Contents

Chemical – Engineering (Industry)

Introduction

What is the meaning of the word "Technology"?

This word has 2 Greek parts

Techno means an art or a trade

Logos means a science

Technology in general is the science dealing with methods and processes for converting products of nature into items of consumption and tools of production. Technology can be subdivided into:

1) Mechanical technology

2) Chemical technology

1- **Mechanical technology.**

Concerning with the processes which, as a rule, do not include any change in the composition and inner structure of material. For instance, wood or cotton are converted first into yarn and then to clothes. Metals are stamped and then used to make apparatus or machine parts.

2- **Chemical technology.**

Concerning with the processes, which include the change in inner structure and composition of material. For instance, wood can be heated without access of air to produce pitch. Natural gas can be made into plastics, rubber or synthetic fibber (i.e. the material produced entirely different in composition, structure and properties from the original material).

However, no sharp dividing line can be drawn between chemical and mechanical technology.

Chemical technology has two main divisions-:

1- Inorganic technology

This deals with production of inorganic acids, alkali, salts including also "fertilizers", cement, glass, ceramic and metallurgy of ferrous and nonferrous metals.

2-Organic technology

This deals with the manufacture of petroleum, basic organic synthetic products, dyes, drugs, plastics and chemical fibers, rubber ……. etc.

Importance of the chemical industry

The chemical industry manufactures thousand of different products. For example: Natural gas, petroleum, fuels-coal are converted into motor fuel, dyes, drugs, explosives, plastics, synthetic fibers, rubber …etc. Textile, clothes, artificial leather and everyday necessities are among the products of chemistry and chemical industry.

The chemical industry is of tremendous importance for agriculture. The demand for mineral fertilizers manufactures protecting the plant against pests and diseases results in increasing (inhibiting) plant growth. The chemical industry provides agriculture with films and other synthetic materials for covering hothouses, for making containers and storehouse…..etc. On the other hand, Fertilizers used for improve the quality of crops (sugar, protein and oil content).

Plastics and chemical fibers are very important. Plastics have excellent electrical insulating properties. They are highly resistant to acids, alkalis and other aggressive chemicals. For such properties plastics are widely used in many branches of the national economy.

Chemical fibers can be made into:

Crease-resistant, water-resistant, and non-shrinking clothes. Chemical fibers mixed with natural fibers such as cotton and wool on ever increasing scale.

At present for example, natural silk has almost completely replaced by synthetic fibers. This situation is due to the fact that the production of natural fibers (cotton and wool) requires considerable labor and may be become uneconomic. For example, labor involved for production of one ton of natural wool is seven times more than for production of one ton of darcon, or acrylic, for this reason, synthetic fibers are cheaper than natural one.

Great advantages can often be gained by using plastics in place of non-ferrous metals in electrical mechanical engineering instruments, and in the building industry.

Raw materials:

The principal items of expenditure which together make up the plant cost are given in percentage as:

1) raw materials, semi-products and basic materials which directly participate in the chemical reactions   (60 – 70%),

2) Fuel and power for technological uses   (10%),

3) Salaries of basic employees   (4%),

4) funds to cover basic items of capital investment (buildings, structures, equipment, etc)   (3—4%),

5) Shop costs, such as salaries of shop management personal, health and safety, etc.

6) General plant expenditures

These figures show that the cost of a chemical product is determined by the cost of the materials used in making it and by the degree of utilization; also important are expenditures on fuel and power.

Materials for chemical processes

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

Raw materials are naturally occurring substances which have not subjected to industrial processing. Semi products are useful secondary products which resulting from primary processing at the plant where they are used. A material proceed at another plant prior to its use in the chemical process is known as a basic material. Waste products are byproducts of other processes.

The raw materials used in chemical industry are divided into the following categories: -

i) Raw materials from upper layer of the earth

Those materials are naturally occurring fuels, employed as chemical materials or as a source of power (coal, peat, petroleum, natural gas). Coal, used either as a source of power or used as a reducing agent during the production of iron.

ii) Ores-rock like material

Which containing metals need to isolate as a pure metal and economically. Iron isolated from magnetite ores, copper also isolated from pyrite ores.

iii) Nonmetallic inorganic naturally occurring materials;

Such materials used as a source of metals (economically produced). Salts of one or more constituents chloride, sulfate, carbonate, phosphate and alumino-silicates as examples.
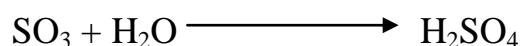
iv) Agriculture crops

Vegetable and animal materials such as ; cotton, wood, fibers, wool, leather and natural products of vegetables.
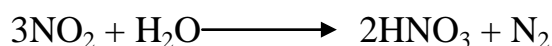
v) Water and air

Water is one of raw materials of the chemical industry. It plays the following roles:

1) In some cases, it participates in the chemical reaction directly.

Ex. (a): (Production of H_2SO_4 acid)

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(b) (Production of HNO_3 acid)

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + N_2$$

2) Water is often used for dissolving solids, liquids or gaseous materials for obtaining suspensions.

3) Water is needed for washing solids and other materials to remove the impurities.

4) It is used for cooling some systems, which react with release of heat.

5) Hot water may be used as a leaching agent to remove some components from wastes, or to increase the reaction or process rate.

Water in its natural state usually contains dissolved impurities. We distinguish three kinds of naturally occurring water:

a) Atmospheric water, one source of water involving rain, snow containing dissolved gases O_2, N_2, CO_2, sometimes H_2S and other gases, organic impurities and dust.

b)Surface water: such as (river, lake, sea water) which contains in addition to dissolved gases, mineral impurities, bicarbonates, sulfates and chlorides of Na, K, Ca, Mg.

c) Underground water: spring, well, like surface water with low content of organic impurities than atmospheric and surface water.

Water is considered to be fresh if its salt content does not exceed 1g/L. According to the salt contained, natural water is classified into:

1) Hard water (which contains 6 mg- equivalent per/L).

2) Moderately hard (which contains 3- 6 mg eq/L).

3) Soft water (contains 3mg eq/L)

Impurities such as gases, salts, organic compounds and micro-organisms, may have important effect on some reactions such as corrosion of equipment of the chemical process or sediment.

Water is conditioned by different operations, depending on the requirements of the chemical process such as:

1) Removal of suspended particles.

2) Softening (reducing the content of Ca^{+2} and Mg^{+2} ions).

3) Desalting.

4) Neutralization.

5) Decontamination (removal of organic impurity, bacteria, fungi, and other microorganisms).

1- Removal of suspended particles:

Removal of suspended particles is carried out by settling or by filtering through a layer of sand. The impurities mainly organic substances present in colloid such impurities removed by precipitation using coagulant reagent $Al_2(SO_4)_3$, then filtered off. Part of bacteria contained in the water is removed by such process.

2-Softening:

Softening or reducing the hardness of water. This process is achieved by adding lime $Ca(OH)_2$ or caustic soda NaOH and soda ash Na_2CO_3, Ca^{+2} and Mg^{+2} ions contained in water are combined into $CaCO_3$ and $Mg(OH)_2$ settle and then is filtered off. If water is softened to 0.03 mg eq/L, Na_3PO_4 is added. In results, the sediment will consist of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$, then filtered off.

3- Desalting of water:

When the water must be desalted more completely this process is achieved by using cation and anion exchange resins. Cation resins contain active group with H^+, Na^+ and NH_4^+ ions, they adsorb ions of metals (Ca^{+2}, Mg^{+2},.. etc) in exchange for these cations. Anion resins contain active groups with OH^- ions which are capable of adsorbing Cl^- , SO_4^{2-}.

4- Neutralization:

This process is necessary when water is contaminated by acids or alkalis. For instance, in cooling sulphuric acid with water some acid will get into it if there is a leak in the cooler. Acid water cannot be recycled without neutralization.

5-Degassing:

This process includes the removal of gases such as H_2S, SO_2, CO_2, which may cause damage (corrosion) of the equipment. The process of degassing is referred as deaeration since inert gas is passed through the water along necessary time-such as nitrogen.

De-pollution of industrial waste water

This is a very important problem in chemical industry, waste water is contaminated by acids, alkalis, salts and various organic impurities, which may destroy vegetables and animals life, and in results it considered as harmful for human. Therefore, methods mentioned before are difficult to use. This problem has not been solved completely and became the problem of staff of chemical plants research laboratories and government agencies.

Fuel and power for the chemical industry

Chemical processes are accompanied by either release of heat "exothermic reaction" or consumption of heat "endothermic reaction".

If a reaction process proceeds with release of heat and only the heat of the reaction is used for maintaining the temperature (i.e) without use of heat from the outside this process is auto-thermic. For instance

$$2SO_2 + O_2 \rightarrow 2SO_3 + Q \ K \ Cal.$$

Where Q, heat released is sufficient to maintain reaction temperature and catalytic effect. However, many exothermic reactions do not produce enough heat for auto-thermicity, and additional heat is necessary to maintain the required process temperature.

Endothermic reactions consume heat (Energy) which must apply from outside the amount of heat necessary is often quite considerable.

However, large additional amount of power are consumed in transporting raw materials, preparing the raw materials such as crushing, grinding and concentrating, moving gaseous liquid and solid materials, compressing gases, etc.

Various kinds of Energy

1) Electric power

This type of energy used for electrolysis of solutions and fused of salts, for electrochemical processes in which the electric energy converted to heat. Electric power is converted in large amounts to mechanical energy such as carrying out physical processes crushing, mixing, moving materials, etc.

2) Thermal energy

This energy used for heating, drying, evaporating, melting and for carrying out endothermic reactions.

3) Energy of light

This energy is used for various photo- chemical reactions as

The synthesis of HCl gas from chlorine and hydrogen, carrying out of polymerization, synthesis of phenol, aniline and other products.

Sources of energy are divided into two groups:

1) Not - renewable:

This group includes coal, petroleum, natural gas and nuclear fuels (uranium, thorium).

2) Renewable group:

Such as the energy of rivers, wind, the sun and heat from the interior of the earth.

Since expenditures on fuel and power usually make up a large part of the cost of the chemical product chemical engineers should solve this problem to increase the efficiency of power utilization, i.e reduce consumption of fuel and power.

The power consumption factor is the ratio of the energy theoretically required for obtaining a unit of the product to the amount actually consumed.

To reduce power consumption, chemical plants utilize the heat carried gases, liquids and solids leaving reaction apparatus and also the heat of compressed gases there by reducing losses of energy to the environment.

Basic laws of chemical technology:

The processing of raw materials into chemical products should be carried out under economically conditions. (i.e) under conditions which result low consumption of raw materials, high quality of products and high process rat.

Cutting the cost of a chemical product means reducing:

-capital investments

-consumption of raw materials

-consumption of power, fuel and labor for unit product.

These factors can be accomplished by introducing the process with high degree of mechanization and automation.

Without knowledge of the laws which govern chemical process it is impossible to control a modern process and to manufacture products economically for ex.:

-determining the sequence of production stages.

-selecting the design of the equipment.

-operating conditions and methods control.

-working out for servicing of equipment and supervising the process.

The basic laws of chemical technology are:

1-Law of conservation of mass discovered by M. Lomonosovc.

2-The periodic law of D. Mendeleyev.

3-Law of conservation of energy.

Law of conservation of mass

This law stated that the total of the materials entering an apparatus for a chemical plant is equal to the mass leaving it (i.e output weight = input weight). It is used to calculate the amounts of materials resulting from a process. On the other hand, it is used to draw up a material balance for the operation of an apparatus (or plant) which is necessary for analyzing the operation of chemical plant and in designing new chemical process.

The physical state of the reacting substances largely determines the group of laws which govern the reactions, as well as the methods, flow diagrams and design of the equipment used for their processing. Therefore, to facilitate the study and discussion of reacting systems and chemical processes, it is convenient to divide them into the two groups of uniform, or uniform or homogeneous group and non-uniform or heterogeneous processes.

Uniform or homogeneous group

Homogeneous processes which include interacting the substances of the same phase gaseous (G), liquids (L) or solids (S).

$$2NO\ (G)\ +\ O_2\ (G) \rightarrow\ 2NO_2\ (G)$$
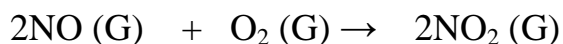
Non-uniform or heterogeneous reaction

Heterogeneous processes: systems consist two are more phases, the reactants may be in the following states; gas- gas, (G-G), gas- liquid (G-L), liquid- solid (L-S), liquid- liquid (L-L immiscible liquids) and solid –solid (S-S).

Example:

$$SO_3\ (G) +\ H_2O\ (L)\ \rightarrow\ H_2SO_4\ (L)$$

$$O_2\ (G) +\ C\ (S)\ \rightarrow\ CO_2\ \ (G)$$
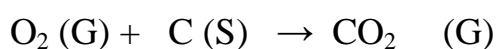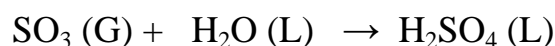
In the chemical industry two-phase systems are the most common.

A chemical processes generally consist the following in the connected elementary processes:

1- feeding the reactants to the reaction zone

2- Chemical reaction.

3- Withdrawal the products from reaction zone.

The overall rate of the process, made up of three elementary processes, will be governed by the slowest of the processes. If the diffusion process is the slowest step, the process is said to lie in the diffusion region. An example of this type, let us consider the heterogeneous reaction, burning pyrite FeS2. The overall reaction equation is given by

$$4FeS_2 +11O_2 \rightarrow 8SO_2 +2Fe_2O_3 +Q\ Kcal$$

For the reaction, the oxygen must first be transported to the surface of pyrite and, after the reaction is completed SO_2 formed must remove from the surface of the particle. In results, the penetration of oxygen becomes slow. This means that the process is lying in the diffusion region. In such a case measures are taken to speed up diffusion, for instance by stirring.

If the overall rate of the process is determined by the rate of chemical reaction. The process said to lie in kinetic region. Then the chemical engineer tries to increase the reaction rate by:

1- Increase the concentration of reactants

2- Raising temperature.

3- Using catalysis.

Chemical processes may be reversible or practically irreversible.

Reversible processes, Chemical equilibrium, and Irreversible processes.

