the two immiscible reactants, which causes an increase in the reaction rate [1, 2, 5].

$$\text{Triglyceride} + 3\,\text{NaOH} \rightarrow 3\,\text{RCOONa} + \text{Glycerin}$$

The flow diagram of the continuous process of converting fatty acids into soap (Fig. 5.1) includes an important component—the hydrolyzer—to which the fats and the catalyst were introduced after mixing and preheating in the blend tank. At the same time, deaerated-demineralized hot water is fed to the top contacting section of the hydrolyzer. The fatty acids are discharged from the top of the splitter and the glycerin is

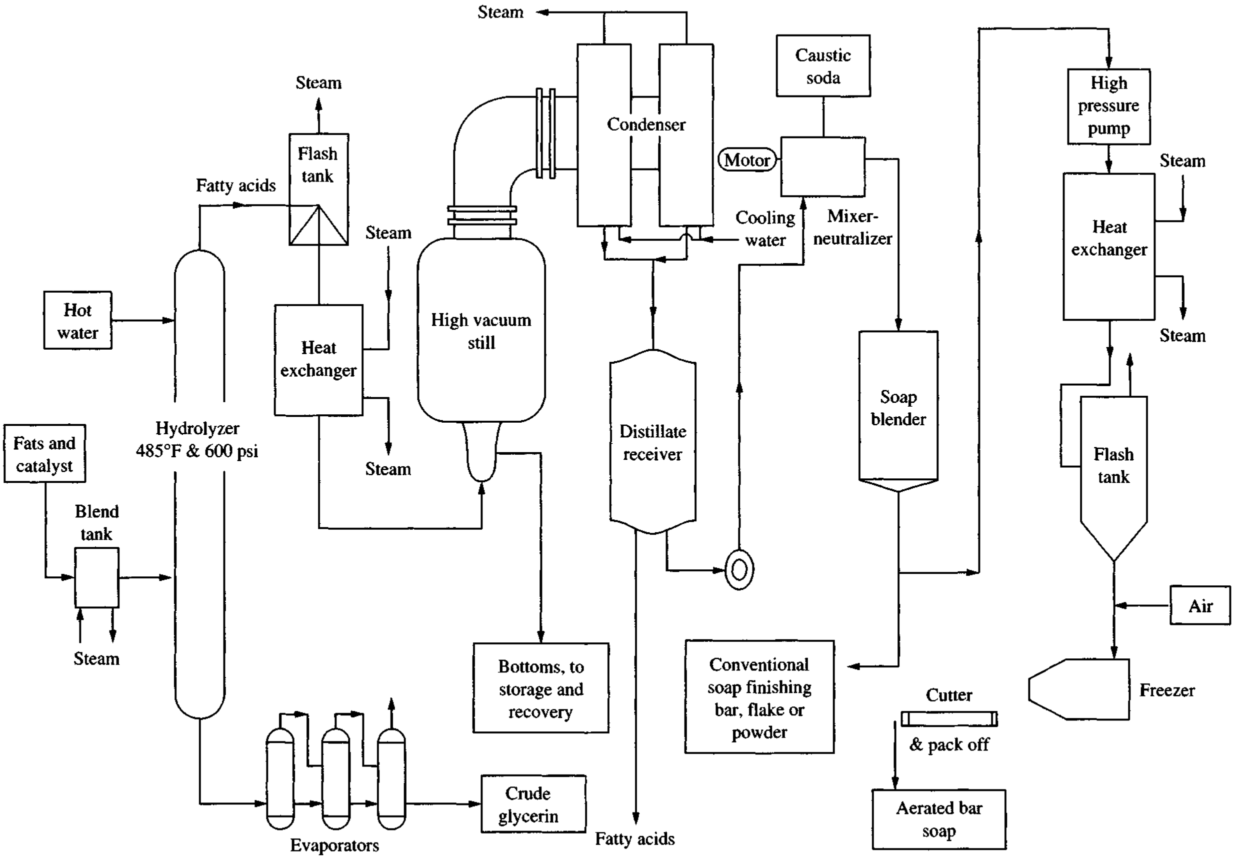


Figure 5.1 Continuous process for fatty acids and soaps.

eliminated from the bottom of the hydrolyzer. The fatty acids are sent to a flash tank, where the water is separated or flushed off.

$$\text{Triglyceride} \xrightarrow[\text{Fat splitting}]{+H_2O} \text{Fatty acids} + \text{Glycerin}$$

The resulting crude mixtures of fatty acids may be used, but a separation into more useful components is made.

The fatty acids are deaerated and distilled in a high-vacuum still. The fatty acids are deaerated to prevent darkening by oxidation during the process. The acids are charged at a controlled rate to the bottom of the high-vacuum still unit. The hot fatty acids are cooled down to room temperature into two parallel condensers prior to neutralization with 50% caustic soda in a high-speed mixer neutralizer. The fatty acids are converted into their corresponding sodium salts that form the soap.

$$\text{Fatty acid} + \text{NaOH} \xrightarrow{\text{Neutralization}} \text{Soap}$$

The amount of caustic soda (NaOH) required for neutralizing a fatty acid blend can be calculated as follows:

$$\text{NaOH} = [\text{weight fatty acid} \times 40]/\text{M fatty acid}$$

The average molecular weight of a fatty acid is calculated from the following equation:

$$M_{\text{fatty acid}} = 56.1 \times 1000/\text{AV}$$

where AV = acid value of fatty acid blend = mg of KOH required to neutralize 1 g of fatty acid.

Neat soap (60 to 63 percent total fatty matter) is discharged into a slowly agitated blender to assure a complete neutralization. The neat soap at this stage may be extracted for conventional soap production (bar, flake, or powder) or undergoes further treatment at high pressure and high temperature in a high-pressure steam exchanger. The heated soap is sent to a flush tank for partial drying. The resulting viscous, pasty soap is then mixed with air in a heat exchanger, where the soap is cooled from 105 to 65°C. The soap is continuously extracted in strip form and is cut into bars. The operation is completed by further cooling, stamping, and wrapping to produce the aerated bar soap.

The advantages of soap manufacturing by this process include the color improvement of the soap, the excellent glycerin recovery, and the need for less space and labor [1, 2, 5].

5.1.7 Environmental aspects

The main atmospheric pollution problem in soap manufacturing is odor. The sources of this odor are from the storage and handling of liquid ingredients such as sulfonic acids and salts, and also from sulfates. The raw materials and product storage, the ventilation lines, the vacuum exhausts, and the waste streams are all potential odor sources. The control of these odors may be achieved by scrubbing exhaust fumes, or by incinerating the remaining volatile organic compounds. The odors originating from the spray dryer may also be controlled by scrubbing with an acid solution. Blending, mixing, drying, packaging, and other operations may involve dust emissions. The dust emission from the finishing operations can be controlled by dry filters such as bag houses. The large sizes of the particulate from the soap powder dryer mean the high-efficiency cyclones installed in a series can achieve a satisfactory control [1, 2, 5, 6, 7].

5.2 Detergent

5.2.1 Introduction and history

It is not easy to determine when the detergent industry came into existence. The problem was to define exactly what is being referred to as a synthetic detergent. For example, in the United States the term *surfactants* was used, while in Europe the term *tenside* was applied to point out the detergent industry.

Many general definitions of a detergent have been suggested [4]:

Detergent. A product that after formulation is devised to promote the development of detergency.

Surface active agent. A chemical compound, which when dissolved or dispersed in a liquid, is absorbed at an interface giving rise to a number of important chemical properties. The compound includes in its molecule one group that has an affinity for polar surfaces, ensuring solubilization in water, and a group that has little affinity for water.

Amphiphilic product. A product that contains in its structure one or more hydrophilic groups and one or more hydrophobic groups.

In the last 1000 years, soap has been used as a general-purpose washing and laundry agent. Soap remained a luxury until the beginning of the 20th century when the first self-acting laundry detergent was introduced in Germany (Persil, 1907). Soap took its place as an ingredient in the multicomponent systems for the routine washing of textiles. Soap was combined with the so-called builders, such as sodium carbonate, sodium silicate, and sodium perborate. The first practical substitutes for soap were fatty alcohol sulfates, discovered in Germany by Bertsch and coworkers in 1928 [4]. The availability of synthetic alkyl sulfates based on natural fats and oils made the introduction of the first neutral detergent for delicate fabrics (Fewa) possible in Germany in 1932. Fatty alcohol sulfates and their derivatives (alkyl ether sulfates, obtained by tracking fatty alcohols with ethylene oxide and subsequent sulfation) still retain their importance in many applications: heavy-duty detergents, dishwashing agents, cosmetics, and toiletries. In 1946, Procter and Gamble introduced the synthetic detergent Tide in the United States. By the 1950s, the widespread availability of tetra propylenebenzene sulfonate (TPS), a product of the petrochemical industry, had largely displaced soap as the key surfactant from the detergent.

In 1977, the German firm Hankel patented the use of synthetic zeolites as a partial replacement for phosphates. The sodium aluminum silicates as zeolites have a particular lattice structure capable of absorbing heavy metal cations through ion exchange process. The role of zeolites that were added to TPS was to soften water by rapid reaction with calcium at normal temperature [4].

Nitrilo triacetic acid (NTA) also represents a partial replacement of phosphate. However, the US Surgeon General issued a report stating that NTA caused birth defects in rats. The use of NTA was immediately phased out in the United States [4].

An important new criterion, the so-called biodegradability of detergents, appeared for surfactants. The insufficient biodegradability of TPS and nonylphenol ethoxylates caused great masses of stable foam to build up in the vicinity of weirs, locks, and other constructions in waterways. Subsequently, the first German Detergent Law was adopted in 1961 [4]. The German precedent was soon followed by the adoption of a similar legislation in France, Italy, and Japan. In the United Kingdom and the United States, voluntary agreement toward the transition to biodegradable surfactants took place between the industry and government [4].

The world production figures of different countries showed that the per capita consumption of detergents varies quite largely (Fig. 5.2). For example, it amounted to 2 to 3 kilograms per year (kg/a) in countries such as Brazil, China, and Russia, and to more than 10 kg/a in Mexico and some European countries in 1997 [8, 9].

The world production of laundry detergents amounted to 21.5×10^6 t in 1998. The total produced volume remained constant in the 1990s worldwide (Table 5.2).