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

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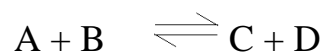
The reversibility of this reaction is indicated by the opposing arrows. At the beginning of the reversible process, when the concentration of the initial substances A and B is high, the rate of the reaction form left to right-the forward reaction will be high, but as the substances C and D are formed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

Reversible reactions do not result in complete conversion of the initial substances A and B into the reaction products C and D. The product yield for given conditions (temperature pressure) is maximum at equilibrium and it is

called the equilibrium yield. If the conditions of the reversible process (temperature, pressure or concentration of one of the reaction components) are changed, the rates of the forward and reverse reactions will change differently and therefore their rates will be equal at other ratios of the concentrations of the initial substances and the reaction products.

Two-phase and poly-phase heterogeneous processes are called reversible if transfer of a substance (or heat) from one phase to the other is possible in both directions.

The effect of temperature and pressure on the chemical equilibrium of homogeneous and heterogeneous processes is determined qualitatively by the Le'Chattier principle when the equilibrium of a system is disturbed the changes which occur are such as to weaken the disturbance.

Thus, when a system in equilibrium is heated the changes will be such that heat is absorbed (the resulting processes will resist a rise in the temperature). While an increase in pressure results in processes which lead to a decrease in the volume of the system. By way of illustration let us consider the effect of temperature and pressure on several reversible exothermic reactions.

A reversible exothermic gas phase reaction without a change in volume, i.e. with the volume of the products obtained equal to that of the initial substances. An example is the reaction of CO with water vapor (CO conversion) to produce hydrogen.

$$CO + H_2O \text{ (Vapor)} \rightleftharpoons H_2 + CO_2 + Q \text{ Kcal.}$$
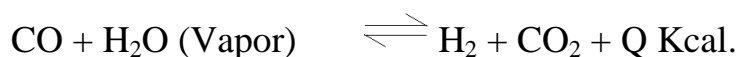
If the temperature is raised, the equilibrium of this reaction will shift in the direction of the initial substances (i. e. to the left), and the equilibrium yield of hydrogen will decrease. Since the volume of the system does not change in the reaction (two molecules of the initial substances produce two molecules of end products) in this case pressure does not affect the equilibrium (does not shift it). However, the degree of conversion of one of the initial products can be increased by using an excess of the other substance (compared with the amount necessary

for the reaction). In this particular reaction by using an excess of water vapor the degree of oxidation of CO to CO_2 can be increased and more hydrogen obtained per unit carbon monoxide (CO) spent.

2- Reversible exothermic gas phase reaction proceeding to the right (forward reaction) with a decrease in volume for instance synthesis of ammonia, NH3 from nitrogen and hydrogen.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + Q \text{ Kcal.}$$
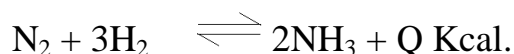
In the case four molecules of the reactants produce two molecules of the end product. The equilibrium of this reaction will be affected both by the temperature and the pressure.

According to the Le' Chatelier principle increase in temperature will shift the equilibrium to the left i.e. toward an increase the concentration of the initial substances. Pressure will exert the opposite effect, i.e. its increase will shift the equilibrium to the right and increase the yield of the product, ammonia.

A reversible endothermic gas phase reaction resulting in an increase in gas volume, for instance interaction of methane, CH4, with vapor (methane conversion) :

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 - Q \text{ K Cal.}$$
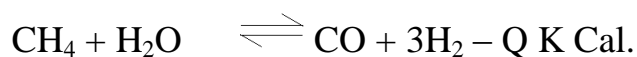
In this reaction two molecules of the reactants produce four molecules of the end products. An increase in temperature will shift the equilibrium of this reaction from left to right, and in pressure from right to left. In practice, high pressure is sometimes used in such reactions to increase the reaction rate and decrease the size of the equipment.

These examples show that by changing the temperature or the pressure the equilibrium of a reversible reaction can be shifted, and by changing the ratio of the reactant concentrations the degree of conversion of one of them can be increased. Reversible reactions play a very important role in industrial chemistry. If one knows the equilibrium relationships, the equilibrium of a reaction can be shifted in the required, economically advantageous, direction.

In practically irreversible processes at equilibrium there is almost complete conversion of the reactants to the reaction products. Among such reactions are, for instance, the combustion of coal ($C+O_2 \rightarrow CO_2+Q$), of sulfur ($S+O_2 \rightarrow SO_2+Q$), etc.

It is much easier to select suitable conditions for irreversible reactions then for reversible ones. An increase in the temperature, as a rule, results in an increased reaction rate. The temperature can, of course, be raised only up to a certain limit depending on the specific nature of the reaction. For instance, the temperature of sintering slugging, thermal decomposition of the reactants.

For reactions in which there is a gas phase an increase in pressure also increases the reaction rate, since an increase in pressure results in an increase in the concentration of the gaseous reactants.

Knowing how the equilibrium of reversible reactions depends on various factors affecting the process, one can determine the conditions at which the reversible reaction will be shifted toward the formation of the reaction product. This will also make it possible to calculate the maximum yield of the reaction product at given conditions. Process kinetics, i.e. the rate of reaction of the initial substances and the laws governing reaction rates, are no less important than the laws of equilibrium.

The Rate of Chemical Processes

The rate of a chemical process is usually expressed in terms of the amount of the product obtained per unit time. Such conditions for a chemical process should be maintained at a rate which is economically most advantageous. The rate of a chemical process is the resultant of the rates of the forward and reverse reactions. The higher the rate of the forward reaction and the lower the rate of the reverse one, the higher will be the rate of the overall process, i.e. the greater the yield of the product per unit time.

At the beginning of a process, when the concentration of the reactants is high, the reaction rate is considerable, but as the reaction approaches equilibrium

it slows down and tends to zero. In industry it is not profitable to conduct a reaction at a low rate and therefore a reversible reaction is not as a rule brought to a state of equilibrium, i. e., in reversible processes the product yield is in practice always below the equilibrium yield.

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

The methods used for increasing the rate of the process depend on the physical state (gaseous, liquid or solid) of the reactants. One of the ways to increase the process rate is to increase the concentration of the reactants, i.e. to enrich solid raw materials and concentrate gaseous or liquid ones. Methods of enriching (concentrating) raw materials are removing impurities. An increase in the concentration of the reactants has a strong effect on the rate of the process. In homogeneous processes the rate of the process. In homogeneous processes the rate of the chemical reaction is directly proportional to the molar concentration of the reactants.

For reversible heterogeneous processes not only the concentration of the reacting component C in the carrier phase at a given moment, but also C_{eq} the concentration of this component in the same phase at equilibrium must be taken into account. The higher the concentration C as compared with the equilibrium concentration (C_{eq}) i. e. the greater the difference $C - C_{eq}$ the higher will the rate of the process be. This difference $C - C_{eq}$ is termed the driving force of the process. At equilibrium the actual concentration and its equilibrium value are equal and consequently, the driving force of the process $C - C_{eq}$ is zero, i.e. the process has reached equilibrium and its rate will be zero.

In reversible reactions the process rate can be increased by removing the product from the reaction zone and thereby decreasing the rate of the reverse reaction.

From a gas mixture the reaction product can be removed by condensation (conversion of the gas to the liquid state) or by sorption with liquids or solids. Sorption of a gas by liquids is called absorption, sorption by solids, adsorption. In many industrial processes removal of the product is achieved by with-drawing the gas mixture from the reaction apparatus, separating the product, and returning the un-reacted substances into the reaction zone. The result is a cyclic process. A typical cyclic process is the synthesis of ammonia.

From a liquid mixture the reaction product can be removed by depositing it in the form of crystals (precipitate), the solution remaining after separation of the precipitate is returned to the reaction. For instance, in production of potassium chloride. The reaction product can also be removed from a liquid mixture by evaporating it or by sorption with liquids or solids.

Usually to increase the reaction rate the temperature and pressure are raised, since they greatly affect many chemical processes. Van't Hoff's law can be applied to most reactions. According to this law the reaction rate is increased 2 to 10 times by a 10 $^{\circ}$C rise in the temperature, while the rate of diffusion-controlled processes increases only 1.1-1.3 times. The large increase in the rate of homogeneous gas reactions with temperature is due to the increased velocity of the gas molecules and the greater number of collisions per unit time. It should, however, be remembered that there is an optimum temperature for many reactions at which the reaction rate ceases to increase and beyond which it begins to drop with a further increase in temperature. This effect of temperature on the rate of some reactions may be caused by various factors one of which is decomposition of the initial substances at high temperatures and a consequent decrease in the concentration of the reactants which greatly affects the rate of the chemical process.

When a gas phase reaction is involved a pressure increase, it is equivalent to an increase in the concentration of the gas component. Pressure is used to increase the rate of a chemical process primarily in cases where it is impossible or irrational to directly increase the concentration. i.e. to add more of one of the reacting substances, for instance in the synthesis of ammonia or methanol.

Temperature and pressure also strongly affect heterogeneous processes. Thus, an increase in pressure or a decrease in temperature will increase the rate and degree of sorption of gases by liquids and solids, while desorption of a gas (vapor) from a liquid or a solid sorbent is accelerated by raising the temperature or lowering the pressure (down to a deep vacuum).

Mixing the Reactants

The degree of mixing of the reactants strongly influences the rate of chemical reactions. In homogeneous (uniform) processes vigorous stirring results in practically uniform concentrations of the initial substances throughout the entire volume and thus in accelerating their interaction. In heterogeneous (non-uniform) systems stirring increases the interface area of the reacting phases. Active stirring of heterogeneous systems is especially helpful in cases where the process lies in the diffusion region as given by the equation represents the burning of pyrite (page 11).

There are a wide variety of methods for increasing the interface area of the phases, depending on the physical state of the reactants, and they are usually aimed at increasing the surface area of the heavier phase. Thus, in gas-solid (G.S) and liquid-solid (L-S) reacting systems the solid initial material is crushed or used in the form of porous lumps, in which the internal area of the pores is many times larger than the external surface area of the lumps. Solids are size reduced in crushers and mills of various types.

Solid reactants may be agitated by different methods. The following methods are used for gas-solid (G.S.) and liquid-solid (L-S) heterogeneous reacting systems.

1- A granular solid with a gas or liquid flowing around the particles can be agitated on shelves by mechanical stirrers an example is the pyrite furnace shown in **Fig. 1**.
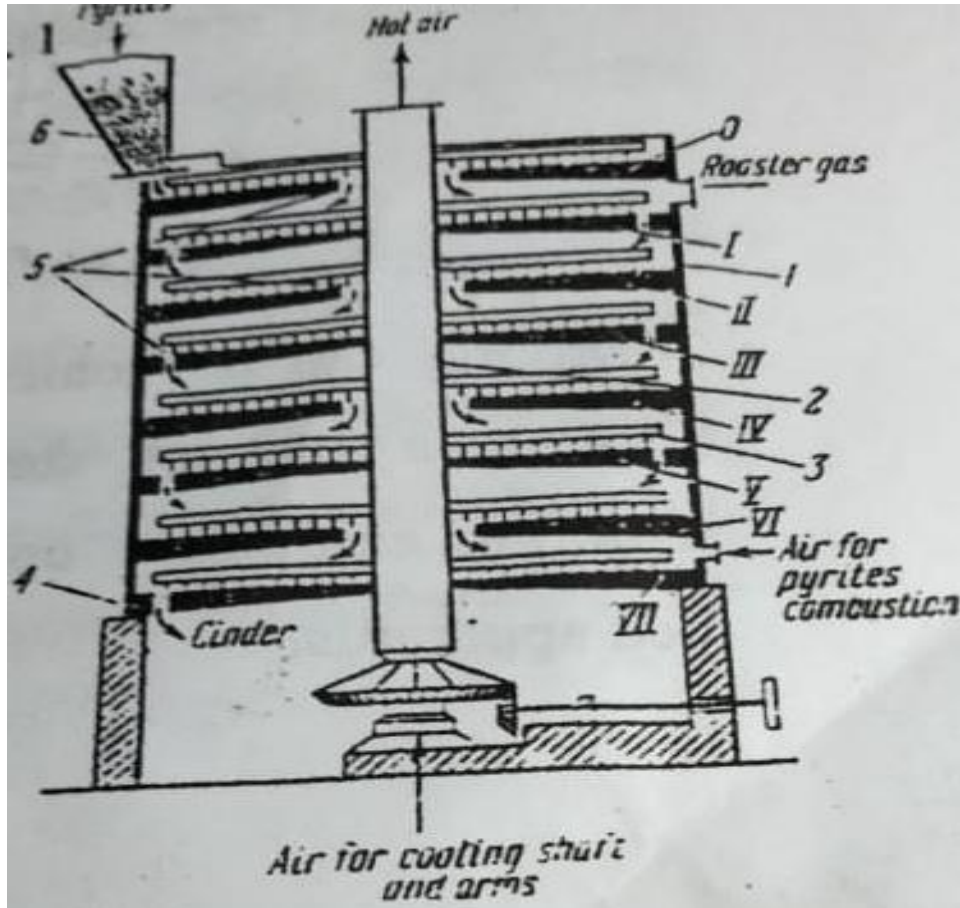

Figure 1

2- If a finely divided solid is to be mixed in a fluid stream, for a G-S system this can be done by spraying the divided material together with the gas into an empty chamber, an example is the pyrite spray furnace of Fig. 2. For an L-S system the solid is mixed with the liquid by means of an agitator, such a mixer for phosphate meal and sulphuric acid, used in manufacturing super-phosphate, is shown in Fig. (see the manufacture of super-phosphate).
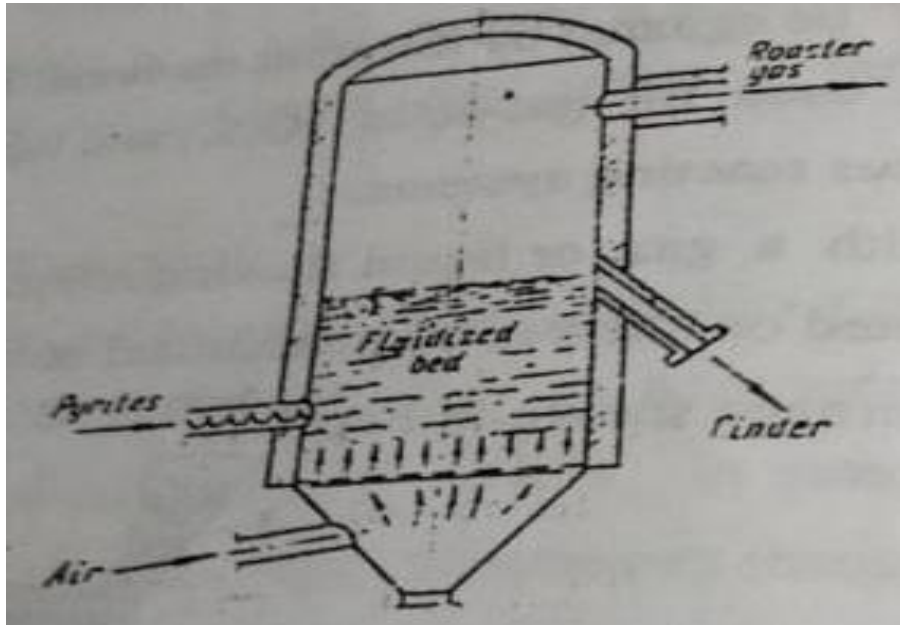
Figure 2

3- Mixing can be achieved by passing a gas or liquid current through a bed of stationary particles of a divided solid material, equipment operating on this principle is called static bed apparatus.

4- A solid granular material can be mixed with a gas or liquid in a suspended, or fluidized, bed (see Fig. 3). In a gas-liquid (G-L) reacting system the gas-liquid interface area is increased by the following methods.
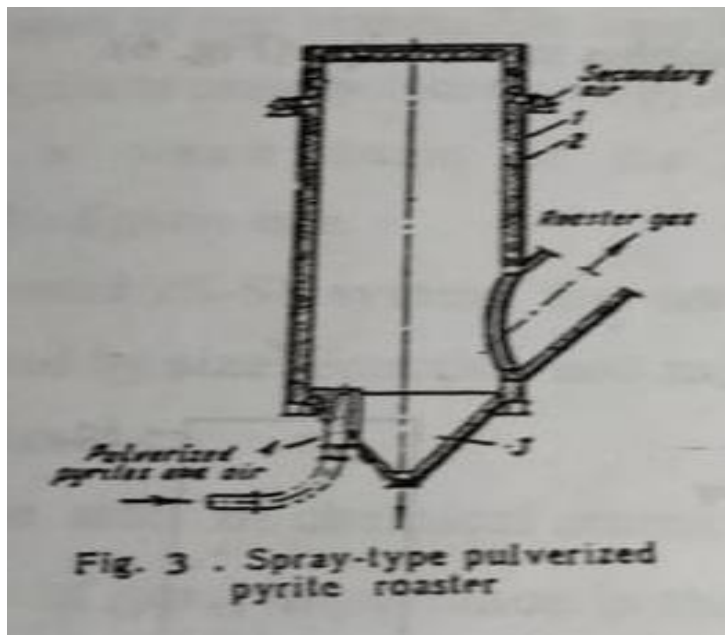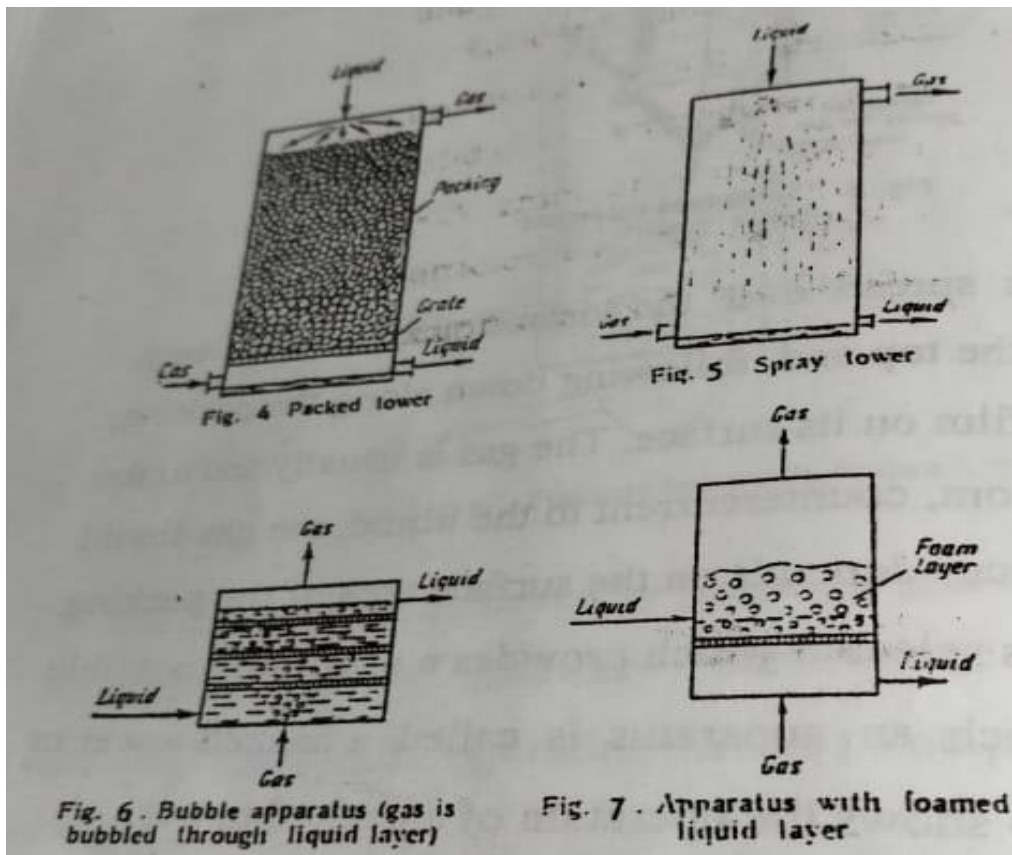

Fig. 3 . Spray-type pulverized pyrite roaster

Figure 3

1- The liquid is spread over the surface of a packing which fills a tower, at the top and, following down along the packing, forms a liquid film on its surface. The gas is usually fed to the tower at the bottom, countercurrent to the liquid, the gas-liquid contacting surface depends on the surface area of the packing and a packing is selected which provides a maximum possible surface area. Such an apparatus is called a packed tower or column. Figure 4 shows the operation of a packed tower.

2- The liquid is sprayed in top a hollow tower, or chamber to which the gas is simultaneously fed (Fig. 5) here the gas-liquid interface is equal to the total surface area of the liquid drops suspended in the apparatus volume.

3- Gas bubbles are passed up through a liquid layer. To break the gas current into small bubbles sieve trays (Fig. 6).

4- The gas is passed through a liquid layer at such a high speed that the liquid foams i.e. suspends in the gas current in the form of films. Jets and drops, figure 7 illustrates the operation of such an apparatus.

Fig. 4 Packed tower

Fig. 5 Spray tower

Fig. 6 . Bubble apparatus (gas is bubbled through liquid layer)

Fig. 7 . Apparatus with foamed liquid layer

In a system of two immiscible liquids (L-L) the interface area of the liquids is usually increased by stirring them to form an emulsion in which drops of the heavier liquid are suspended in the lighter one.

In a solid-solid (S-S) system the area of contact of the solids is increased by size reduction and mixing.

Catalytic Processes

Increasing the rate of chemical reactions by means of so-called catalysis is of great importance in the chemical industry. The utilization of catalysts in almost all new chemical processes has made it possible to use new raw materials and to obtain various complex products from hydrogen nitrogen, carbon monoxide, methane, ethylene etc. It is due to the development of catalytic processes that the dream of the Great Russian scientist D. Mendeleyev has come true coal, petroleum and gases have become valuable raw materials for the chemical industry.

Catalytic processes came into wide use at the beginning of this century. These catalytic syntheses of ammonia and methanol, reactions of hydrogenation, oxidation and polymerization are used extensively in the chemical industry.

One of the features of a catalyst is that after taking part in a reaction it normally is not changed chemically. One of the examples is the commercial synthesis of ammonia from nitrogen and hydrogen. If we mix nitrogen and hydrogen, no appreciable amount of ammonia can be obtained, even if we raise the pressure to 1000 atm. or use high temperatures. This process has become possible solely due to the use as a catalyst of ordinary iron, with small additions of oxides of potassium aluminum, calcium, silicon, which are called promoters or activators.

An iron catalyst for ammonia synthesis lives a long time and its activity decreases only as a result of mechanical damage, high temperature or impurities in the gas (catalyst poisons).

An important property of catalysts is their selectivity. Of the many possible reactions between the initial substances, the catalyst as a rule speeds up only one reaction, without noticeably affecting the rate of the others. Thus , the following products can be obtained from carbon monoxide and hydrogen, depending on the catalyst used.

Table 1

Initial substances	catalyst	Products obtained
$mCO + nH_2$	Copper or Zinc-chromium	Methanol
	Alkaline	Methane land water
	Iron and	Olefins and paraffins
	Cobalt	
	Ruthenium	High-molecular paraffins
	Aluminium-Thorium	Isobutane
	Zinc-thorium	Isopropane

All these products are used in the chemical industry.

We distinguish two basic kinds of catalytic processes: homogeneous and heterogeneous catalysis.

Homogeneous catalysis is a catalytic process in which the catalyst and the reactants are in the same physical state: gas-gas, liquid-liquid.

Heterogeneous catalysis is a catalytic process in which the catalyst and the reactants are in different physical states. In industrial heterogeneous catalytic processes the reactants are usually in the gaseous phase and the catalysts are solids.

Among such processes are ammonia synthesis, oxidation of SO_2 to SO_3 (the production of sulphuric acid) and oxidation of ammonia (the production of nitric acid).

Some reactions are accelerated in the presence of catalysts thousands and millions of times and proceed at lower temperatures, which results in the saving of power. Catalysts do not change the equilibrium of the reaction, but they speed up approach to equilibrium. The nature of catalytic action is not yet fully understood, and therefore experimental data are of primary importance in selecting a catalyst for a particular reaction.

For a heterogeneous catalytic process in which the reactants are gases and the catalyst is a solid the accelerating effect of the catalyst can be explained in the following simplified way. The molecules of a gaseous substance are in constant chaotic linear motion. When they collide the velocity of the individual molecules changes and they begin to move about at various speeds, from very high to very low ones.

In many cases colliding molecules in a gas mixture lack the necessary kinetic energy to overcome the forces hindering chemical interaction. Therefore the reaction between the gases will proceed very slowly. A rise in temperature will increase the number of molecules of high kinetic energy and thus increase the rate of reaction between them, but this is not always sufficient. Speaking of such gas reactions we say that their activation energy is very high, i. e. for a reaction between such gases to occur high energy of the molecules is necessary to overcome the forces of mutual repulsion between the molecules and to weaken the bonds between the atoms in the molecules. The catalyst reduces the activation energy of the reaction.

Schematically, this can be represented as follows:

Two molecules A and B reacting in the gas phase to form a new substance AB by the reaction A + B = AB

The activation energy of the reaction is high and therefore it proceeds very slowly.

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

$$A + B + K \rightarrow AK + B \rightarrow AB + K$$

Where K is the catalyst.

It is seem from the above scheme, that at first the catalyst reacted with the molecule A to form an intermediate compound AK, then the second reacting molecule B combined with AK to form the substance AB. After the reaction is completed the catalyst is returned to its original form. With this course of the reaction the activation energy is less and the reaction rate increases.

In heterogeneous catalysts, as a rule, have a developed surface area. The surface are of an iron catalyst in ammonia synthesis amounts to about 101 m^2/g. there are catalysts with as area of up to 400 m^2/g.

Substances which do not speed up the reaction, but retard (inhibit) it, are called negative catalysts, or inhibitors. For instance, when motor fuel are put away for storage it is advisable to add a small amount of substances which retard oxidation and polymerization processes.

Manufacture of Ammonia

Nitrogen plays its part in the life of plants and animals in the form of compounds, and not as elemental nitrogen. Ammonia is the most important of the nitrogen compounds taking part in nitrogen metabolism.

The bulk of ammonia made is used in the production of fertilizers. Ammonia serves as a raw material for manufacturing nitric acid, which is employed (in addition to make fertilizers) in the production of dyes and their intermediates, plastics, chemical fibers, photographic materials, drugs, explosives, etc.

There are only a few industrially important natural sources of combined nitrogen. The known deposits of sodium nitrate $NaNO_3$ are located in Chile and South Africa. Small amounts of ammonia sulphate, $(NH_4)_2SO_4$, are obtained in the process of purification of coke-oven gas. These sources, however, could not satisfy the rapidly growing demand for combined nitrogen in agriculture and industry. At the end of the 19th century an urgent need for the production of nitrogen compounds from atmospheric nitrogen.

The air surrounds us is an rich source of uncombined nitrogen. However, combining atmospheric nitrogen into compounds proved to be a difficult problem. Atmospheric nitrogen is in the form of stable N_2 molecules, which react withother elements very difficult and nitrogen is considered an inert gas.

At the beginning of 20th century by joint efforts of scientists and engineers of many countries the problem of combining atmospheric nitrogen was developed. The following methods for manufacturing nitrogen compounds from atmospheric nitrogen were developed:

1- Arc process:

In this method nitrogen is combined with atmospheric oxygen at high temperature (2500- 3000 C^o) in the flame of an electric are furnace according to the following reaction.
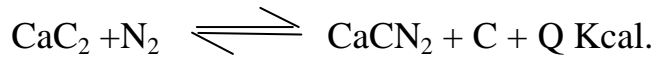
$$N_2 + O_2 \rightleftharpoons 2NO + Q \text{ Kcal.}$$
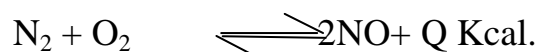
The NO is oxidized to NO_2

$$2NO + O_2 \rightleftharpoons 2NO_2$$
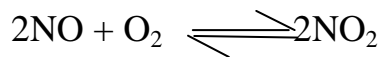
Then NO_2 adsorbed by H_2O to form HNO_3 or adsorbed by $Ca(OH)_2$ to form $Ca(NO)_2$ power consumption for this method is 60.000 K W h per ten

2- Cyanamid process:

This process is carried out by combining N2 with calcium carbide ($CaC2$) at 1000 Co according to the following equation:

$$CaC_2 + N_2 \rightleftharpoons CaCN_2 + C + Q \text{ Kcal.}$$

Power consumption for this method 10.000 to 12000 Kwhr per ton.