The use of enzyme additives was the most important and revolutionary trend in the detergent industry in the past decade. The lower-temperature washes of the new high-efficiency machines are expected to give a boost to the demand for enzymes. As catalysts, enzymes are efficient and effective at low doses and at low temperatures where surfactant

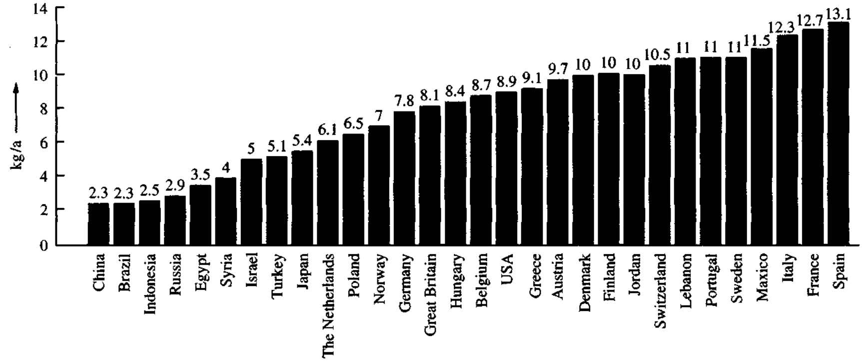


Figure 5.2 Per capita consumption of detergents in 1996 (kg/a) [8, 9].

activity is challenged. Enzymes continue to be popular additives for stain removal and fabric care.

The Freedonie group pegged the US demand for detergent enzymes at US$155 million in 1996 and anticipated that it will grow to US$260 million by 2001 [10].

5.2.2 Principle groups of synthetic detergents

Detergents are complex formulations that contain more than 25 different ingredients that can be categorized into the following main groups:

1. Surfactants
2. Builders
3. Bleaching agents
4. Additives

TABLE 5.2 Worldwide Production Detergent Industry [4]

Production 10^3 t	1994	1998
Soap bars	4579	3651
Detergent bars	1251	968
Powders	13,310	14,137
Pastes	496	505
Liquids	2052	2372
Total	21,688	21,633
World average Per capita consumption, kg/a	4.5	3.9

SOURCE: Ciba Specialty Chemicals Ltd., Switzerland.

Each group of detergents has its own specific functions during the washing process. They have synergistic effect on one another [1–4].

5.2.3 Surfactants

Surfactants represent the most important group of detergent components. They are present in all types of detergents. In general, surfactants are water-soluble surface-active agents comprising a hydrophobic group (a long alkyl chain) attached to a hydrophilic group.

The hydrophilic group is usually added synthetically to a hydrophobic material to produce a compound that is soluble in water. However, this solubilization does not necessarily produce a detergent, because detergency depends on the balance of the molecular weight of the hydrophobic portion to that of the hydrophilic portion.

Therefore, there are four main groups of surfactants: anionic, cationic, nonionic, and amphoteric[1–4].

Anionic surfactants. These are compounds in which the detergency is realized in the anion that has to be neutralized with a basic material before the full detergency is developed.

$$R-SO_3^-Na^+$$

Alkylsulfonates (anionic surfactants)

Cationic surfactants. These are compounds in which the detergency is in the cation, and although in the manufacturing process no neutralization takes place, the material is in effect neutralized by a strong acid.

$$R_2\,N^+(CH_3)_2\,Cl^-$$

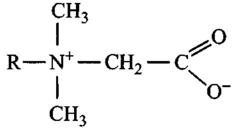
Dialkyl dimethylammonium chlorides (cationic surfactants)

Nonionic surfactants. These contain nonionic constituents.

$$RO-(CH_2-CH_2-O)_n\,H$$

Alkyl poly(ethylene glycol)ethers (non-ionic surfactants)

Amphoteric surfactants. They include both acidic and basic groups in the same molecule.

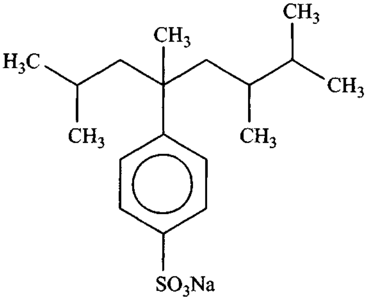


$$R-N^+(CH_3)_2-CH_2-COO^-$$

Betain (amphoteric surfactants)

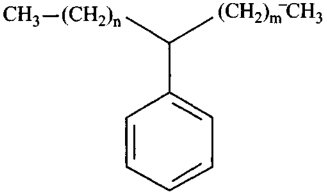
Anionic surfactants

Alkylbenzene sulphonates (LAS andTPS). Alkylbenzene suofonates represent the largest class of synthetic surfactants and until the mid-1960s tetra propylene benzene sulfonate (TPS) was the most prominent detergent.



TPS

TPS has largely replaced soap as an active ingredient in laundry detergents in Europe, the United States, and Japan. However, the branched side present in TPS prevents the compounds from undergoing sufficient biodegradation. The replacement of TPS by more degradable straight-chain homologues was an urgent task for scientists in the 1950s. Economic circumstances have permitted the straight-chain or linear alkylbenzenesulfonates (LASs) to take the lead in the detergent industry in Europe, the Americas, and Asia [1–4].



LAS (m + n = 7 – 10)

LASs were found to possess interesting foaming characteristics, which are very significant for their application as detergents. However, LAS can be controlled by foam regulators. Also, the foam produced is stabilized by form stabilizers. The basic processes have been applied for the manufacture of LAS. The dehydrogenation of paraffins, followed by alkylation of benzene with a mixed olefin or paraffin feedstock, represents the most important route for the production of LAS. This process is catalyzed by hydrogen fluoride (HF) [1–4].

The partial chlorination of paraffins, followed by alkylation of the chloroparaffin or paraffin feedstock using aluminum chloride ($AlCl_3$) as a catalyst, represents another important route toward LAS.

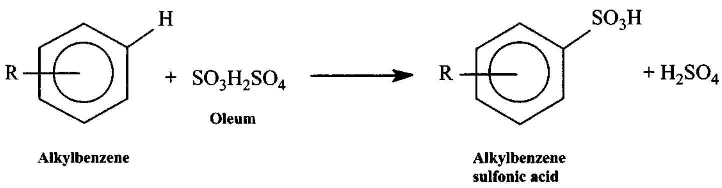
The third process implicates partial chlorination, but includes a dehydrochlorination to olefins prior to alkylation, with $AlCl_3$ or HF as a catalyst.

Universal Oil Products Company (UOP) offers processes, catalysts, adsorbents, and equipment for the production of linear alkylbenzenes (LAB) from kerosene or normal paraffins. The UOP LAB processes consist of a combination of several UOP processes, including the kerosene prefractionation and detergent alkylate. The LAB technology is the most economical technology available today, and over 70 percent of the world's LAB is produced using UOP technologies. Until 1995, alkylation used hydrofluoric (HF) acid as the catalyst. In 1995, the first commercial Detal process unit using a solid best catalyst alkylation process was commissioned. This revolutionary technology abolished the use of liquid acid in the plant, reducing capital investments, maintenance costs, and waste treatment [1–4].

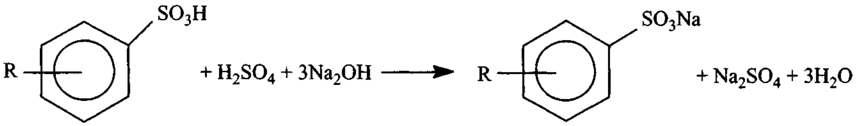
The continued worldwide demand for LAB creates new growth and development of new technologies to improve the process. LAS made from sulfonation of LAB is the most cost-effective surfactant available for use in detergent formulation. Environmentally proven LAS has the largest volume of existing surfactants [1–4].

Sulfonation of LAB. The sulfonation of alkylbenzenes leads to sulfonic acid tyre product, which is then neutralized with a base such as sodium hydroxide to produce sodium alkylbenzene sulfonate. The sulfonation reaction is highly exothermic and instantaneous. An efficient reactor heat removal system is used to prevent the decomposition of the resultant sulfonic acid. The sulfonation reaction takes place by using oleum ($SO_3H_2SO_4$) or sulfur trioxide (SO_3). Although, the oleum sulfonation requires relatively inexpensive equipment, the oleum process has major disadvantages compared to sulfur trioxide. The need for spent acid stream disposal and the potential corrosion owing to sulfuric acid generation increased the problems related to oleum process [1].

Sulfonation

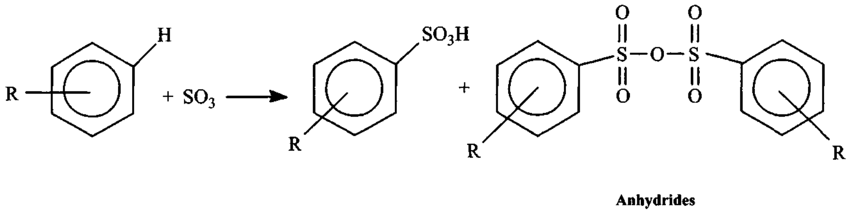


Neutralization

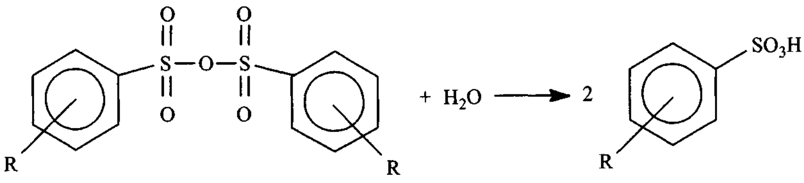


The gaseous air or SO_3 sulfonation process leads to high yields of sulfonic acid (95 to 98 percent). This process comprises three major steps. The sulfonation of alkylbenzene with air or SO_3 forms the alkylbenzene sulfonic acid and anhydride. The latter is decomposed into the alkylbenzene sulfonic acid by hydration. The neutralization of the sulfonic acid into the corresponding sodium salt represents the last chemical step in the process of formation of detergents [1].

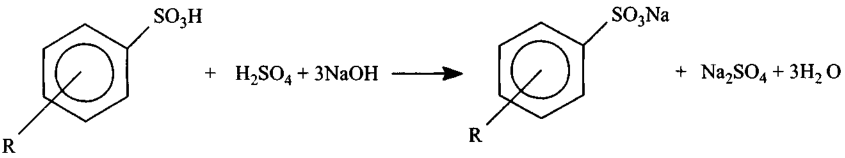
Sulfonation



Hydration

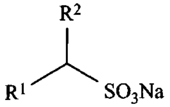


Neutralization



Secondary alkanesulfonates (SAS). The large-scale production of sodium alkanesulfonates (SAS) began in the late 1960s.