3- Ammonia process:

This process has advantages over the arc and Cyanamid processes. Power consumption per ton of combined nitrogen is several times less than in the Cyanamid process. The ammonia process is today the principal method used for producing combined nitrogen. Ammonia serves as the basis for manufacture of all the other nitrogen compounds. Ammonia is made in this process by reversible reaction

$$N_2 + 3H_2 \rightleftharpoons NH_3 + Q \text{ Kcal.}$$
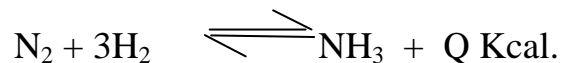
i.e the ammonia is synthesized from nitrogen and hydrogen. The process is conducted in the presence of an iron catalyst at high pressure and temperature of about 500 Co.

The first step in the process is to obtain the initial gases, nitrogen and hydrogen.

Source of nitrogen

Air is the name given to the mixture of gases which form the gaseous layer encircling the earth, i.e its atmosphere. The gases making up the bulk of the air are nitogen (78.03%) by volume in dry air, oxygen (20.99%), and argon (0.94%). Hydrogen, neon, helium, krypton, xenon and carbon dioxide are also present in the air in the small amount.

Separation of air into nitrogen and oxygen is based on the difference in the boiling points of liquid nitrogen and liquid oxygen as given in table 2.

Table 2: Air components in percentage per volume and the boiling points of N_2 and O_2

Gas	Volume %	Boiling point of liquid gas Co
N2	78.03	-195.8
O2	20.99	-182.9
Ar	0.94	-

**Separation of N_2 and O_2**

According to the values of O_2 and N_2 (liquids) boiling point, If we evaporate the liquefy air, N_2- well evaporate before O_2. The process is conducted through the following stages:

1) Air purification and drying.

2) Air liquefy and drying

3) Air distillation and drying

1- Purification and drying

Air subject and liquefy may contain the dust, water vapors (humidity) and CO_2 gas. The dust is separated by passing air through oil filters. These filters are consisting of columns filled with mineral oil, metal rings wetted with this oil.

The carbon dioxide is eliminated by adsorption using (caustic soda) sodium hydroxide .

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$
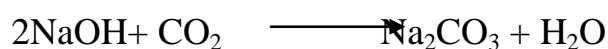
Humidity (the water vapors) is eliminated by adsorption using solid adsorbents such as: Silca gel, activated aluminia or caustic soda.

2- Liquefaction of air

This process is achieved by deep cooling (-70 C^o) at high pressure. As a results of high pressure exposed, the mixture temperature is raised. In chemical industry cooling air to low temperatures one of the following way used.

a)Throttling method.

Expansion of compressed air by allowing it to flow through throttle into a space at lower pressure.

b)Expand methode

In this method the air compressed and causing it to do work, such as compress gas engine or turbine type.

If the expansion of the compressed air is carried out in an apparatus provided with good heat insulation, the temperature of the air expand by throttling or in a compressed gas engine will be lowered.

The idea of these methods depend on that air expand exhaust part of internal energy, in the first case, acting against the gas molecules in front of the throttle, and in the second moving the piston or the turbine. In results, the temperature will drop. Repeating the process and using thermal of exchangeable way, further reduction of air temperature is attained. Finally, at a point reached, condensation of mixture begins and air liquefies.

3- Air liquid distillation

Liquid – air is in equilibrium with it vapor. In the vapor in equilibrium with a liquid mixture there will always be more of the lower-boiling component than in the liquid. In the case of liquid air the vapor over boiling air will contain 93% nitrogen and 7% oxygen. Full separation of liquid air. According to the boiling point of N_2 and O_2 the separations occur by rectification of air – liquefied. The complete separation achieved by double rectification columns.

Source of H_2

Hydrogen- synthesis by one of the following ways:

1- Conversion of CO in water gas

$$CO + H_2O \longrightarrow H_2 + CO+Q \text{ Kcal.}$$

Water gas obtained by or gasifying solid or liquid fuels yields hydrogen, whereas production of a hydrogen-nitrogen mixture results when producer gas

obtained by employing a mixture of air and steam for gasification, is used. For ammonia synthesis using this method, producer gas of approximately the following composition: 37%H_2, 22%N_2, 6% CO_2 and about 1% of CH_4 and H_2S. The conversion of carbon monoxide proceeds by the reversible reaction; this process conducted, according to the reversible reaction

$$CO + H_2O \; \underset{\longrightarrow}{\longleftarrow} \; H_2 \; + CO_2 \; + Q \; Kcal.$$

Chromium-activated iron catalysts are employed, which are easily poisoned by hydrogen sulphide H_2S whose presence in the gas and result in metal corrosion. For this reason H_2S must be removed from reaction zone by :

1- Dry purification process , the gas mixture pass through a solid adsorbent using Fe $(OH)_3$ and CaO.

2- A widely used method is the arsenic-soda process using alkaline solution of oxy-thioarsenic salt.

$$Na_4As_2S_5O_2 + H_2S \rightarrow \; Na_4As_2S_6O + H_2O$$
$$Na_4As_2S_6O + 0.5 \; O_2 \; \rightarrow \; Na_4As_2S_5O_2 + S$$
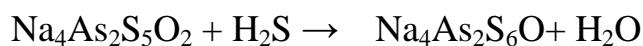
Recently, most of hydrogen used in NH_3 manufacture was obtained form coke by gasifying to CO. This drop the cost of NH_3- production, since coke fuel has been replaced as a raw material of gases, such as natural gas, and gases of petroleum refining.

Conversion of methane of natural gas

Natural gases of some fields contain a high percentage of CH_4. Hydrogen is obtained from natural gas by reacting the latter with steam and oxygen as follows:

$$CH_4 + H_2O \; \longrightarrow \; 3H_2 + CO - Q \; Kcal.$$
$$CH_4 + \tfrac{1}{2} \, O_2 \; \longrightarrow \; 2H_2 + CO + Q \; Kcal.$$
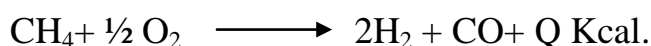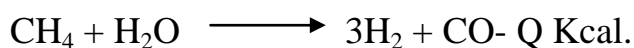
The CO is then oxidized by steam to CO2 and hydrogen (conversion of CO). The conversion of methane by steam is conducted by either2- ways:

(i) Pressure close to atmospheric pressure

(ii) At elevated pressure.

The second way is better one, since the natural gas delivered to the plant is at high pressure. In results reduction of the power consumption for subsequent compression of gas in the process of ammonia production. In addition, reduce the size of equipment and piping.

On the other hand, the reaction is carried out at high temperature 1300-1400 ^{o}C (high- temperature conversion of methane) or, in the presence of a catalyst. Also, the reaction carried out at temperature 300-900 ^{o}C in the presence of catalysis Ni-deposited on alumina (Catalytic conversion).

The second process (including catalysis) meets poison effect of catalysis by H$_2$S. The life time of catalyst is about 4- years.

In the high-temperature methane conversion process the temperature is maintained at 1300-1400°C by using proper steam-gas-oxygen ratio. The following Figure is the diagram of combined steam-oxygen conversion of methane and carbon monoxide at atmospheric pressure.

The natural gas first passes through saturating tower 1 countercurrent to hot water (85°C): here it is saturated with water vapour. At the exit from the tower steam is added to it and the steam –gas mixture is directed to exchanger 2, where it is heated to 500-6000°C. From the heat exchanger the mixture goes to mixer chamber 3, into which oxygen or oxygen-enriched air (about 40% O$_2$) is also introduced. The steamed-gas mixture obtained, at a temperature of 4500$^{°}$C, enters methane converter 4.

After passing through the catalyst the gas leaving the converter has a temperature of 8000°C. The residual content of methane is 0.4 to 0.5%. The gas flows to humidifier 5, where water vapour is added by the evaporation of steam condensate and the temperature is reduced to 7500°C. Then the converted gas passes through heat exchanger 2, where it gives up available heat to the gas going to the mixer chamber and converter and, 4000°C, it enters carbon monoxide converter 6. The available heat of the gas leaving this converter is used to produce

steam in waste-heat boiler 7. The gas is passed further through water heating tower 8, spray cooler 9, and is sent on for removal of CO_2 and remaining CO.

Purifying the converted gas

Besides the nitrogen and hydrogen for ammonia synthesis, the converted gas contains other gases, which are impurities. For instance, gas obtained by steam-oxygen conversion of methane at atmospheric pressure, after nitrogen is added to it, contains 68% nitrogen and hydrogen, about 28% CO_2, 3% CO, 0.4% CH_4, 0.3% Ar, and traces of O_2 and H_2S. The oxygen-containing impurities (CO, CO_2, and H_2O) and hydrogen sulphide are poisons for ammonia synthesis catalysts, methane and argon are inert impurities which accumulate in ammonia synthesis equipment and reduce its output. The catalyst poisons are especially harmful and these impurities must be removed from the converted gas.

The following methods of purification are used: - condensation of the impurities by subjecting the gas to deep cooling and then washing it with liquid nitrogen; removing the impurities by absorption with liquids or adsorption on solid sorbents; purification by catalytic hydrogenation.

The CO_2 is usually removed from the gas using liquid sorbents. This is based on the solubility of CO_2 in water, ammonia liquor, solutions of alkalis, monoethanolamine, etc. When water is employed, the gas, at 16-28 atm, is fed to the bottom of a packed tower countercurrent to cold water. The water containing the dissolved carbon dioxide goes from the tower to a turbine, which, together with an electric motor, rotates the shaft of the pump delivering water to the tower. In this way the electic power consumed in pumping dioxide, which is released from the water when the pressure is reduced, is utilized in the production of urea and dry ice. After the water purification procedure the gas contains from 2 to 3% carbon dioxide, which is removed by washing with a caustic soda solution. In recent years water is being replaced as the solvent for CO_2 by solutions of ethanolamines-monoethanolamine, $NH_2CH_2CH_2OH$, and diethanolamine, $NH(CH_2CH_2OH)_2$. The amine carbonates and bicarbonates formed when CO_2 is

absorbed are decomposed with release of CO_2 by heating. After it undergoes such regeneration the ethanolamine solution is recycled to the packed absorption tower.

The carbon monoxide is usually removed from the gas by absorption with aqueous solutions of copper ammonium salts complex compounds. CO absorption is conducted at a high pressure (100 to 300 atm) and at a temperature of 0 to 200°C. The copper-ammonium solution is regenerated by heating it and reducing the pressure to the atmospheric level. By such procedures the CO content of the hydrogen–nitrogen mixture is reduced to 0.004% and that of CO_2 to 0.003%.

Electrolytic method of manufacturing hydrogen and oxygen

Hydrogen and oxygen can be obtained by electrolysis of H_2O. Pure water is a poor conductor of electricity (Weak electrolyte) and therefore not used for electrolysis, aqueous solution of alkalis NaOH, KOH or acids H_2SO_4 being used instead of H_2O. When a direct current at 1.9 to 2.5 V is passed through such solutions the water decomposes. In results O_2 and H_2 evolved at anode and cathode respectively. This method results in producing high purity of O_2 and H_2 gases. Because of the high consumption of the electrolysis procedure it is rarely used at present for producing hydrogen used in NH_3 synthesis.

Fundamental theory of ammonia synthesis

Ammonia synthesis represented by the follow reversible reaction.

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + Q \text{ Kcal.}$$
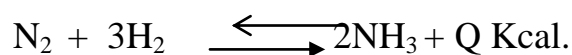
According to Le' Chatelier principle,

a) Decrease of temperature shifted the equilibrium toward ammonia formation (Exothermic reaction).

b) Rise the pressure shifted the equilibrium toward ammonia formation (reaction accompanied by decrease of volume).

Without a catalyst, ammonia synthesis proceeds at an extremely slow rate even at very high temperatures. An increase in temperature reduces the equilibrium content of the ammonia. Consequently, a catalyst which increases the rate

synthesis at low temperatures must be used. The following table illustrates the % NH_3 per volume at different temperature and pressure.

Table 3: NH_3% per volume at different pressure and temperature

Temperature.^{o}C	NH_3% per volume at different pressure, atm.				
	100	300	1000	2000	3500
200	-----	89.94	98.29	--------	--------
300	-----	70.96	92.55	--------	--------
400	25.12	47.00	79.82	93.07	97.73
500	10.61	26.44	57.47	-------	-------
600	4.52	13.77	31.43	-------	-------
700	------	7.28	12.83	-------	--------

Iron is used to employ as a catalyst and obtained from the reduction of Fe_2O_3 and Fe_3O_4. As results, at higher temperatures, the reaction products affect the activity of the catalysis. At present to ensure high, stable activity of catalyst promoters (Al_2O_3, K_2O, CaO, and SiO_2) are added to Fe. It was found that the catalyst used for ammonia synthesis sensitive to different impurities in (N_2-H_2) mixture. There are 2-types of catalyst poison.

1- Reversible Poison:

This type caused by O_2 containing compounds in the (N_2-H_2) Mixture, such as CO, CO_2, H_2O. This impurities result in sharply drop of catalyst activity but the catalyst restored, and the activity increased to the former level.

2- Irreversible Poison:

These type caused by S containing compounds such as ((H2S) is the activity of catalyst not return to the formed level.

Factors affect the ammonia process rate:

Kinetically, we know that the slowest step in a chemical reaction is the rate determining. In the given process is, N_2 adsorption is the slowest step (i.e) the process, is catalysis controlled.

The rate of ammonia synthesis is depending on the following factors:

1- Temperature
2- Pressure, concentration of $N_2 - H_2$ mixture
3- present of an inert gas such a argon or methane.
4- Activity of catalyst use
5- Space velocity

Space velocity

Space velocity is defined as the volume of N_2- H_2 mixture in m^3 pass through $1m^3$ of catalyst in one hour. The following table recorded the results obtained for NH_3

Table 5: NH_3% content per volume at different temperature and space velocity.