These sulfonates are still valued as anionic surfactants for consumer products. The secondary alkanesulfonates are known to have high solubility, fast wetting properties, chemical stability to alkali, acids, and strong oxidants such as chlorine.



$R^1, R^2 = C_{11\text{-}17}$

Sodium alkanesulfonates are produced by photochemical sulfoxidation or sulfochlorination of suitable C_{12}–C_{18} paraffin cuts. SAS can largely be substituted for LAS in formulations because of the similarity in terms of solubility, solubilizing properties, and wetting power [4].

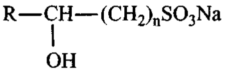
Sulfonated olefins

$R—CH{=}CHCH_2SO_3Na$

$R{=}C_8 \quad C_{12}$

Alkenesulfonates

and



$$R—\underset{\displaystyle OH}{\underset{|}{CH}}—(CH_2)_nSO_3Na$$

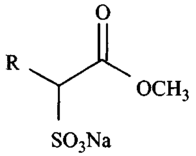
$R{=}C_7—C_{13}$

Hydroxyalkanesulfonates

The first commercial sulfonation of olefins with SO_3 involved the use of an SO_3-organo compound complex. Nowadays best results are obtained by sulfonating with uncomplexed diluted SO_3 in a film reactor [3, 4].

The reaction between α-olefins and SO_3 is not straightforward because of the formation of mixtures of alkene sulfonic acids, sultones, alkene disulfonic acids, and sultone sulfonic acids. Alkaline hydrolysis of sultone intermediates results in Ca 60 to 65 percent alkenesulfonates and Ca 35 to 40 percent hydroxyalkanesulfonates. The materials are sold as α-olefinsulfonates (AOS) because of the use of olefinic precursors. AOS has not yet made great strides in the heavy-duty laundry field but is being used successfully for light-duty detergents, hand dishwashing, shampoos, bubble baths, and synthetic soap bars [3, 4].

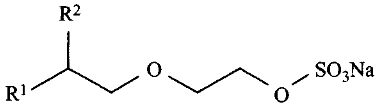
α-Sulfo fatty acid ester (MES)



$R{=}C_{12\text{-}16}$

The α-sulfo fatty acid esters represent another class of anionic surfactants. Methyl ester sulfonates (MES) are surfactants that are derived from a variety of methyl ester feedstocks such as coconut, palm kernel, palm stearin, beef tallow, and soy. Palmitic and stearic acid derivatives lead to good detergency because of the long hydrophobic residues [3, 4]. The sensitivity of MES to water hardness is similar to AOS and small compared to LAS and SAS. MES have exceptional dispersion power with respect to lime soap. They have only been used in a few Japanese detergents [3, 4].

Alkyl ether sulfates (AES)



$R^1 = H, R^2 = C_{10\text{-}12}$	Fatty alcohol ether sulfates
$R^1 + R^2 = C_{11\text{-}13}$	Oxo alcohol ether sulfates

Alkyl ether sulfates (AES) are anionic surfactants obtained by ethoxylation and subsequent salfation of alcohols derived from feedstock or synthetic alcohol. AES, also known as alcohol ether sulfates, have low sensitivity to water hardness (Fig. 5.3), high solubility, and good storage stability at low temperature [4, 11].

The main components of the commercial AES are alkyl ether sulfates and alkyl sulfates. Other by-products such as unsulfated alcohols, alcohol ethoxylates, inorganic salts, and polyethylene oxide sulfates are also present in the commercial product [4, 12].

Sodium C_{12-14} n-alkyl diethylene glycol ether sulfates demonstrate increased detergency performance as the hardness increases. This is a result of the positive electrolyte effects attributable to calcium or magnesium ions.

AES are very intensively foaming compounds, which increased their use in high-foam detergents for vertical-axis washing machines. AES are suitable components of detergents for delicate or wool washables, as well as foam baths, hair shampoos, and manual dishwashing agents because of their specific properties. The optimal carbon chain length has been established to be C_{12-14} with 2 mol of ethylene oxide.

AES have been used in the United States and Japan because of their critical micelle concentration, which is lower than LAS, resulting in very satisfactory washing power. In Europe, the use of alcohol ether sulfates has been largely restricted to specialty detergents [3, 4].

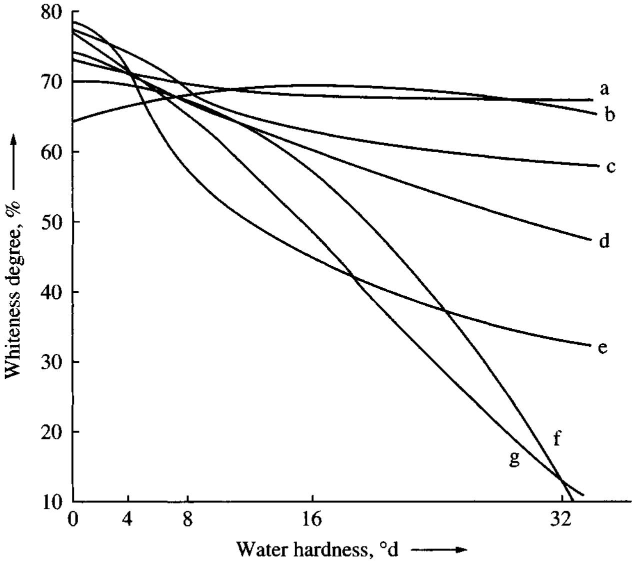


Figure 5.3 Detergency performance on wool by various surfactants as a function of water hardness [4]. Time: 15 min; temperature: 30°C; bath ratio: 1:50; concentration: 0.5 g/L surfactant + 1.5 g/L sodium sulfate; (a) Nonylphenol 9 EO; (b) C_{12-14} alcohol 2 EO sulfates; (c) C_{15-18} α-olefinsulfonates; (d) C_{16-18} a-sulfo fatty acid esters; (e) C_{12-18} Alcohol sulfates; (f) C_{10-13} alkylbenzenesulfonates; (g) C_{13-18} alkanesulfonates.

Nonionic surfactants. The majority of nonionic surfactants are condensation products of ethylene oxide with a hydrophobe. This hydrophobe is invariably a high molecular weight material with an active hydrogen atom, and the nonionic material can be one of the following reaction products [1–4]:

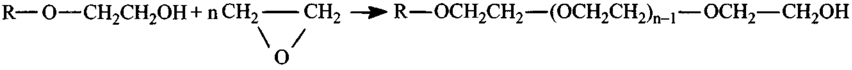
1. Fatty alcohol and alkylphenol condensates
2. Fatty acid condensates
3. Condensates of ethylene oxide with an amine
4. Condensates of ethylene oxide with an amide

Fatty alcohol and alkylphenol condensates

$$R-O-CH_2-CH_2\,(OCH_2CH_2)_{n-1}OCH_2CH_2OH$$

R = alkyl or phenyl

The alcohol ethoxylates and alkylphenol ethoxylates are produced by the reaction of alcohol with an excess of ethylene oxide. The reaction of one molecule of ethylene oxide is not sufficient to produce a water-soluble detergent product.



$$R{-}O{-}CH_2CH_2OH + n\,\underset{O}{CH_2{-}CH_2} \rightarrow R{-}OCH_2CH_2{-}(OCH_2CH_2)_{n-1}{-}OCH_2{-}CH_2OH$$

R = alkyl or phenyl; n = 16–50

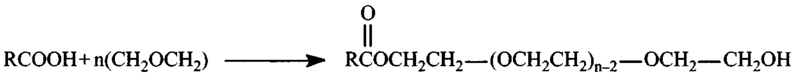
The ether linkage is a strong bond, therefore, the material cannot be hydrolyzed and there is no possibility of ionization and subsequently it is not affected by metal ions. In practice, the optimum detergency is found in the range of 10 to 15 molecules of ethylene oxide per molecule of fatty alcohol. The source of the alcohol varies greatly, but natural, Ziegler and OXO alcohols of various molecular weights are being used. Another source of alcohols is the one used by Union Carbide. These alcohols are obtained from n-paraffins that are oxidized to secondary alcohols. The ethoxylation of these alcohols is done in two stages [3]. The product containing 1 mol of ethylene oxide is produced first with an acid catalyst. After this stage the catalyst and the unreacted alcohol are removed and ethoxylation takes place as usual [3].

The alkylphenols behave in the same manner as fatty alcohols. The nonyl (or octyl) phenol is widely used with 8 to 12 molecules of ethylene oxide. Nonylphenol is completely soluble in water at room temperature and exhibits excellent detergency. Dodecylphenol ethoxylate is used in certain agriculture emulsifiers and dinonylphenol as low or nonfoaming ingredients of household washing machine powders [3, 4].

The alkylphenol ethylene oxide condensates have been the most widely produced nonionic detergent. These condensates are solubilized by the ethylene oxide units forming hydrates with water. Compared with all other materials that dissolve in water, these products show an apparent anomaly: their solutions are completely clear in the cold, but when heated they become turbid and, if the temperature is raised sufficiently, separation into two phases can take place. This is explained by the fact that at an elevated temperature the hydrates are destroyed.

The important use of polyester fibers in clothing and bedding increased the nonionic constituent in laundering as it was found that nonionics remove soil from these fibers better than the anionics.

Fatty acid condensates. Fatty acid condensates are another type of nonionic surfactants that are prepared by the reaction of fatty acids with ethylene oxide.

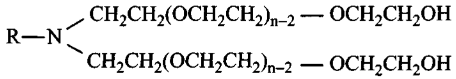


$$RCOOH + n(CH_2OCH_2) \longrightarrow R\overset{O}{\overset{\|}{C}}OCH_2CH_2{-}(OCH_2CH_2)_{n-2}{-}OCH_2{-}CH_2OH$$

These condensates can also be produced by the esterification of a fatty acid with a polyethylene glycol, $HOCH_2(CH_2CH_2)_nCH_2OH$. Esters are materials that have some disadvantages compared to other nonionic detergents. In general, nonionic detergents are not affected by metallic ions, acids, or alkalis. However, the fatty acid condensates of ethylene oxide are readily hydrolyzed by acids or alkaline solutions to the corresponding fatty acid and polyethylene glycol. In strong alkaline solutions the esters are no better than the soap of the corresponding fatty acid, and in strong acid solution they are much affected. However, they do perform well as components of household detergent powders [3, 4].