Space velocity m^3/m^3.hr	NH_3% content per volume at different temperature, ^oC			
	450	475	500	525
15,000	19.6	21.6	23.0	19.3
30,000	14.6	17.7	18.2	16.7
45,000	12.7	15.2	16.5	15.7

From this table its clear that with increasing the space velocity of $H_2 - N_2$ Mixture to 3 times (25,000 - 45,000) NH_3% content is slightly decrease with increasing the space velocity at the same temperature However, higher the space velocity, lower catalyst consumption, (catalyst utilized with more efficiency long life time of catalyst).

This is based on economic considerations even the low amount of NH_3 produced. In addition, the heat released is not sufficient for autothermic synthesis and may used outside source of heat.

Industrial ammonia synthesis

According to the pressure employed, ammonia synthesis is divided into 3 types.

a) Low pressure synthesis 100 atm.

b) Medium pressure synthesis 200-250 atm

c) High pressure synthesis 600-1000 atm.

Commonly, medium pressure synthesis is used in those systems not all N_2–H_2 mixture completely converted to ammonia. For such reason the recycle schemes are used, where fresh H_2-N_2 mixture feed with the remaining port of un-reacted N_2–H_2 to the converter. Exchangeable processes take place by evaporate of ammonia to cool the other part.

The process was simplified in following flow sheet :
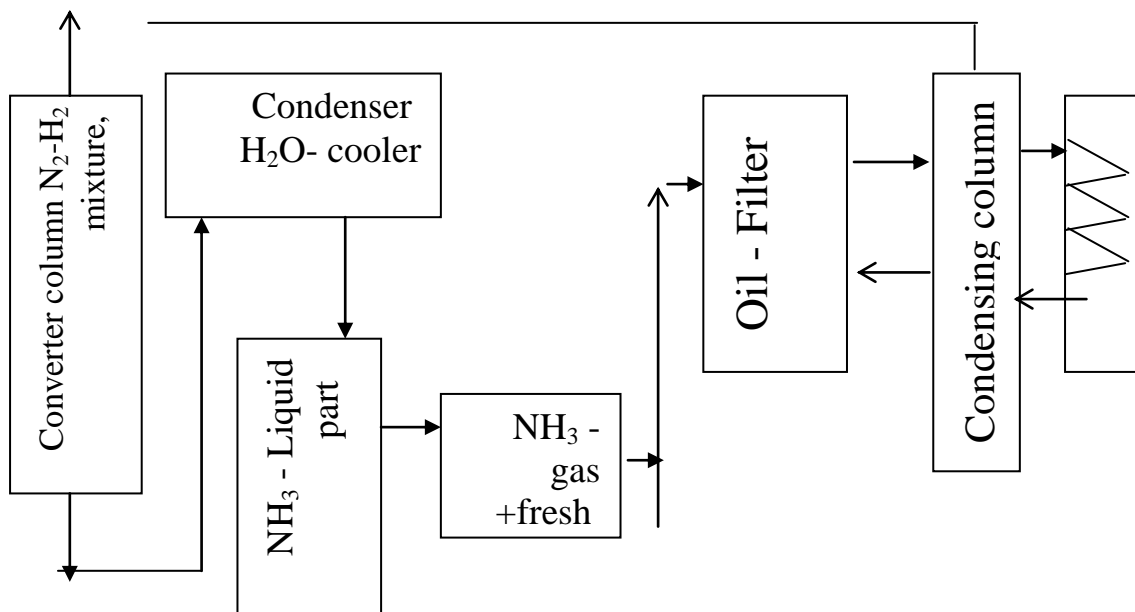
Manufacture of Caustic Soda

Caustic soda, chlorine and HCl acid found wide application in a number of branches of the economy.

Caustic soda (NaOH) is strong alkali. It's used in soap making, production of aluminum, a semi-product from which aluminum metal is smelted, manufacture of artificial silk, in organic synthesis, and other branches of industry.

There are two methods for production of caustic soda. :

(I) Chemical method: (Chemical method including 2-ways)

a) Lime – soda method

This method consists, treating of soda solution with milk of lime according to the following equation:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$$
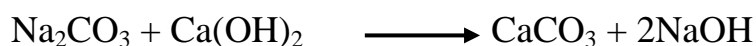
This process is carried out at a temperature of 80 ^{o}C in reactors with agitators. The precipitate $CaCO_3$ is filtered off and the resulting solution evaporated in a vacuum evaporator and then concentrated to 92% in caste-iron pots the molten soda is poured into iron drums to solidify.

(b) Ferrite Method

This method consists, sintering a mixture of solid soda ash Na_2CO_3 with Fe_2O_3 1100 to 1200 ^{o}C in rotating drums – type furance

$$Na_2CO_3 + Fe_2O_3 \longrightarrow Na_2OFe_2O_3 \text{ (sodium ferrite)} + CO_2$$

The cake containing sodium ferrite then treated with H_2O as follows:

$$Na_2OF_2O_3 + 4H_2O \longrightarrow 2NaOH + 2Fe(OH)_2$$

The solution containing 400 g/L of NaOH evaporated to concentrate as in lime-soda method $Fe(OH)_2$ produced charged once more in other process.

The chemical methods have serious disadvantages: the fuel consumption is high, the caustic soda obtained is polluted with other impurities, servicing the equipment laborious, etc.

At present electrochemical processes are widely used to produce caustic soda and gaseous manufacture

(II) Electrochemical method:

The raw materials for the production of caustic soda by electrochemical methods are saturated solutions of sodium chloride (310 – 315 g/L NaCl) obtained by dissolving solid common salt. Usually these solutions contain calcium and magnesium salt impurities which, when alkali is formed in the electrolyser, will react with it and yield precipitates which disrupt the normal course of electrolysis. Therefore, prior to being subjected by precipitating them with a soda solution and milk of lime. The precipitates are filtered off and clarified solution is used for electrolysis.

The electrolyser cells for electrolysis of salt solution may be classified into two types:

a- Cells with solid – iron cathode, graphite anode and vertical or horizontal diaphragm (asbestos) to separate the cathodic and anodic compartments.

b- Cells with liquid Hg - cathode.

When dissolved in water NaCl forms positively charged Na^+ ions and a negatively charged Cl^- ions. The water in which the NaCl is dissolved is a very weak electrolyte, slightly dissociated into H_3O^+ ions and OH^- group. If a direct current pass through the aqueous solution of NaCl, i.e we have the following ions

Na^+ , H_3O^+ , Cl^- , OH^-
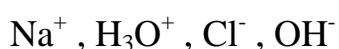
H^+ - ions give up their charge at Fe-cathode because H^+ ions require a lower voltage than Na^+

Cl^- - ions give up their charge at graphite anode O^{2-} release at graphite anode is negligible since the voltage required for OH^-

$$OH^- - e \longrightarrow O_2 + H_2O$$
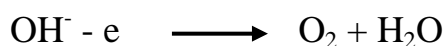
is higher than Cl^- ions . On other hand $Cl^- > OH^-$

In results H_2 and Cl_2 are removed separately at the cathode and anode respectively. Remaining $Na^+ + OH^-$ ions give raise to caustic soda

$$Na^+ + OH^- \longrightarrow NaOH$$

It is discharged from the electrolyser as a solution containing about 120 g/L NaOH and about 180 g/L of NaCl which do not undergo electrolysis. As this solution is evaporated NaCl precipitates out and the concentration of NaOH in the end product is raised to 92%.

For electrochemical decomposition of a certain substance, the electrolyser is connected to a d-c power source of a definite voltage. The minimum voltage required for the decomposition of a substance is called the theoretical decomposition voltage. It is equal to the difference of the equilibrium potentials of the anode and cathode reactions under given conditions. For common salt the theoretical voltage is 2.166 V. Electrolysis begins when the voltage applied to the electrolyte exceeds the theoretical decomposition voltage.

The economics of an electrochemical process depend to a great extent on the rational utilization of electric power. The electrolysis of common salt is accompanied by side reactions, which entails waste power.

The ratio of the actual product yield, A_{actual} to the theoretically possible yield, $A_{theoretical}$.

The current efficiency K of the given process;

$$K = \frac{A_{actual}}{A_{theoretical}} \times 100, \text{ yield actual} < \text{yield theoretical}$$

and defined as the minimum voltage of decomposition expressed in percentage.

All those processes take place according to faradays laws, who formulated the basic laws of electrolysis processes:

1- The amount of substances released at electrode is directly proportional to the amount of electricity pass through electrolyte.

2- Electrochemical equivalent, the amount of a substance released by expending 1A- hr (electricity).

The production of one gram-equivalent of substance theoretically 1 Faraday (96500 coloumb) and $1F \sim 26.8$ A.hr

For example Cl_2: (Cl_2 gram equivalent 35.46gm)

How much electrochemical equivalent:

1 faraday   equivalent weight

26.4 A.hr   35.46 gm Cl_2

1 A.hr   X gm Cl_2

The electrochemical equivalent of Cl_2 amount produced for 1A.hr (electricity)

Elect. Equivalent = 1.323 gm

NaOH, M.wt = 40

1F   ---------   40 gm NaOH

26.4A.hr   40 gm

1Ah.hr   X gm

Electrochemical equivalent of NaOH = 40 / 26.4 = 1.492 gm.

The electrolytic cells for manufacture of NaOH are shown in the figures
First Type

NaCl solution
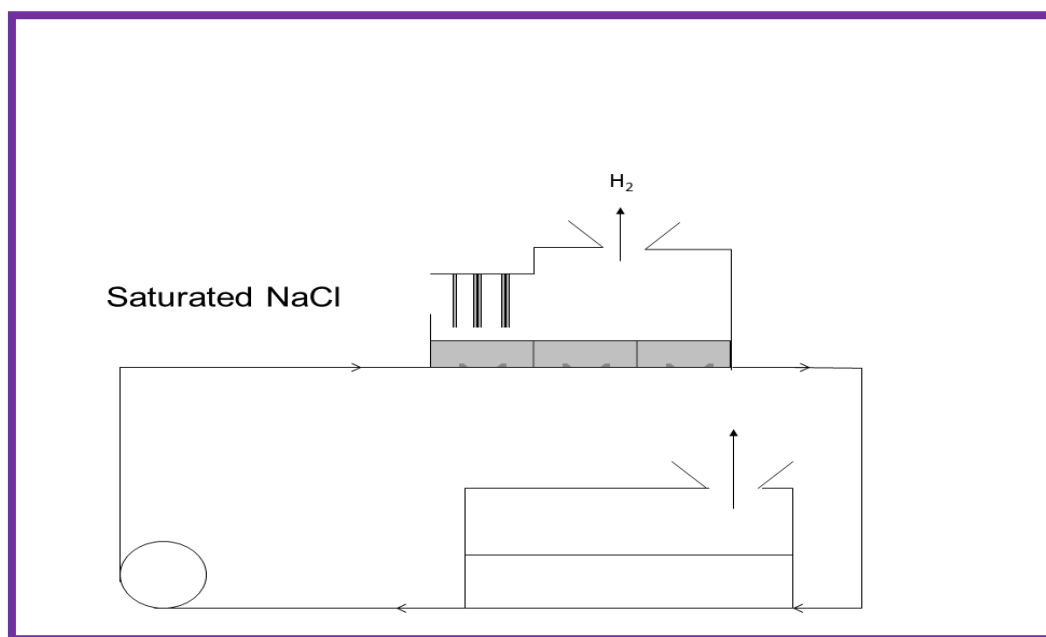
310 – 315 gm/l

Solution,   diaphragm (asbestos)
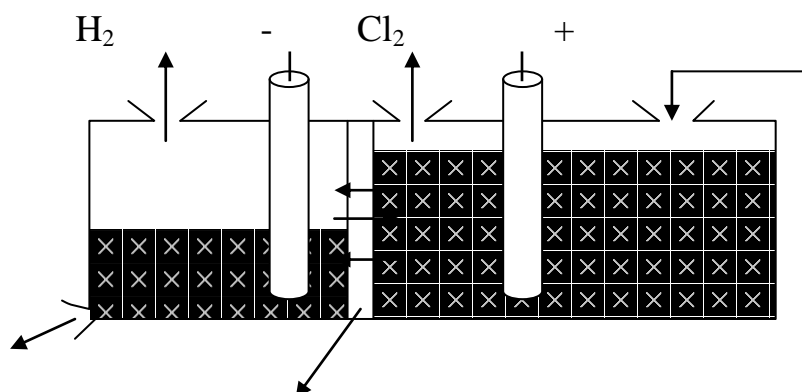
NaOH 110 – 120 gm/L, NaCl 170 –180 gm/L

## Manufacture NaOH using cells of Second type.

The electrolysis of NaCl solutions in cells with a liquid – Hg cathode is shown in the following figure,

Saturated solution of NaCl is continuously fed to the cell at chamber containing graphite anodes immersed in Hg- moving bed. When direct current passes through the solution Cl^- - ions give up their charge at anode

$$2Cl^- \longrightarrow Cl_2 + 2e$$
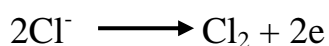
Na^+ - ions react at cathode

$$Na^+ + e \longrightarrow Na$$
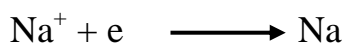
The sodium element released at cathode make amalgam with Hg, which dissolve in excess of Hg as follows

$$Na + nHg \text{ (excess)} \longrightarrow NaHgn$$

Practically no H_2 will be released at cathode because the potential of sodium release at the Hg cathode is lower than that for hydrogen release. The sodium amalgam is removed and treated with water according to the following reaction:

$$NaHg_n + H_2O \longrightarrow NaOH + n\,Hg + 0.5\,H_2$$
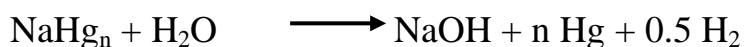
The caustic soda solution formed in the decomposer is concentrated by evaporation; the gaseous hydrogen goes to the consumer, while the mercury released as a result of decomposition of the amalgam with water is returned to the electrolyser by means of a lift or pump.