Condensates of ethylene oxide with an amine. The condensation of alkylamines with ethylene oxide leads to secondary or tertiary substituted amines depending on the concentration of ethylene oxide.

$$R{-}NH{-}CH_2{-}CH_2(OCH_2CH_2)_{n-2}{-}OCH_2{-}CH_2OH$$

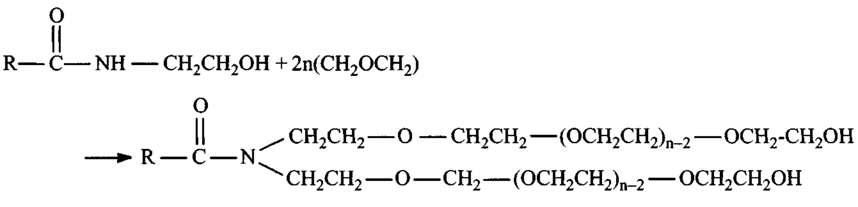


$$R{-}N\begin{cases}CH_2CH_2(OCH_2CH_2)_{n-2}{-}OCH_2CH_2OH\\ CH_2CH_2(OCH_2CH_2)_{n-2}{-}OCH_2CH_2OH\end{cases}$$

R = 11-17

This class of nonionic surfactants has not been used largely in cleaning detergents. However, it is noteworthy that these materials in acidic solution can exhibit cationic characteristics, whereas, in neutral or alkaline solution, they are nonionic [3, 4].

Condensates of ethylene oxides with an amide. Fatty acid alkanolamides are amides of alkylolamines and fatty acids. Certain members of this class exhibit detergency and others do not. The nondetergent materials are converted into detergents by condensation with ethylene oxide.



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2CH_2OH + 2n(CH_2OCH_2)$$

$$\longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N\begin{cases}CH_2CH_2{-}O{-}CH_2CH_2{-}(OCH_2CH_2)_{n-2}{-}OCH_2\text{-}CH_2OH\\ CH_2CH_2{-}O{-}CH_2{-}(OCH_2CH_2)_{n-2}{-}OCH_2CH_2OH\end{cases}$$

$R = C_{11\text{-}17}$
$n = 1, 2$

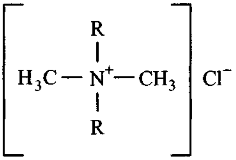
Fatty acids alkanolamides find only a little application in laundry detergents. They are used as foam booting, that is, adding desired stability to the foam produced by detergents. Small amounts of these materials as cosurfactants are capable of enhancing the soil removal properties of the classical detergent components at low washing temperatures [3, 4].

Cationic surfactants. Long chain cationic surfactants such as disteral diamethyl ammonium chloride (DSDMAC) exhibit extraordinarily high sorption power with respect to a wide variety of surfaces [13–15]. These surfactants are very strongly absorbed by the surface of natural fibers, such as cotton, wool, and linen [4].

Cationic surfactants are mainly employed for the purpose of achieving certain special effects, which include applications in rinse-cycle fabric softeners, antistatic agents, and microbicides [4].

Nonionic surfactants are more tolerant of the presence of cationic surfactants than anionic surfactants. Mixtures of the two are sometimes used in the production of specialty detergents that are powerful antistatic products.

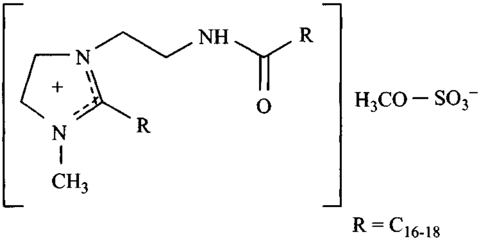
The cationic detergents invariably contain amino compounds. The most widely used would be the quaternary ammonium salts, such as cetyltrimethylammonium chloride, a well-known germicide and distearyldimethylammonium chloride (DSDMAC), known as fabric softener for cotton diapers and as a laundry rinse-cycle fabric softener [4].



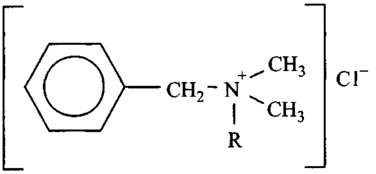
$$\left[H_3C-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{N^+}}-CH_3 \right] Cl^- \qquad R = C_{16-18}$$

DSDMAC

Imidazolinium salts, such as 1-alkylamidoethyl-2-alkyl-3-methylimidazolinium methylsulfate have been used as rinse-cycle softening agents, but in less significance compared to DSDMAC [4].

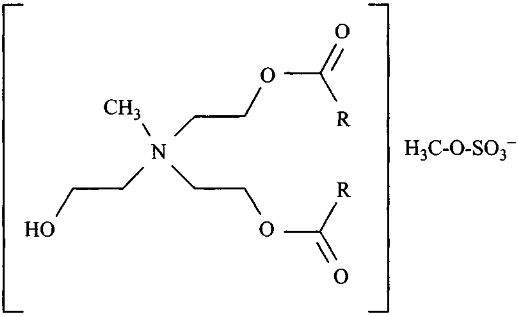


The compounds based on alkyldimethylbenzylammonium chloride type have been used as laundry disinfecting agents. They show limited fabric softening character [4].



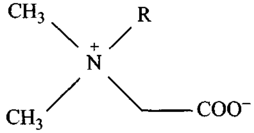
R = C_{8-18}

Esterquats represent a new generation of fabric softeners that have been developed in the 1980s or 1990s and have replaced DSDMAC [4, 16].

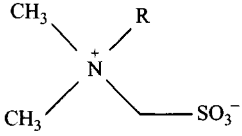


N-Methyl-N,N-bis[2-($C_{16\text{-}18}$-acyloxy)ethyl]-N-(2-hydroethyl) ammonium methosulfate. (Esterquat) EQ

Amphoteric surfactants. These compounds have the characteristics of both anionic detergents and cationic fabric softeners. They tend to work best at neutral pH, and are found in shampoos, skin cleaners, and carpet shampoos. They are very stable in strong acidic conditions and are favorably used with hydrofluoric acid. For example, compounds of alkylbetain or alkylsulfobetaine type possess both anionic and cationic groups in the same molecule even in aqueous solution. These surfactants are rarely employed in laundry detergents because of their high costs [3, 4].



R = C_{12-18} **Alkylbetaines**



R = C_{12-18} **Alkylsulfobetaines**

5.2.4 Inorganic builders

The use of the detergents mentioned so far as end products, would be costly, and so water is used to dilute these ingredients into the more consumer useable form. Sodium sulphate that is used as a diluting agent in powder detergents is cheap and user friendly.

Builders enhance the detergency action so that less can be used of the more expensive detergents of high activity. The combination of builders and surfactants exhibits a synergistic effect to boost total detergency and cleaning efficacy. Detergent builders should have the ability to control water hardness and other metal ions by eliminating calcium and magnesium ions that arise from the water and soil. Builders should also be compatible with other formulation ingredients and detergent additives. Consumer safety and environmental acceptability are important characteristics of builders [3, 4].

The inorganic constituents fall into the five following groups:

1. Phosphates
2. Silicates
3. Carbonates
4. Zeolites
5. Bleach-active compounds

Phosphates. There are two classes of phosphates—orthophosphates and complex phosphates. The orthophosphates used in the detergent industry are trisodium phosphate in hydrated and anhydrous forms (Na_3PO_4 and $Na_3PO_4 \cdot 12H_2O$), disodium phosphate, another form of orthophosphates in anhydrous form (Na_2HPO_4), and crystalline $Na_2HPO_4 \cdot 12H_2O$· In the past, trisodium phosphate was used as a soap builder, but it is seldom used in detergent formulations nowadays because phosphates cause eutrophication of water. It has the property of softening water by precipitating metallic ions, as a gelatinous precipitate [3,4].

Trisodium phosphate can cocrystallize with sodium hypochlorite to produce the material called commercially *chlorinated trisodium phosphate* that has a formula approximating to ($Na_3PO_4 \cdot 12H_2O$) NaOCl. This material is added to the cleaning detergents that require the bleaching and sterilizing effect of NaOCl together with the high alkalinity and water-softening of trisodium phosphate [3, 4].

The detergent industry has introduced another form of phosphate the so-called *condensed phosphates*. These materials have a higher proportion of P_2O_5 and a lower proportion of Na_2O in the molecule. These phosphates have a lower alkalinity than trisodium phosphate. The commonly used complex phosphates are:

Tetrasodium pyrophosphate, $Na_4P_2O_7$ (TSPP)

Sodium tripolyphosphate, $Na_5P_3O_{10}$ (STP)

Sodium tetraphosphate, $Na_6P_4O_{13}$

Sodium hexametaphosphate, $(NaPO_3)_6$

Both sodium tetraphosphate and sodium hexametaphosphate are hygroscopic and are unsuitable for formulation into dry powders. Tetrasodium pyrophosphate (TSPP) is now used for specialized purposes only, but its potassium analogue is used in liquids. The combination of TSPP and sodium carbonate was more effective than either ingredient used separately [3, 4].

Sodium tripolyphosphate (STP) was commercially available in the mid-1940s and had replaced TSPP because of its superior detergent processing, solubility, and hardness ion-sequestering characteristics. Sequestration is defined as the reaction of a cation with an anion to form a soluble complex. The sequestration of Ca^{2+} and Mg^{2+} ions leads to softened water and is the most important function of any detergent builder [3, 4].

STP is the major builder ingredient in heavy duty laundry detergents, automatic dishwashing compounds, and industrial and institutional cleaners [3, 4].

Silicates. The addition of sodium and potassium silicates to synthetic detergent has proved very beneficial. They have in solid or solution form important characteristics such as emulsification, buffering, deflocculation, and antiredeposition ability.

Sodium silicate is prepared by the fusion of sand that contains a high amount of silica with soda ash according to the following equation:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

The proportion of silica, sand, and soda ash is important in providing a variety of alkalinity. The molecular formula of silicates has been adopted according to the method of Berzlins and is written as $Na_2O{:}SiO_2$ [3].

Silicates are produced in liquid, crystalline, or powdered form. The ratio of $Na_2O{:}SiO_2$ is usually selected to meet the product requirement and its application. The sodium metasilicate ($Na_2O/SiO_2 = 1/1$) is used in dry blending. The liquid silicates having $Na_2O{:}SiO_2$ ratio of 1:2 or higher are used in laundry and automatic dishwashing applications.

Soluble glass and soluble powders are the two forms of detergents that are prepared in the ratios of $Na_2O{:}SiO_2$ of 1:2 and 1:33, respectively. A ratio of 1:2.4 is commonly used in making detergent powders and is produced by blending the neutral soluble powder and the alkaline soluble glasses or by adding caustic soda to neutral glass [3].

A *wet method* for the production of soluble detergents of up to 40 percent disilicate by the reaction of fine sand and caustic soda (3 to 50 percent) is as follows.

$$2\,SiO_2 + 2NaOH \rightarrow Na_2O.2SiO_2 + H_2O$$

Potassium silicate, available commercially in colloidal ratios, is used nowadays for specialized liquid detergents. It is available in weight ratios of 1:1.5 to 1:2.5. Silicates soften water by the formation of precipitates that can be easily rinsed away. Silicates are corrosion inhibitors of stainless steel and aluminum that can be caused by synthetic detergents and complex phosphates [3].

Carbonates. Carbonates are being used because of the restriction in the use of phosphates in certain areas of the United States. Sodium carbonate (Na_2CO_3) or a combination of Na_2CO_3 and zeolite has replaced sodium tripolyphosphate (STP) as a builder in granular laundry products [3].

Sodium carbonate provides high alkalinity because only sodium hydroxide is high on a weight per volume basis. Na_2CO_3 softens water by the precipitation of calcium and magnesium carbonates, provided the pH of the solution is greater than 9.

Synthetic soda is of superior quality compared to mined natural soda ash. There are two important grades of carbonates: light soda ash and dense soda ash. Light soda ash can absorb large amounts of liquid material onto its surface and remains dry [3].

Sodium carbonate is commonly used in powdered laundry detergent, automatic dishwashing compounds, and hand surface cleaners.

Sodium carbonate is produced by the Solvay process, which uses sodium dichloride, carbon dioxide, and ammonia. Carbon dioxide obtained from burning limestone to lime is introduced in countercurrent to the solution of sodium chloride (known as brine) saturated with ammonia. Sodium bicarbonate, which is almost insoluble in solution and precipitates, is separated and roasted to sodium carbonate [3].

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CO_2 + NaCl + NH_4OH \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

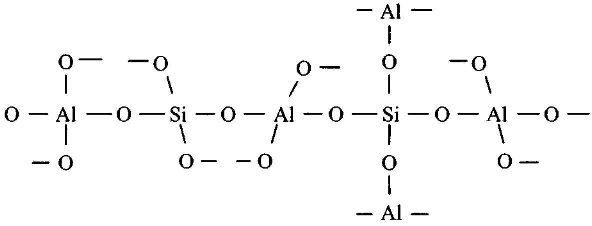
The carbon dioxide released from the conversion of the bicarbonate to carbonate is reused in the absorption tower in addition to CO_2 obtained from the burning of the lime.

Zeolites. Silicon is the second most abundant element in the earth's crust after oxygen. Silicon, which is never found free, is invariably associated with oxygen (silica, quartz) and with metallic oxides.

Zeolites, also known as molecular sieves, are important alternative builders for powdered laundry detergents and replaced phosphate salts that were banned for legislative reasons. Zeolites exist in the form of calcium, sodium, magnesium, potassium, and barium salts.

The most widely used form of zeolites is type A—which are hydrated sodium aluminum silicates of empirical formula $Na_2O{\cdot}Al_2O_3{\cdot}x\,SiO_2{\cdot}yH_2O$.

The crystalline material of type-A zeolites has a three-dimensional lattice structure of a simplified formula:



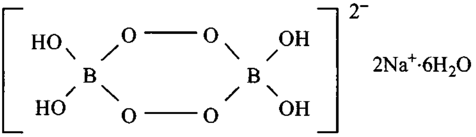
Type-A zeolites are the most widely used form for laundry detergents.

The main advantage of zeolites compared to phosphates is nonsolubility in water, and they subsequently remove heavy metal ions such as manganese and iron readily and rapidly from the solution. However, magnesium ions are not totally removed by zeolites because of the size of magnesium; therefore, zeolites are then used in association with other builders such as sodium carbonate [3, 4].

Bleach-active compounds. Oxygen-releasing compounds are added to detergent powders as bleach-active materials. Peroxide-active compounds are the most used bleaches in Europe and many other regions of the world. Among these peroxides, hydrogen peroxide (H_2O_2) is converted by alkaline medium into hydrogen peroxide anion as active intermediate [4].

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^-$$

HOO^- oxidizes bleachable soils and stains. The most used source of hydrogen peroxide is sodium perborate, known as sodium peroxoborate tetrahydrate, $NaBO_3{\cdot}4H_2O$, that in crystalline form contains the peroxodiborate anion [4, 17].

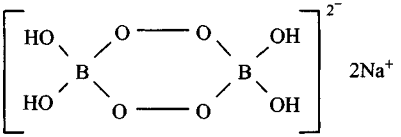


Peroxodiborate anion

Peroxodiborate is hydrolyzed in water to form hydrogen peroxide.

$$(NaBO_2H_2O_2)_2 \cdot XH_2O \longrightarrow 2NaBO_2 + 2H_2O_2 + XH_2O$$

In solution, sodium perborate monohydrate is similar in action to that of hydrogen peroxide. At elevated temperatures, active oxygen is released and has a bleaching effect but does not affect animal, vegetable, and synthetic fibers [3, 4].



Sodium perborate

Sodium perborate can be used as the universal laundry bleach and has been used in Europe for the past 50 years [3, 4].

Sodium perborate is a stable material when mixed with other dry ingredients. However, the presence of traces of water and certain heavy metals will catalyze the decomposition of the perborate. Therefore, magnesium sulphate or silicate, or tetrasodium pyrophosphate is added to adsorb traces of water and metal to prolong the storage life of the powders [3, 4].

Hypochlorite is another effective bleaching compound at normal temperature. The use of liquid hypochlorite has gained importance in many countries where laundry habits, such as cold water washing, made the sodium perborate less effective. Hypochlorite reacts with an alkaline to produce hypochlorite anions [4, 18, 19].

$$HOCl + OH^- \rightleftharpoons ClO^- + H_2O$$

The aqueous solution of sodium hypochlorite (NaOCl) is used as a source of active chlorine that can be used in either the wash or the rinse cycle.

Powdered sodium perborate has some advantages over liquid sodium hypochlorite (NaOCl). NaOCl must be added separately in either the wash or the rinse cycle whereas perborate can be included directly in the powder laundry product. Also, a high dosage of NaOCl may cause significant damage to laundry and colors. In addition, sodium hypochlorite solutions have limited storage stability especially in the presence of impurities such as heavy metal ions. Sodium hypochlorite has a high reactivity and oxidation potential and may cause problems with textile dyes and most fluorescent whitening agents.

Studies showed that chlorine bleach is used predominantly in the Mediterranean countries whereas peroxide bleach use dominates in Europe. However, hypochlorite bleach in either the wash or the rinse cycle is still a preferred bleaching agent in a large part of the world (Table 5.3) [4].

TABLE 5.3 Washing Habits in Different Regions of the World [4]

Washing conditions	United States	Japan	Europe
Washing machine	vertical axis or agitator type	vertical axis or pulsator type	horizontal axis drum type
Heating equipment	no	no	yes
Fabric load, kg	23–25	4–8	2–5
Amount of water, L	medium loads: approx. 50–60 large loads: approx. 65–75	low: 30 high: 65	low: 10–16 high: 20–25
Total water consumption, L (regular cycle)	120	120–150	55–90
Wash liquor ratio	approx. 1:25	approx. 1:10 to 1:15	approx. 1:4 to 1:10
Washing time, min	8–18	5–15	50–60 (90°C) 20–30 (30°C)
Washing rinsing, and spinning time, min	20–35	15–35	100–120 (90°C) 50–70 (30°C)
Washing temperature, °C	hot: 55 (130°F) warm: 30–45 (90–110°F) cold: 10–25 (50–80°F)	5–25	90 60 40
Water hardness (average), ppm $CaCO_3$	relatively low, 100	very low, 30	relatively high, 250
Detergent dispenser	mostly no	mostly no	yes
Recommended detergent	1.0–1.2	0.5–0.8	4.5–8.0
Dosage*, g/L g/kg laundry	15–30	5–7	15–35
Peroxide bleach	mostly added separately	mostly dosed separately	mostly incorporated in detergent
Chlorine bleach	added separately	dosed separately	predominantly in the Mediterranean countries

*In the United States and Japan mostly without bleaching components.

5.2.5 Sundry organic builders

Antiredeposition agents. The detergent has an important characteristic that allows the removal of the soil from textile fibers during the washing process. Furthermore, the redeposition of displaced soil can be prevented by the addition of special antiredeposition agents. The role of these agents is to be adsorbed on the surface of the textile, there by creating a protective layer that strictly inhibits redeposition of the removed soil. For example, the adsorption behavior of gelatin on glass, both in the presence and in the absence of sodium n-dodecyl sulfate, clearly showed the effect of the