Mercury cells operate at a voltage of about 4.5 V, the load on the bath reaches 200,000 A, the electrolyte temperature being between 70 –80 ^{o}C. The current efficiency if from 94 to 96%, the alkali concentration at the decomposer outlet 450 to 500 g/L, power consumption per ton of NaOH 3,100 – 3,200 KWh.

The advantages of mercury cells are the high concentration of the alkali solution obtained, which reduces the consumption of fuel for its evaporation, and the high purity of the alkali. The disadvantages, as compared with porous – diaphragm cells are higher power consumption per unit products, large amounts of mercury in the cells, mercury loses, potentially dangerous working conditions because of penetration of harmful mercury vapours into the workshop atmosphere, etc.

Manufacture of Mineral Fertilizers

Fertilizers are substances which are introduced into the soil to increase the yield of agricultural crops. With each harvest part of the nutrients is withdrawn from the soil, gradually exhausting it, and these results in reduced crops. To obtain stable harvests the losses must be offset by systematic application of fertilizer. In this way not only can the crop be maintained at a fixed level, but it can be raised as well.

In addition to increasing the amount of agricultural produce, fertilizers also improve their quality. Thus, with the use of fertilizers the starch, sugar, protein and oil content of plants is raised, this in turn increases the content of fats and proteins in livestock products. The use of fertilizers increases the strength of such products as flax, cotton, and wool.

Fertilizers increase the resistance of plants to diseases, low temperatures and other conditions which hinder the development of the plant. The use of fertilizers results in a great increase in labor productivity.

To live and develop normally plants require many different substances. of the 103 elements of the Mendeleyev periodic system about 60 are present in the compounds of which plants are made up. They must all be contained in the soil in the upper fertile layer of the earth, and in the atmosphere surrounding the plants.

The principal role in plant life is played by carbon, hydrogen, oxygen (these are contained in the cellular tissue), nitrogen, potassium, phosphorus, magnesium, sulphur, calcium, and iron. These 10 elements account for over 99 % of the plant weight. The other elements, although contained in plants in very small quantities, are of great importance in the vital processes.

The bulk of the carbon is received by the plants from the air in the carbon dioxide assimilated by photosynthesis, with a small amount of it supplied from the soil through the root system.

Oxygen and hydrogen enter into the plant mainly from the soil as ingredients of water the other elements are contained in water-soluble mineral salts or weak organic acids. Usually the soil quickly becomes impoverished in the water-soluble mineral salts of nitrogen, potassium and phosphorus, because agricultural crops consume relatively larger amounts of them.

As for the remaining elements (about 50), their consumption by plants is comparatively small, but if there is a deficiency of any of them in the soil (especially of boron, manganese, cobalt, zinc, copper, etc.) normal development of the plant is disturbed. Therefore, where there is an insufficient amount of these elements in the soil they should also be introduced in small quantities as so-called minor-element fertilizers.

To make rational use of fertilizers, one must know the composition of the soil and the nutrient requirements of the individual agricultural crops. This makes it possible to introduce the fertilizers into the soil in the amounts essential for normal development and life of the plants.

The Classes of Fertilizers

Fertilizers are usually classified into two groups:

(1) Organic fertilizers (manure, peat, industrial waste, green manure, etc.);

(2) Mineral or artificial fertilizers, i.e. specially manufactured products.

In this chapter the production of mineral fertilizers, is discussed. With respect to their agricultural effects mineral fertilizers are divided into direct and indirect ones.

Direct fertilizers are substances containing elements essential to plant life in the form of their compounds.

Indirect fertilizers are substances introduced into the soil mainly with the purpose of improving its physical and biological properties. For instance, ground limestone and dolomite reduce the acidity of the soil; gypsum improves the properties of saline soils, etc.

With respect to the nutrients contained in them, mineral fertilizers are divided into phosphorous, nitrogenous, and potassium fertilizers. The minor-element fertilizers are usually treated as a separate group. Fertilizers containing only one nutrient are called simple; those with two or more nutrients in them are termed multiple-element fertilizers. If such fertilizers are produced by mixing simple (single) fertilizers, they are called mixed fertilizers. The most important mineral fertilizers used in agriculture are listed in the following Table.

Phosphorous Fertilizers

The raw materials for the manufacture of phosphorous fertilizers are naturally occurring minerals phosphate rock and apatite-whose basic component is tricalcium phosphate $Ca_3(PO_4)_2$, which is insoluble in water and in weak organic acids. In addition to tricalcium phosphate, phosphate rock and apatite contain calcium fluoride, CaF_2. Apatite containing CaF_2–$3Ca_3(PO)_2$. CaF_2 or $Ca_5F(PO_4)_3$. is called fluor- apatite.

The Soviet Union has over 200 industrial phosphate rock deposits. Phosphate rock occurs either in the form of nodules of various shapes and colours (nodular deposits) or in seams. Most of the phosphate rock deposits are of sedimentary origin. They were formed from animal or plant organisms rich in phosphorus compounds and are deposited in seams. Of the greatest commercial importance in the Soviet Union are the deposits in Kare-Tau (Southern Kazakhstan)-the richest deposit in the world, in Vyatka, Aktyubinsk, Yegor` yevsk, etc. Phosphate rock contains various impurities which reduce the per cent content of the useful ingredient, tricalcium phosphate, in them (it is usually given in terms of per cent of P_2O_5). Phosphate rock is often concentrated to remove the impurities and increase the P_2O_5 content of concentrated phosphate rock ranges from 20 to 30 %.

Apatite ores are predominantly of igneous (volcnic) origin and made up of large crystals. The world's richest deposit of apatites is in the Soviet Union, in the vicinity of Kirovsk. In this deposit the apatite occurs together with nepheline, (Na or K)$_2$O.Al$_2$O$_3$.2SiO$_2$.2H$_2$O, and other valuable minerals. The apaitie-nepheline rock is separated at an ore-beneficiation factory into an apatite concentrate containing 39 to 41 % P$_2$O$_5$ and a nepheline fraction, used as a raw material from which aluminium, soda products and cement are made.

More than half or the world's reserves of phosphate raw material are located in the Soviet Union and it has therefore tremendous potentialities for developing the production of phosphorous fertilizers.

Plants can only assimilate the phosphorus in compounds which are soluble in water or weak organic acids. Tricalcium phosphate, Ca$_3$(PO$_4$)$_2$, contained in phosphate rock and apatite, is insoluble both in water and in weak organic acid. Since plants cannot assimilate the phosphorus in such a compound it must be converted into other compounds available to the plants, such compounds as, for example, acid calcium salts of phosphoric acid – monocalcium phosphate, CaH$_4$(PO$_4$)$_2$, which is readily soluble in water or dicalcium phosphate, CaHPO$_4$, which is insoluble in water but soluble in weak organic acids (for instance, citric acid). The P$_2$O$_5$ in dicalcium phosphate, CaHPO$_4$, is said to be in an available citrate-soluble form. Water-soluble compounds of phosphorus are more rapidly assimilated by plants than citrate-soluble ones. However, in sandy soils, through which rain water easily penetrates, citrate-soluble phosphorus compounds are not quickly washed away and will be more fully, although slowly, utilized by the plants.

For highly acid soils it is advisable to use ground phosphate rock as the fertilizer. In this case the conversion of tricalcium phosphate to compounds available to the plants is by the action of the contained in the soil.

Simultaneously, the acidity of the soil will be reduced and the physical and chemical conditions for plant growth will improve. Animal bones contain phosphorus as tricalcium phosphate, and therefore after the fat and glue have been removed from them by extraction, they can be used in the form of bone meal in the same way as phosphate rock and apatite meals.

Naturally occurring phosphate rock and apatites are processed industrially on a large scale into phosphorous fertilizers, i. e. into phosphorus compounds available to plants. Naturally occurring phosphates are also used for producing elemental phosphorus and phosphoric acid – semi-products from which concentrated phosphorous fertilizers are made.

In short, the main purpose in the technology of phosphorous fertilizers is to convert insoluble natural compounds of phosphorus into soluble ones by decomposing phosphate rock or apatite with acids, alkalis, or in other ways.
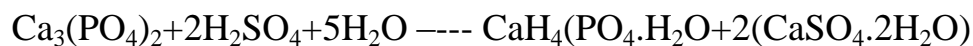
The production of super-phosphate

Super-phosphate is the product of decomposition of phosphate rock or apatite by sulphuric acid. It may be in the form of a grey powder or of granules consisting practically of the water-soluble phosphorus compound- the mono-hydratre of mono-calcium phosphate, $CaH_4(PO_4)_2,.H_2O$, and the low-solubility calcium sulphate dihydrate, $CaSO_4.2H_2O$—gypsum.

Super-phosphate is a phosphorous fertilizer with a low P_2O_5 content (maximum 20 to 22 %). The gypsum ($CaSO_4.2H_2O$) in the superphosphate has no nutrient value for plants.

To make super-phosphate, ground phosphate rock or apatite and sulphuric acid are mixed in a definite ratio, and the mixture obtained in the form of pulp, is poured into a chamber, or den. In this den the mixture gradually solidifies and matures, i. e. the phosphoric and the sulphuric acid react. Then the superphosphate is cut into flakes and sent to the warehouse.

The reaction between the phosphate rock and the sulphuric acid is described by the following equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \text{ ---- } CaH_4(PO_4.H_2O + 2(CaSO_4.2H_2O)$$

As can be seen, water is also a participant in the reaction of superphosphate formation. Therefore dilute sulphric acid of 68% concentration is used in making superphosphate. One molecule of the water in the acid combines with one molecule of the mono-calcium phosphate, four others with calcium sulphate to form two molecules of gypsum, $CaSO_4 \times 2H_2O$, this promotes setting of the pulp and solidification of the super-phosphate formed in the den. The reaction of apatite with sulphuric acid to yield super-phosphate can be represented in this way:

$$3Ca_3(PO_4)_2.CaF_2 + 7H_2SO_4 + 17H_2O \rightarrow$$

$$3CaH_4(PO_4)2.H_2O + 7(CaSO_4.2H_2O) + 2HF$$
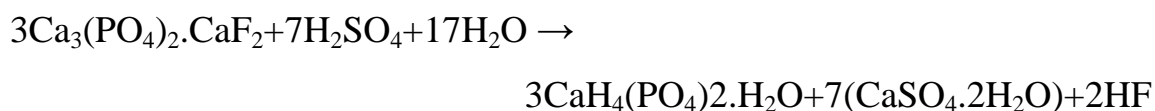
The process of super-phosphate formation in the den is a complicated one, it involves chemical reactions, diffusion of the acid into the particles of the phosphate raw material and crystallization of mono-calcium phosphate. All these individual processes are affected by the temperature and the concentration of the reacting substances. A temperature of about 110 ^{o}C is maintained in the den (by the heat released in the decomposition reaction. Curing of the super-phosphate does not terminate in the den, but continues during storage. The oxides Al_2O_3 and Fe_2O_3 in the phosphate raw material are harmful impurities. In the process of treating the phosphate with sulphuric acid the sesquioxides form aluminum sulphate and iron sulphate. During storage of the super-phosphate these compounds react with the mono-calcium phosphate to convert the phosphorus into compounds which cannot be assimilated by plants. This very undesirable process, which lowers the quality of the superphosphate.

The principal stages in manufacturing super-phosphate are proportioning of ground phosphate rock or apatite and sulphuric acid, obtaining a pulp by agitating the ground phosphate with sulphuric acid in a mixer, setting, solidification and maturing of the mix in the den, final curing of the superphosphate formed in the storage premises.

A schematic diagram of the process of production of super-phosphate is given in the following Figure.
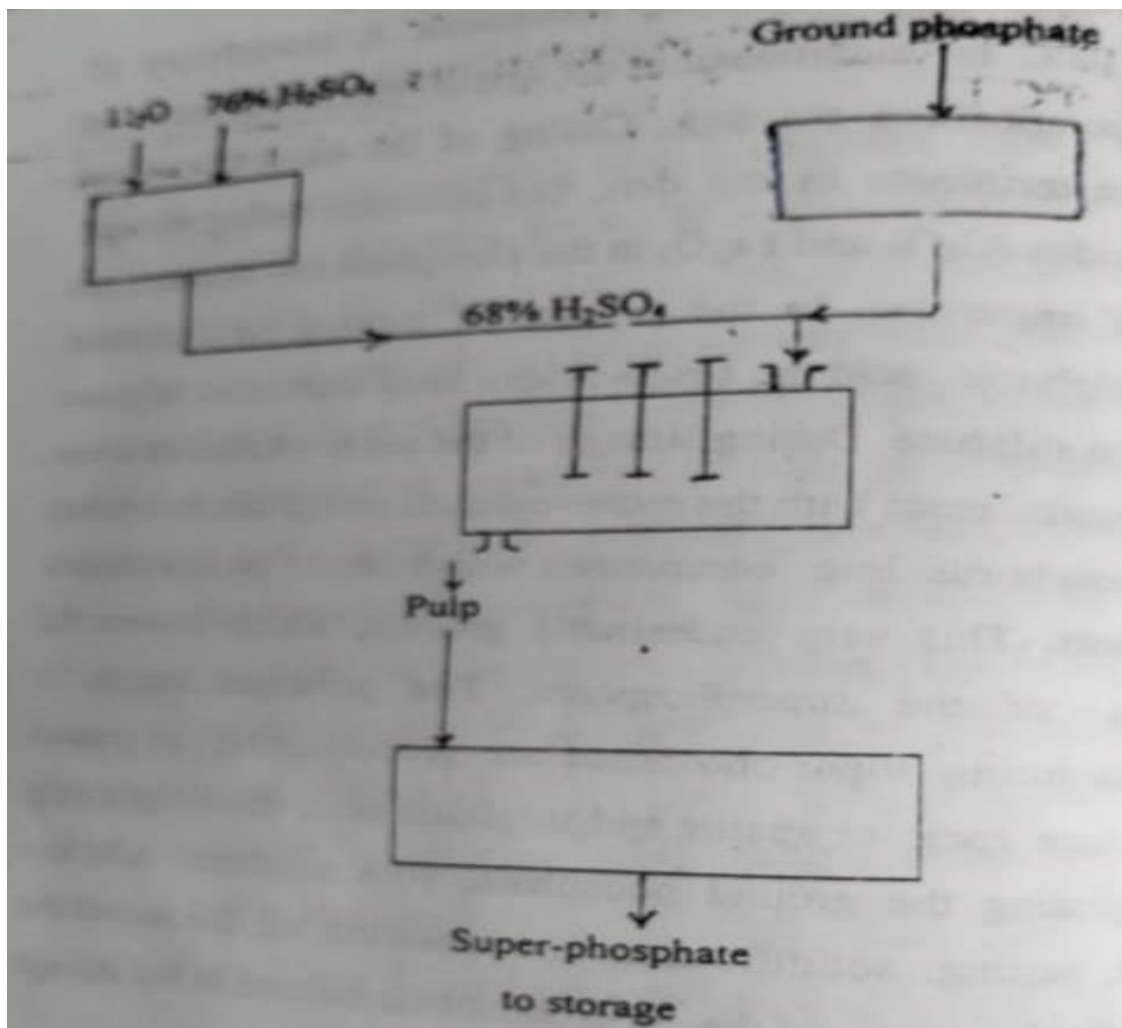
Sulphuric acid from a tower (76% concentration) is continuously supplied to proportional l, where it is diluted with water to a concentration of 68%, and then it is fed into mixer 3. Ground phosphate rock or apatite from the warehouse is measured out with the aid of automatic scale 2. The ground phosphate is mixed with the sulphuric acid in continuous action mixer 3. Ordinarily, use is made of

screw-type mixers or chamber-type mixers, in which mixing is by means of high-speed agitators. The pulp obtained in the mixer is fed to continuous-action maturing den 4, where it sets (solidifies), and then is cut up and sent to the storage room. Formerly, setting and maturing of super-phosphate were carried out in batch-type dens. After such a den was filled with the mix and when the superphosphate had solidified, the den was opened and the superphosphate was cut up. After the den was freed from the superphosphate it was refilled with the mixture, etc. batch-type dens have serous disadvantages: their capacity is small, the product obtained is not of uniform composition and properties, the dens are not hermetically sealed and therefore the plant atmosphere may contain noxious gases and dust. Such dens are still in operation, but most newly built and reconstructed plants are equipped with improved, continuous-action, dens.