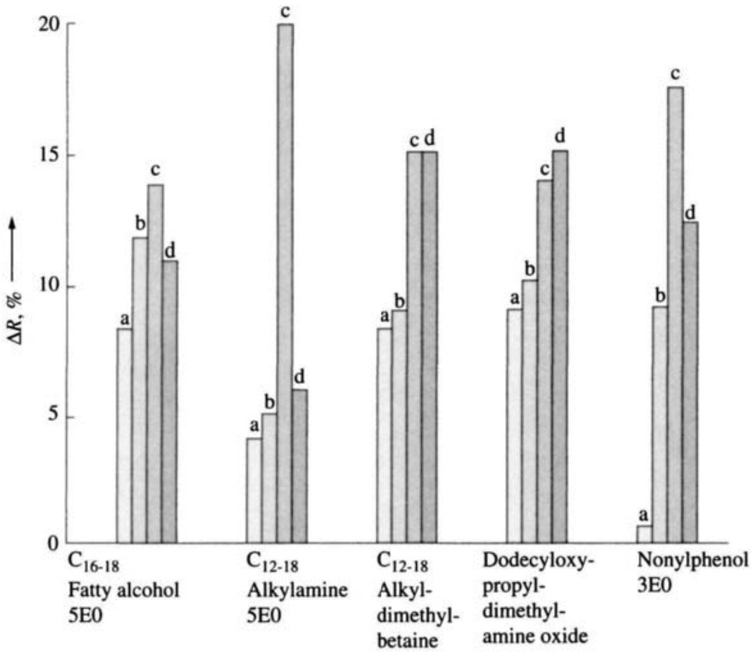
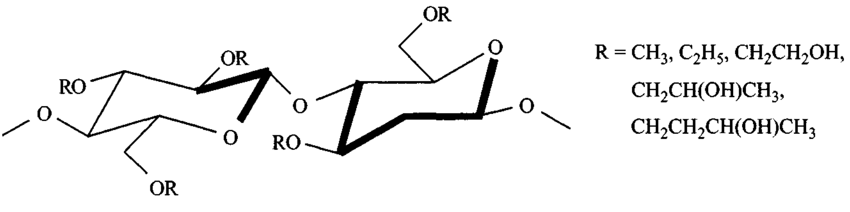


Figure 5.4 Influence of specific surfactants on the oil antiredeposition capability of detergents [20]. ΔR indicates the improvement in the soil antiredeposition capability against the additive [20]. (a) Cotton, 95°C; (b) Permanent-press cotton, 95°C; (c) Polyester, 60°C; (d) Polyester or cotton, 60°C. 5g/L detergent; 0.2 g/L surfactant; number of wash cycles = 3; time = 30 min [20].

addition of the surfactant. The presence of n-dodecyl sulfate eliminates the adsorption of the macromolecules onto the substrate [3, 4].

The carboxymethyl cellulose (CMC) derivatives and carboxymethyl starch (CMS) are effective antiredeposition agents that are cellulose-containing fibers such as cotton and blends of cotton and synthetic fibers. However, CMC has virtually no effect on pure synthetic fibers. Other effective antiredeposition agents and soil repellents have been developed (Fig. 5.4) [20].

The nonionic cellulose ethers have been found suitable for use with synthetic fibers [3, 4].



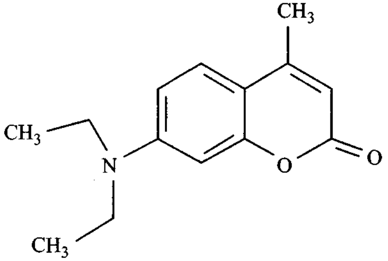
Nonionic cellulose ethers

The modern detergents are provided with mixtures of anionic and nonionic polymers (e.g., carboxymethylcellulose-methylcellulose) and also with polymers from polyethylene glycol and terephthalic acid [3, 4].

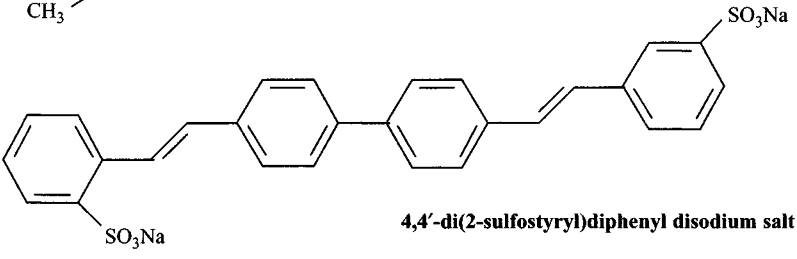
Thickening agents. Carboxymethyl cellulose (CMC) is also used as a thickening agent in addition to its characteristic as a soil antiredeposition agent. Modified nonionic celluloses, methyl cellulose, hydroxyethyl cellulose methylhydroxy propyl cellulose are being used as thickening agents. All these modified celluloses are soluble in cold water and insoluble in hot water and most organic solvents [3, 4].

Optical brighteners. Optical brighteners are an integral part of laundry products, whether laundry powders or laundry liquids. They are organic compounds capable of converting a portion of the invisible ultraviolet light into longer wavelength visible blue light. They are dyestuffs, which are absorbed by textile fibers, but are not easily rinsed off. The reflection of the blue light makes the clothes look brighter than they actually are.

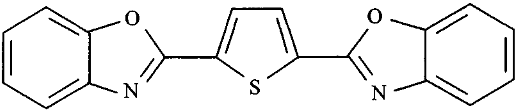
Optical brighteners are usually derivatives of coumarin, stilbene, distyrylbipheny, and bis(benzoxazole). Examples of chemical structures of some important optical brighteners are given:



7-diethylamino-4-methyl coumarin



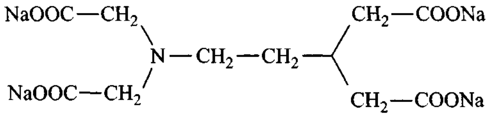
4,4′-di(2-sulfostyryl)diphenyl disodium salt



2,5-bis(benzoxazol-2-yl)thiophene

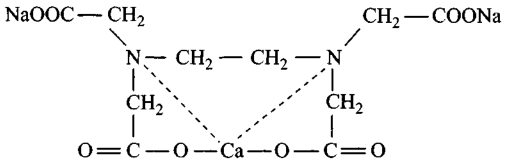
The optical brighteners binding occur, in the case of cotton and chlorine-resistant materials, through the formation of hydrogen bond to the fibers. Whitening effects achieved with polyamide brighteners are largely because of the diffusing power of whitening agent molecules present at the fiber surfaces [3, 4].

Chelating agents. The role of the chelating agents is to block the polyvalent ions and to make them undetectable and ineffective. Sodium salts of ethylene diamine tetraacetic acid (EDTA) and of nitrilo triacetic acid (NTA) are members of the group of chelating agents and their use has increased in the last few years.



Sodium salt of EDTA

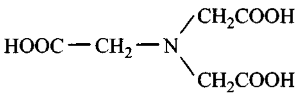
The sodium salt of EDTA reacts with calcium ions to give a complex in which Ca is bidentated to nitrogen atoms of EDTA. Two sodium ions are released from the reaction [3, 4].



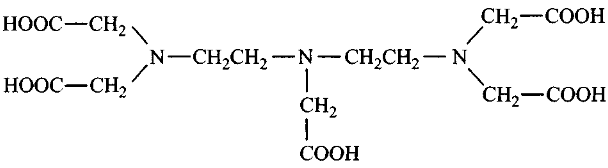
There are three main groups of the chelating agents.
Aminocarboxylic acids:

a. Ethylene diamine tetraacetic acid

b. Nintrilo triacetic acid



c. Diethylene triamine pentacetic acid (DTPA)



NTA sequestrates more calcium ions per unit weight than EDTA because of its lowest molecular weight. However, both will sequester more calcium ions than magnesium because the molecular weight of magnesium is smaller than that of calcium. EDTA and NTA are used in laundering formulations to chelate trivalent ions, thus preventing iron stains in laundering [3, 4].

Enzymes. Enzymes are defined as organic catalysts that promote specific chemical reactions in the body upon which all life depends. Naturally occurring enzymes are related to proteins and are largely composed of amino acids.

The most significant development in the detergent industry in recent years is the introduction of enzyme additives.

Enzymes catalyze destruction and removal of stubborn proteinaceous stains and specific types of soils by detergent. Chocolate and starch-based food stains as well as greasy stains that are difficult to remove in low-temperature washing, are eliminated by detergent-enzymes [1–4].

There are four types of enzymes of interest to the detergent industry:

1. Proteases: act on protein to form amino acids
2. Amyloses: convert starches into dextrins
3. Lipases: attack fats and oils
4. Celluloses: hydrolyze cellulose of broken surface fibers and remove micro-pills from cotton and restore color

The mechanism of the enzymes is to cleave the protein into smaller peptide fraction that is soluble in water. Even if the conversion is not complete, the protein is degraded into a product that can be easily removed by the detergent. The activity of enzymes depends on temperature and pH value. At a certain temperature of the wash bath (mostly above 55°C) the activity of enzymes decreases. The proper choice of the type of enzyme and the appropriate formulation has led to detergent-grade enzymes that are not significantly damaged during the storage or in the wash liquor [1–4].

5.2.6 Manufacturing of detergents

Production of alkylbenzene sulfonates [1, 2]. The alkylbenzene sulfonates, used as liquid surfactants in making the detergent slurry, are produced by the sulfonation of linear alkylates followed by the neutralization step with a caustic solution containing sodium hydroxide (NaOH). The process of sulfonation of alkylbenzenes with oleum takes

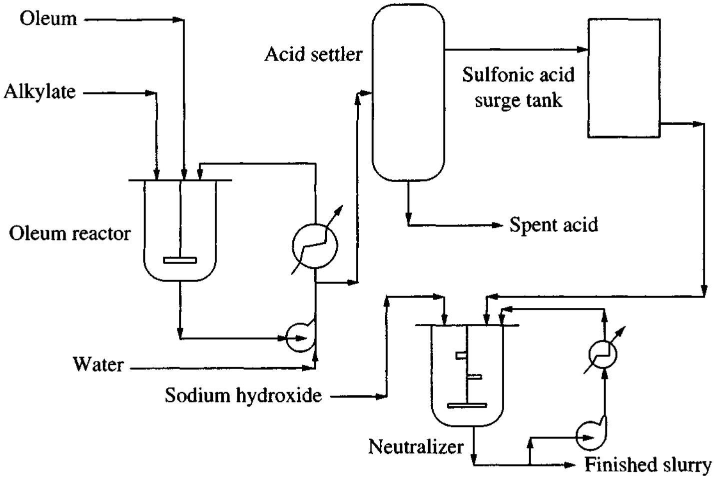


Figure 5.5 Oleum sulfonation process.

place in a batch system where five basic processing operations are used (Fig. 5.5):

1. Sulfonation
2. Digestion
3. Dilution
4. Phase separation
5. Neutralization

The sulfonation stage includes mixing of alkylate with oleum that leads to an exothermic reaction. The removal of heat is done by reactor jacketing. The key parameters that control the reaction of sulfonation are temperature, acid strength, reaction time, and oleum-to-alkylate ratio. The reaction was completed at the digestion stage where the product from the sulfonation zone is aged for 15 to 30 min. The mixture of sulfonic acid and sulfuric acid is diluted with water to quench the reaction. The reaction mixture is sent to a separator to allow gravity settling of the spent sulfuric acid from the lighter sulfonic acid. The lower spent acid layer contains, approximately, 75 to 80 percent sulfuric acid. The upper layer contains, approximately, 88 to 91 percent sulfonic acid and 6 to 10 percent sulfuric acid [1, 2].

The linear alkyl sulfonates can be neutralized with aqueous solutions of base such as NaOH, KOH, NH_4OH, or alkanolamines. The sodium salts are used in the formulation process to produce spray-dried detergents

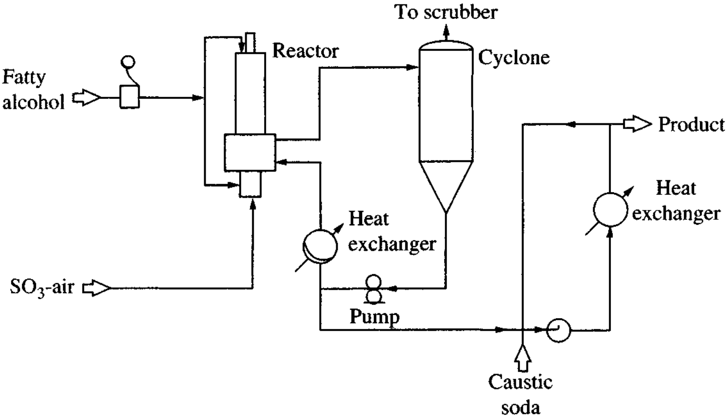


Figure 5.6 Fatty alcohol sulfation process.

for household laundry. However, ammonium and alkanolamine neutralized salts are usually employed in light duty liquid detergents [1, 2].

Fatty alcohols sulfation [1, 2]. The sulfation of fatty alcohols takes place in falling film reactors but cooling water and sulfation temperatures are adjusted to lower values. The sulfonic acids obtained are neutralized immediately to minimize degradation and side reactions in storage [1, 2].

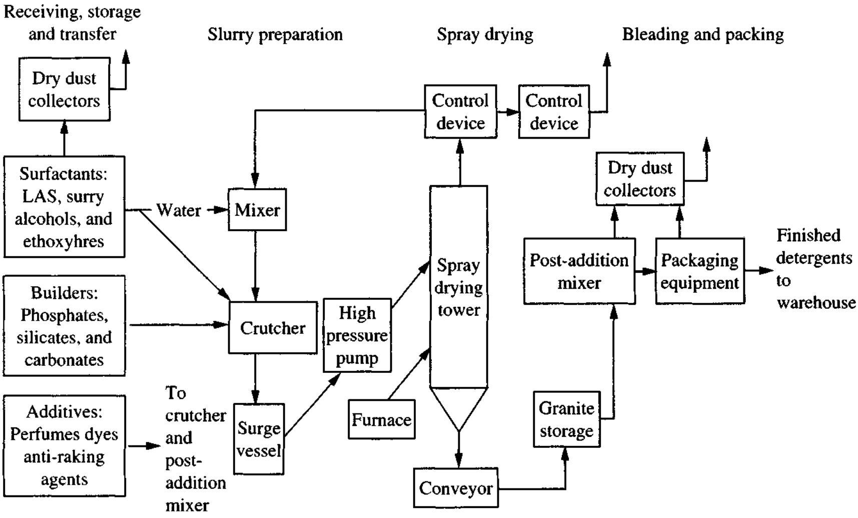
$$R{-}OH + SO_3 \longrightarrow R{-}O{-}SO_3H$$

A typical process for the sulfation of fatty alcohols is shown in Fig. 5.6. A posthydrolysis step includes bleaching to remove color before neutralization. The neutralization step of the sulfonic acid is similar to the case of oleum sulfonation process [1, 2].

The surfactant slurry, builders, and other miscellaneous additives are introduced in the crutcher. A considerable amount of water is removed, and the paste is thickened by the tripolyphosphate (used as a builder) hydration reaction:

$$Na_5P_3O_{10} + 6H_2O \longrightarrow Na_5P_3O_{10} \cdot 6H_2O$$

Spray-drying process. The first step in the spray-drying process includes the preparation of slurry of thermally stable and chemically compatible ingredients of the detergent (Fig. 5.7)[1–4]. The slurry, the builder, and other additives are mixed in a crutcher. The blended slurry is transferred and held in a stirred storage vessel for continuous pumping to a spray dryer. The slurry is sprayed through nozzles into the tower at pressures of 4.1 to 6.9 kilopascals (kPa) in single-fluid nozzles and at



LAS = Linear alkyl salfonate

Figure 5.7 Spray-drying process.

pressures of 340 to 690 kPa in 2-fluid nozzles. Steam or air is used as the atomizing fluid in the 2-fluid nozzles. The slurry is sprayed at high pressure into a vertical drying tower having a steam of hot air at 315 to 400°C. The dried powder flows off the tower at a temperature of 90 to 100°C. An airlift is used for cooling to prevent lumping. The most common towers designed for detergent production are countercurrent. The slurry is introduced at the top of the tower and heated air is introduced at the bottom. The detergent granules are conveyed mechanically or by air from the tower to a mixer to incorporate additional ingredients, such as a perfume, and finally to packaging and storage [1–4].

5.3 Environmental Aspects

5.3.1 Emissions and controls

The exhaust air from detergent towers contains two types of contaminants:

1. Fine detergent particles
2. Organics vaporized in the higher zone of the tower

Dust emissions are generated at scale hoppers, mixers, and crutchers during the batching and mixing of fine dry ingredients to form slurry. Conveying, mixing, and packaging of detergent granules can also cause dust emissions. For this process, fabric filters are used, not only to reduce or eliminate dust emission, but also to recover raw materials [1–4].

Dry cyclones are the primary collection equipment used to capture the detergent dust in the spray dryer exhaust and recycle it back to the crutcher. The dry cyclones can remove up to 90 percent by weight of the detergent product fines from the exhaust air. Fabric filters have been used after cyclones but have limited applicability, especially on efficient spray dryers, because of condensing water and organic aerosols binding the fabric filters [4, 21].

In addition to particulate emissions, volatile organic compounds (VOCs) may also be emitted when the slurry contains organic materials with low vapor pressures. The surfactants included in the slurry represent the origin of the VOCs. The vaporized organic materials condense in the tower exhaust air stream into droplets or particles. Paraffin alcohols and amides in the exhaust stream can result in highly visible plume that persists after the condensed water vapor plume has dissipated [4, 21]. Some of the VOCs identified in the organic emissions are: hexane, methyl alcohol, 1,1,1-trichloroethane, perchloroethylene, benzene, and toluene [1–4].

A method for controlling visible emissions would be to remove by substitution the offending organic compounds from the slurry.

5.3.2 Wastewater and the environment

Wastewater is the by-product that has the potential for causing a number of undesirable effects in sewage treatment plants in the environment. In fact, the clean water, which was brought into the process, is later released to the sewage system in the form of contaminated wastewater containing additional energy, soil from the laundry, lint, dyes, finishing agents, and detergents. Detergents are released as the products of reaction with other material during the washing cycle or in unchanged form [4].

The variations in laundry soil levels affect the concentration and the composition of laundry wastewater considerably. Laundry wastewater is generally a heavy source of contamination; therefore, it should not be returned to receiving waters in untreated form [4].

Fortunately, the laundry wastewater is mixed with general water in the public sewage and in the sewage treatment plants. As a result of dilution, both temperature and the high pH value of wastewater are considerably decreased. In addition, if laundry wastewater was treated separately, major problems would be encountered in dealing with the load of organic pollutants introduced by household and commercial laundry operations [4].

5.3.3 Biodegradation

The removal of organic compounds from sewages, surface waters, and soils can be done by the biodegradation process. This is a stepwise process that is mainly affected by aerobic microorganisms (Fig. 5.8). The first step involves the transformation of the sodium sulfonate to a first degradation product (primary degradation). The subsequent degradation to the second, third, and so on, intermediate steps takes place with the decreasing of molecular mass and structural complexity. The ultimate biodegradation represents the total decomposition of the total organic structure into carbon dioxide, water, inorganic salts, and at the same time, partly into bacterial biomass.

Since 1973, the regulation in Europe requires a minimum of 80 percent biodegradability for the anionic and nonionic surfactants in a package detergent. Anionic surfactants are determined as *methylene blue active substance* (MBAS), that is, materials forming a chloroform soluble complex with cationic dye methylene blue. Nonionic surfactants are defined as *bismuth active substance* (BiAS), that is, materials forming an insoluble complex with the bismuth-containing Drangendorff reagent [4]. The primary biodegradation of anionic and nonionic surfactants is determined in standardized tests by measuring the removal of MBAS and BiAS, respectively. The ultimate biodegradation of chemicals can be followed in the tests by means of nonspecific analytical parameters such as carbon dioxide evolution (BOD) or the removal of dissolved organic carbon (DOC).

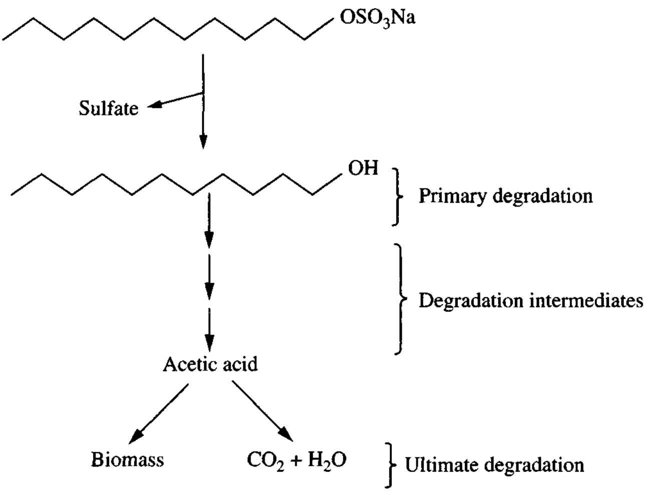


Figure 5.8 Biodegradation pathway of fatty alcohol sulfates.

Primary and ultimate biodegradability of test substances is normally evaluated by applying standardized and internationally used (OECD, ISO, EU) test procedures [4].