The following Figure is a diagram of a continuous-action den; this is a vertical reinforced-concrete cylinder, 1, and a bottom, 2 which rotates slowly (one revolution per 1.5-2.5 hr) on rollers 5. The den has a stationary reinforced concrete lid, 8, resting on supports 6. Inside the den there is a cast-iron tube 4 coaxial with the cylinder and attached to the fixed lid, the tube passes through a packed gland in the bottom of the den, it is used for discharging the superphosphate from the den. Partition 11 is also rigidly fixed to and "suspended" from the den lid. There is a sliding fit between the edges of the partition and the bottom and wall of the den. The partition separates the zone into which the mix is charged from the zone out of which the superphosphate is discharged. From mixer 10 through hatch 9 the mix of ground phosphate and sulphuric acid is continuously fed into the den, where it sets. As the den rotates in the clockwise direction, the solidified mix slowly moves toward the discharge zone, maturing goes. The vacated apace at the fixed partition is continuously filled with fresh mix.
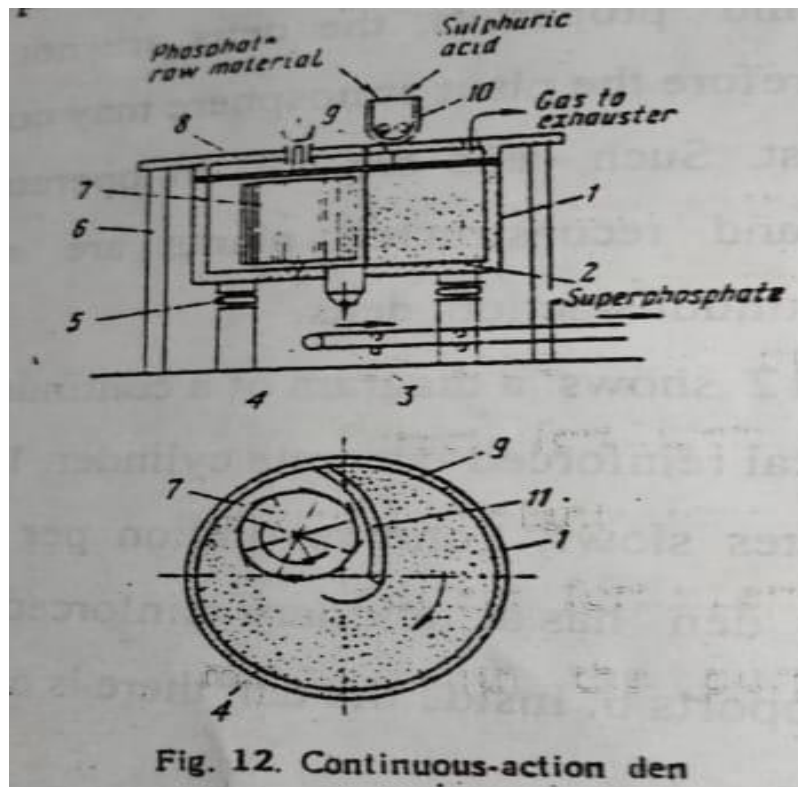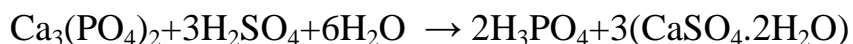
Fig. 12. Continuous-action den

The manufacture of phosphoric acid

Phosphoric acid, H_3PO_4, is obtained from naturally occurring phosphates (phosphorite or apatite) by extraction or by electro thermal procedures.

In the extraction process phosphoric acid is made from the phosphates mainly using sulphuric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$$

The phosphoric acid (solution) is separated from the precipitate (gypsum) by filtering. The precipitate is washed with water for complete removal of the phosphoric acid from it. However, even after the washing operation part of the phosphorus compounds remain in the gypsum, called phospho-gypsum for this reason.

The unit for the production of phosphoric acid by extraction is of relatively simple design. The principal items of equipment are extractors (tanks with an agitator) and vacuum filters. Extraction-process phosphoric acid contains a maximum of 36% H_3PO_4. For use in making triple super phosphate and other fertilizers extraction-process phosphoric acid is sometimes evaporated to

concentrations of 50-75% in drum-type concentrators, which are very similar in design and operation to the concentrators for the evaporation of sulphuric acid.

In the electrothermal process the phosphoric acid is usually obtained in two stages. The first stage yield, elemental (yellow) phosphorus. For this purpose phosphorite or apatite, carbon (coke and anthracite), and silicon dioxide (quartzite) are charged into an electric furnace. Upon heating the mixture to a temperature of about 1500 °C the following reaction takes place:

$Ca_3(PO_4)_2 + 5C + nSiO_2 \rightarrow P_2 + 3CaO.nSiO_2 + 5CO$
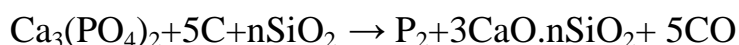
Gas containing the phosphorus in the vapour phase is with drawn from the electric furnace at a temperature of about 600 °C and cooled, first by steam and then by water the phosphorus condenses and accumulates under the water in the yellow phosphorus form.

The residual gas, which contains carbon monoxide, can be used as a fuel or in the synthesis of organic compounds.

In the second stage molten yellow phosphorus is pumped from a heated storage tank through an atomizer nozzle into a combustion chamber. Where it burns (is oxidized) to P_2O_5. The phosphorus pentoxide combines avidly with the water vapour contained in the flue gases to form phosphoic acid.

Phosphoric acid obtained by the electrothermal process is distinguished by high purity and high concentration (up to 80-95%). It can be used in manufacturing a number of different phosphoric acid salts and for synthesizing organic compounds. Where electric power is inexpensive thermal – process phosphoric acid can be used to advantage in the production of concentrated fertilizers (double superphosphate precipitate, ammophos, etc.).

The manufacture of concentrated phosphorous fertilizers (triple superphosphate)

Triple superphosphate is made by decomposing the natural phosphates not with sulphuric acid as in the production of simple superphosphate, but with phosphoric acid containing up to 70% H_3PO_4:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O \text{---} 3Ca(H_2PO_4)2H_2O + Q$$
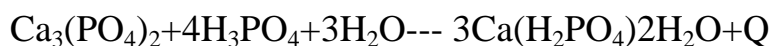
The product, consisting almost entirely of monocalcium phosphate, is soluble in water and is called triple superphosphate. Its P_2O_5 content (40 to 50%) is 2 to 2.5 times that of simple super-phosphate. Extraction process of phosphoric acid, of about 36% concentration, is now widely used in manufacturing triple super-phosphate.

Precipitated phosphate, dicalciumphosphate

Precipitated phosphate, dicalciumphosphate, is obtained by neutralization of phosphoric acid with limestone and or with milk of lime:

$$H_3PO_4 + CaCO_3 + H_2O \longrightarrow CaHPO_4.H_2O + CO_2$$

$$H_3PO_4 + Ca(OH)_2 \longrightarrow CaHPO_4.H_2O$$
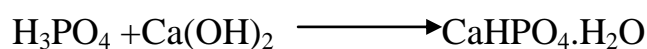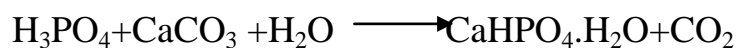
The precipitated phosphate is filtered, dried and packed. The product contains up to 42% P_2O_5 in an available (citrate-soluble) form.

Ammophos, $(NH_4) H_2PO_4$ and $(NH_4)_2HPO_4$

Ammophos is obtained by the neutralization of phosphoric acid with gaseous ammonia. Phosphate rock and apatite can also be decomposed with nitric acid; the resulting complex fertilizer contains both nitrogen and phosphorus. By adding potassium salts to the product of nitric acid decomposition of phosphates, fertilizers containing nitrogen can be obtained. These are called nitrophoskas. Natural phosphates cab converted into products available to plants by sintering them with soda ash at high temperature (1000 to 12000 °C). These fertilizers are called thermal phosphates. The fusing of phosphates and silicon dioxide, magnesium silicates or alkaline alumino-silicates results in a fertilizer called fused phosphate. Thermal phosphates and fused phosphates contain 20 to 35 % P_2O_5 in an available (citrate-soluble) form. They are only slightly hygroscope, comparatively inexpensive and are used to advantage as phosphorous fertilizers, especially on acid soils.

Nitrogenous Fertilizers

The nitrogen in nitrogenous fertilizers can be either the form of the cation NH^+ i. e. in the ammonia form, or the form of the anion NO_3 i.e. in the nitrate form; some fertilizers contain both ammonia and nitrate nitrogen. Another nitrogenous fertilizer is carbamide (urea), $CO(NH_2)_2$. All the nitrogenous fertilizers are soluble in water and are readily assimilated by plants.

The most commonly used nitrogenous fertilizers in the USSR are ammonium nitrate, NH_4NO_3, which contains up to 35% nitrogen, and carbamide (urea), $CO(NH_2)_2$ which has the highest nitrogen concentration (up to 46%) of all the nitrogenous fertilizers.

Ammonium sulphate, $(NH_4)_2SO_4$ containing 20 to 21% nitrogen is also used as a nitrogenous fertilizer.

The manufacture of ammonium nitrate. Ammonium nitrate, NH_4NO_3 contains nitrogen in both the ammonia and nitrate forms and is successfully used for all types of soils and agricultural crops. It is an extremely valuable nitrogenous fertilizer. However there are some physical properties of ammonium nitrate which impede its application. In a damp atmosphere ammonium nitrate crystals tend to deliquesce and cake, cease to flow and form into large agglomerates. To reduce caking, ammonium nitrate crystals are either granulated or "dusted "with finely divided non-hygroscopic additives (lime, phosphate rock, apatite or bone meal, etc.).

On heating, ammonium nitrate loses ammonia. At temperatures above 200 °C decomposition of the nitrate speeds up, oxygen is released; the nitrate may explode and is a fire hazard. Decomposition is accelerated in the presence of certain substances (graphite, glass, etc.). Ammonium nitrate may explode in improper storage conditions. It should be remembered that during storage of ammonium nitrate its crystalline structure may undergo transformations from one form to another (recrystallization), this also promotes caking. When transformation to a new crystalline form occurs there is a considerable increase in

the volume of the ammonium nitrate and as a result the bags in which it is stored are split open.

Ammonium nitrate is, as a rule, made at plants which produce ammonia and nitric acid. The manufacture of ammonium nitrate includes the following stages, neutralization of dilute nitric acid with gaseous ammonia, evaporating the ammonium nitrate solution to a melt containing 98 to 99% NH_4NO_3 granulation.
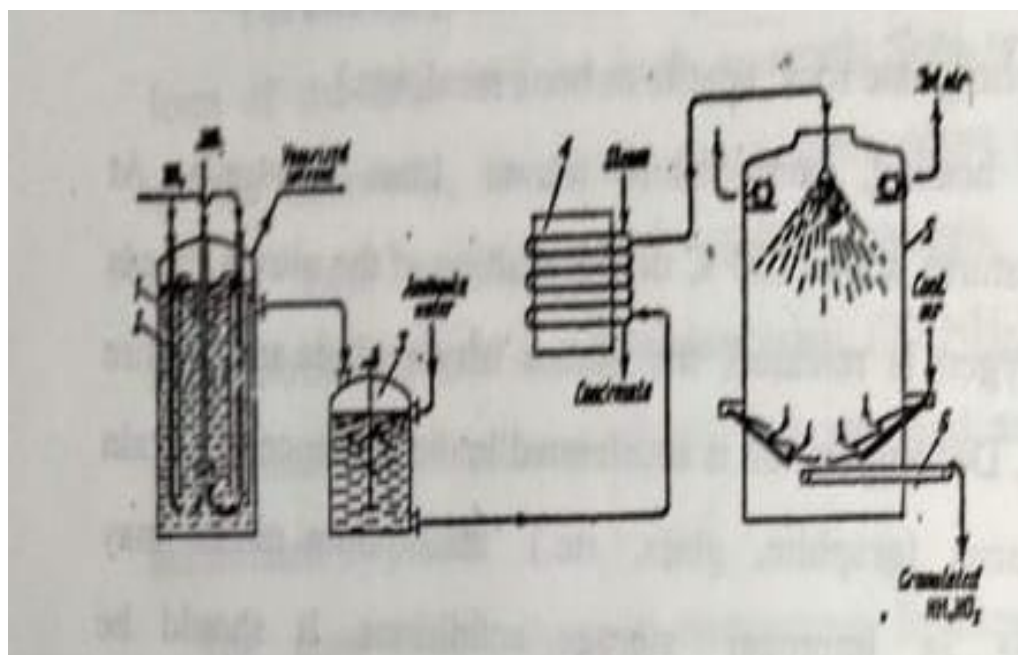

Fig. 13. Flowsheet of ammonium nitrate manufacturing process

Neutralization of dilute nitric acid with gaseous ammonia proceeds by the reaction.