5.4 Economic Aspects

The role of detergents represents an important factor in the worldwide economy. The increase of the standards of living in the last 40 years was accompanied with a tremendous growth in the world consumption of the detergents. The absolute quantity has increased from approximately 10×10^6 t in the late 1950s to 21.5×10^6 t worldwide in 1988 [4]. For example, the total consumption of laundry, dishwashing, and cleaning detergents in Europe was 6.4×10^6 t in 1991. The quantity has increased to 6.8×10^6 t in 1999 (Table 5.4) [4, 22].

TABLE 5.4 The Total Consumption of Surfactants Worldwide (10^3 t) [4, 22]

End use	1992	1998
Household		
North America	866	1115
Western Europe	1061	1119
Asia	1208	1599
Other regions	998	1235
Total	**4133**	**5068**
Personal care		
North America	204	210
Western Europe	143	163
Asia	119	194
Other regions	86	155
Total	**552**	**722**
Industrial and institutional cleaners		
North America	263	311
Western Europe	155	192
Asia	60	75
Other regions	42	53
Total	**520**	**631**
Industrial process aids		
North America	1191	1316
Western Europe	644	676
Asia	858	1085
Other regions	355	364
Total*	**3048**	**3441**
Grand total	**8253**	**9862**

*Does not include soap.

TABLE 5.5 The Major Surfactant Consumption by Type Worldwide (10^3 t) [4, 22]

Surfactant type	1992	1998
Linear alkylbenzene sulfonates	2385	3027
Branched alkylbenzene sulfonates	411	148
Alcohol sulfates	466	479
Alcohol ethoxy sulfates	511	911
Alcohol ethoxylates	742	849
Alkyl phenol ethoxylates	652	701
Quaternaries	312	434
Others	2774	3263
Total	**8253**	**9862**

The two largest end uses, which are household products and industrial processing aids, together account for 86 percent of the total production of surfactants [4, 22]. Household products include heavy-duty powder and liquid detergents, light-duty liquids, and fabric softeners.

Industrial processing materials are covered by the following major end uses: plastics and elastomers, textiles, agricultural chemicals, leather and paper chemicals, and other miscellaneous uses.

The anionic surfactants, such as linear alkyl-benzene surfactants, represent the largest consumed type of surfactants worldwide followed by alcohol ethoxylate, and alkylphenol ethoxylates (Table 5.5) [4, 22].

For legal restrictions, the use of sodium triphosphate as a builder has sharply decreased mainly in the United States, Europe, and Japan. The application of sodium triphosphate in detergents dropped by more than 50 percent within 10 years in these countries [4, 23].

Zeolite A, the most important phosphate substitute, became the highly demanded builder worldwide. The worldwide production of zeolite A increased in western Europe in the 1990s. Detergent builder zeolites represent the largest application field for zeolite. Almost 90 percent of zeolites produced worldwide (or ~ 215,000 tons/year) in 2003 were used for detergents. Meanwhile, production capacities for detergent-grade zeolites have largely surpassed the demand [4].

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Sugar Industry

Introduction

Sugar, which refers usually to sucrose, is natural and nontoxic, sweet testing, water soluble crystalline carbohydrates, and every 1 gram of sugar provide body 4 K.calories. The main source for sugar is the beet sugar or cane sugar; also there are several sources such as honey, corn syrup, fruits, and vegetables….etc. The primary function of sugar in food products is to provide sweetness and energy, in addition, sugar plays a very important role in preservation, fermentation, color and texture. At last years, the increase of consuming sugar leads to several disease especially obesity, cardiovascular disease and diabetes type 2, so food organizations issued strict instructions about determining the sugar intake in diets.

History of Sugar

Since ancient times, sugar has been produced in India; it was expensive at first so honey was more often used for sweetening in the world. Sugarcane was a native of tropical South Asia and Southeast Asia, and people chewed it to extract its. In Europe, sugar was found by the 1st century and used as an imported medicine not as a food. Sugar stayed relatively unimportant until the Indians discovered methods to turning sugarcane juice into granulated crystals which is easier to store and to transport around the 5th century. In the 15th century, Venice was the chief sugar refining and distribution centre in Europe. China established its first sugarcane plantations in the 17th century. Chinese documents confirm at least two missions to India, initiated in 647 AD, to obtain technology for sugar refining. When Arab armies conquered the region, they carried away the knowledge of sugar manufacture and love of sugar as a food, condiment and medicine. In the early 700s Islamic armies had conquered much of Spain, bringing the culture of sugar with them. [10] In 19th century, sugar became more widely available, popular and considered a necessity. This evolution of taste and demand for sugar as an essential food ingredient unleashed major economic and social changes.

Manufacturing process

- Mill house:
- Sugar canes are cut into pieces and crushed in a series of rollers to extract the juice in the mill house.
- Lime Treatment
- The milk of lime is added to the juice and heated.
- When colloidal and suspended impurities are coagulated, most of colour is also removed during lime treatment.
- The coagulated juice is clarified to remove sludge.
- The sludge is further filtered through filter press and then disposed off as solid waste (press mud).

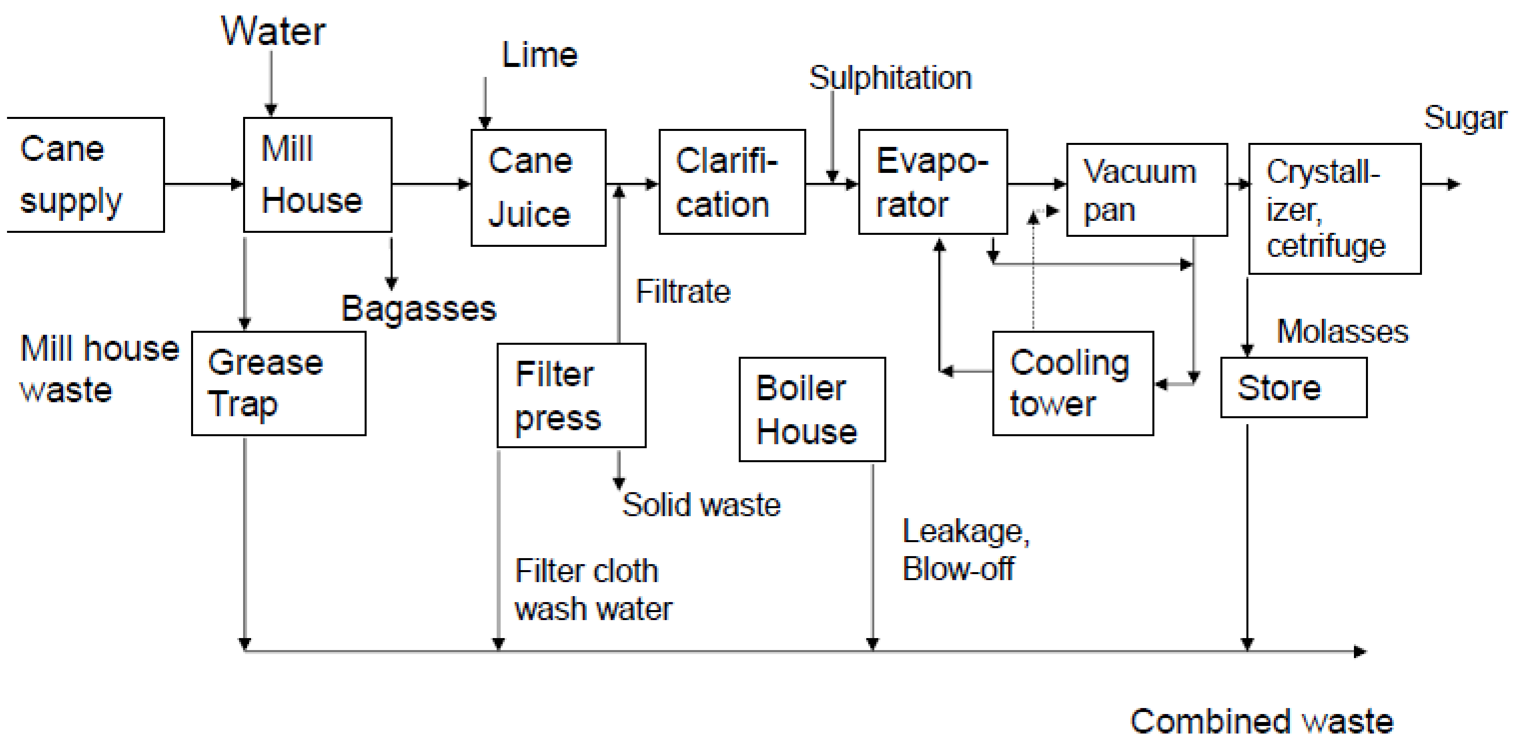
Sulphitation Process

- The filtrate is recycled to process along with entire quantity of clarified juice.
- This juice is treated by passing sulphur dioxide gas through it. This is known as sulphitation process.
- Colour of juice is completely bleached out due to this process.
- The clarified juice is then preheated and concentrated in evaporators and vacuum pans. The partially crystallized syrup from vacuum pan known as '**massecuite**' is transferred to the crystallizers.

Crystallizers

- In crystallizers **complete crystallization** of sugar occurs. The massecuite is then centrifuged to separate the sugar crystals from liquor.
- The spent liquor is discarded as '**black strap molasses**'.
- Sugar is then dried and bagged for transport.
- The fibrous residue of the mill house, known as '**bagasses**' is burnt in the boilers or may be used as raw-materials for paper products.
- Black strap molasses is used as raw material in distilleries.

Manufacturing process



Flow diagram of cane sugar manufacturing process

Treatment of the wastes

- Pollution load in sugar mills can be reduced with better water and material economy practiced in plant.
- Recycling will reduce the volume of waste to great extent. e.g. volume of mill house waste can be reduced by recycling the water used for splashing.
- Dry floor cleaning and reducing quantity of floor wash water can reduce the volume of waste.
- Proper control of operation can reduce the pollution load e. g. overloading of evaporators and vacuum pans, extensive boiling of the syrup leads to loss of sugar through condenser water thus increase in volume and strength of effluent.
- COD/BOD ratio (approx. 1.6 - 2) makes it biodegradable wastewater.
- Conventional aerobic treatment (ASP and TF) are not too efficient even at low organic loading rate.
- Due to seasonal nature of waste conventional treatment may not be economical.
- Anaerobic treatment (digestion and lagoon) can give > 70% to 90% efficiency. Effluent from anaerobic treatment can be treated by stabilization pond.
- Two stage biological treatments (anaerobic lagoon + stabilization pond) is common. Overall BOD > 90% can be removed.