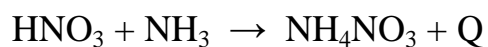$$HNO_3 + NH_3 \rightarrow NH_4NO_3 + Q$$

Figure 13 is a flowsheet of the manufacture of ammonium nitrate. Neutralizer 1 is a vertical cylindrical vessel of stainless steel in which another cylinder, 2, is enclosed. Nitric acid and gaseous ammonia are continuously fed to the bottom part of cylinder 2, in which neutralization takes place.

The absorption of ammonia by nitric acid is accompanied by an abundant release of heat. The heated solution rises to the top and flows over the brim of

cylinder 2 into the space between the first and second cylinders. This space is the evaporating section of the apparatus. Here a considerable fraction of the water is evaporated from the ammonium nitrate solution and as a result the temperature in the neutralizer drops. The so-called juice steam which is released is withdrawn from the apparatus and used as a heating agent for the further evaporation of the solution. After leaving the neutralizer the solution enters the second-stage neutralizer 3 to which the necessary amount of ammonia liquor is added for the final neutralization of the solution. Then the solution is directed to vacuum evaporator 4, where its concentration is brought up to 97-98% .The melt obtained is fed to granulation tower 5. Granulation is effected by spraying the melt in a hollow reinforced concrete granulation tower, 30 to 35 m high. Cold air is sucked in at the bottom of the tower by fans at the top. The drops of the melt solidify into granules as they fall through the current of cold air, and collect at the bottom of the tower in a hopper, from which they are removed by conveyer 6 for drying, and then go to the storage. Ammonium nitrate is packed in multi-layer paper bags impregnated with bitumen.

A single-stage process for manufacturing ammonium nitrate without the use of evaporators has been developed in which ammonia and 60% nitric acid, preheated in heat exchangers, are reacted at a pressure of 4 atm.

The vapour-liquid mixture produced in the reactor is separated in an apparatus, from which the melt, which contains 97 to 98% NH_4NO_3, is sent on for granulation.

The manufacture of Carbamide (urea)

Carbamide, $CO(NH_2)_2$, contains 46% nitrogen, readily available to plants. It is therefore, a very valuable fertilizer. It is also used as anitrogenous addition to livestock feed. In industry carbamide is used in making aminoplastics.

Carbamide is made from ammonia and carbon dioxide. The reaction proceeds in two stages. In the first stage ammonium carbamate, NH_2COONH_4 , is obtained.

$$2NH_2 + CO_2 \rightarrow NH_2COONH_4 + Q$$

In the second stage water is removed from the carbamate (dehydration), and the carbamide is formed :

$$NH_2COONH_4 \rightarrow CO(NH_2)_2 + H_2O \longrightarrow Q$$

The carbamide yield increases with the concentration of the initial materials. An excess of NH_3 prevents the formation of undesirable by-products.

Carbamide is synthesized at a pressure of 180 to 200 atm (procedures using pressures of 400 to 500 atm have also been developed) and at a temperature of 180 to 200 C. If the initial product are 100% carbon dioxide and liquid ammonia taken in excess, the yield of carbamide (with respect to the CO_2) is 60 to 70 , i. e. even with an excess of ammonia the CO_2 is not fully converted to carbamide. The melt obtained by dehydration of the carbamate contains about 35% carbanide. In the production of carbamide the utilization of the unreacted initial materials is problem of great importance. The ammonia contained in the gas can be absorbed with nitric acid to produce ammonium nitrate. Another method consists in separating the gases by selective absorption with various absorbents and returning the CO_2 and NH_3 to the process.

A simplified flowsheet of the manufacture of carbamide (urea) is presented in Fig. 14. Ammonia and carbon dioxide enter synthesis column 1 made of alloyed steel. The column contains cylindrical sleeve 2, inside which the reaction takes place. The liquid ammonia first enters the annular apace between the outer (1) and inner (2) cylinders. In this way the wall of main cylinder 1, designed to withstand the high pressure, is protected against corrosion by the reaction products. A solution containing about 35% carbamide is with-drawn at the top of the column and after its pressure is reduced to atmospheric it goes to distillation column 3, where the excess ammonia and the products of decomposition of ammonium carbonates are distilled from the carbamide solution. The bottom part of the distillation column is used for heating the carbamid solution, which goes from here to evaporator 4. The melt obtained is collected in reservoir 5, from which it is

pumped for crystallization or to tower 6 for granulation. The granulated carbamide is delivered to the storage premises by conveyer 7.

Fig. 14 Flowsheet of carbamide (urea) manufacturing process
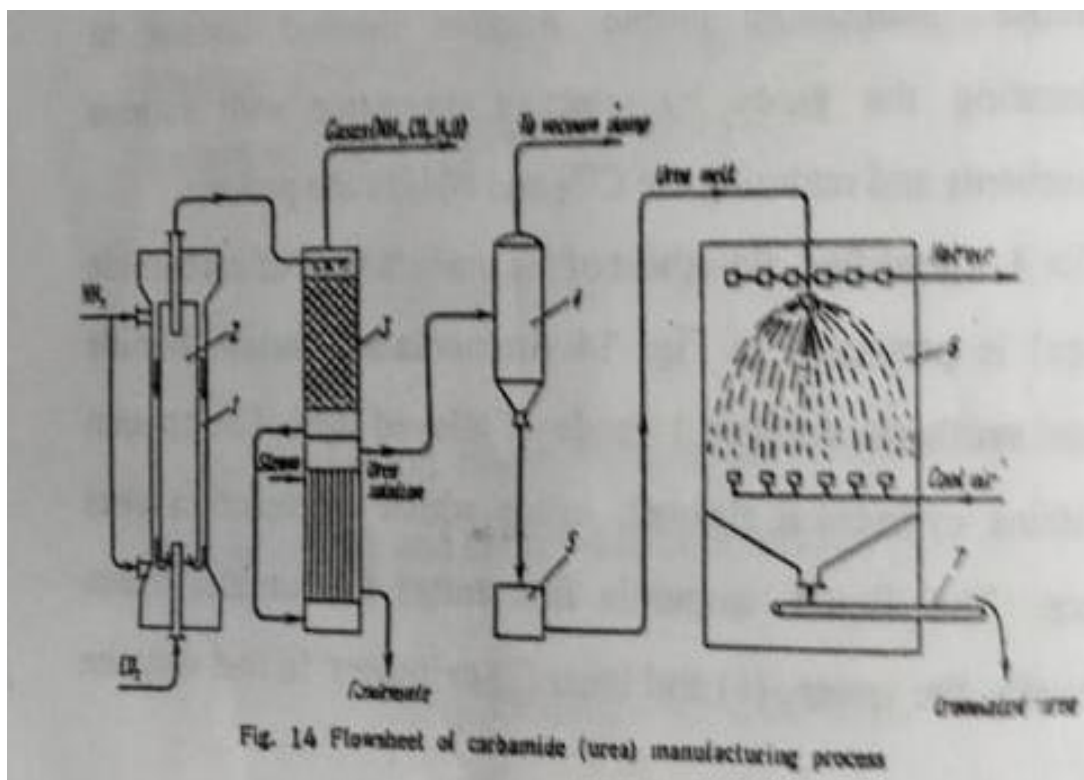
Manufacture of ammonium sulphate

Ammonium sulphate, $(NH_4)_2SO_4$ contains up to 20-21% nitrogen and is therefore a low-concentration nitrogenous fertilizer. Its repeated use as a fertilizer results in acidification of the soil and therefore the soil must be neutralized from time to time by introducing lime (liming). Ammonium sulphate is obtained as by-product when ammonia is removed from coke-oven gas with the aid of sulphuric acid:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + Q$$
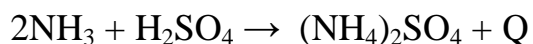
Potassium Fertilizers

Potassium fertilizers are obtained from minerals which contain potassium salts. Of greatest importance are the minerals sylvinite, KCl-NaCl and carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$.

The Verkhnekamsk deposit of potassium salts is the richest in the world. In recent years deposits of potassium salts have been discovered in Byelorussia.

Verkhmekamsk sylvinite contains 23 to 30% KCl and 65 to 70% NaCl. Ground sylvinite can be used directly as a fertilizer. However, the high NaCl content of sylvinite restricts its use since introduction of chlorine compounds into the soil has an adverse effect on some agricultural crops. Laarge amounts of sylvinite are processed into potassium chloride, which is used as fertilizer either separately or mixed with other with other fertilizers.

The isolation of potassium chloride from sylvinite is based on the different ration of the solubilities of potassium chloride and sodium chloride in water at different temperatures. This is showm in Fig. 43. As can be seen, the solubility of NaCl remains practically unchanged from 0 to 100 °C, whereas the solubility of KCl increases with the temperature. At about 25 °C the solubility curves of KCl and NaCl intersect, i. e. at this temperature the solubilities of the salts become equal. At a temperature of 80 or 100 °C there will be more KCl in solution than NaCl. If a solution saturated at 100 °C is cooled to 25 °C, only KCl will precipitate from it., If the remaining solution is reheated to 100 °C, it is no longer saturated with respect to KCl, i. e. it is capable of dissolving more of it.

By treatment of mew portions ofsylvinite with this solution at 100 °C KCl only will be dissolved. NaCl remains as a waste product of the production process.
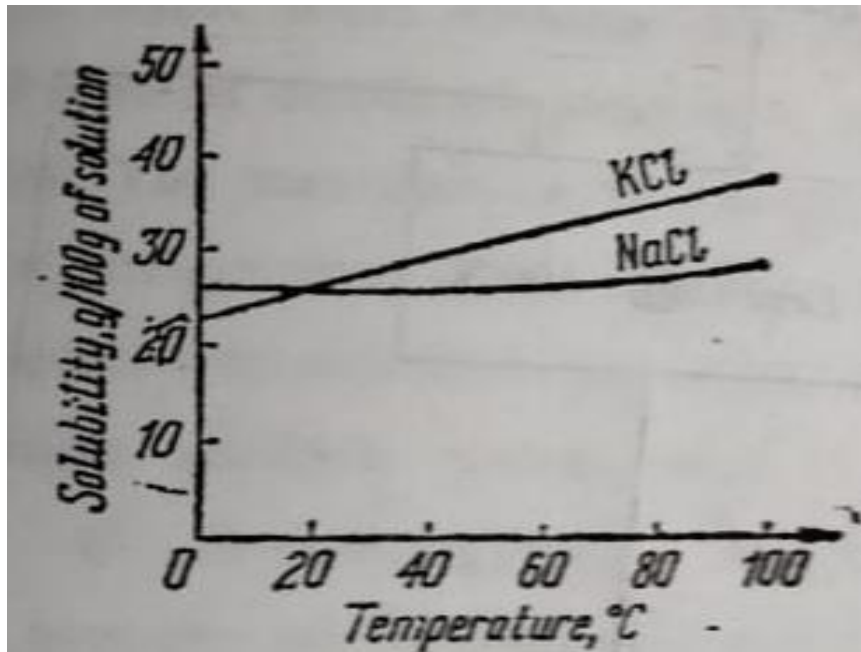
Figure 16 is a flowsheet of separation of sylvirite into KCl and NaCl.

Potassium chloride can also be obtained from carnallite ($KCl.MgCl_2.6H_2O$).

However, carnallite separation is more complicated as compared with separation of sylvinite. By comprehensive utilization of carnnallite not only potassium chloride can be obtained, but also magnesium salts, metallic magnesium magnesium bromine, and other valuable products. Potassium chloride is also separated from sylvinite and carnallite by flotation procedures.
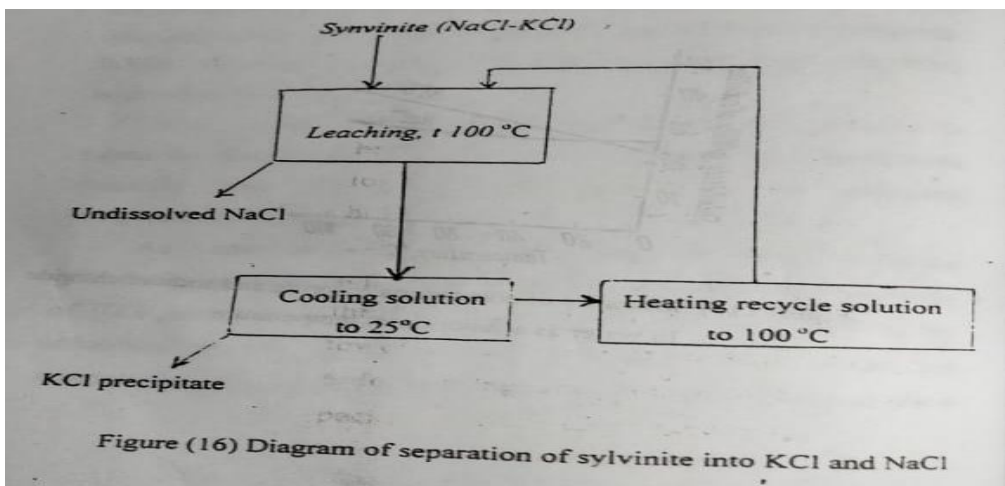

Figure (16) Diagram of separation of sylvinite into KCl and NaCl

Fig. 16 Diagram of separation of sylvinite into KCl and NaCl

Prospective Development in Mineral Fertilizers Manufacturein

Mineral fertilizers are the most important means for increasing agricultural productivity. Their wide utilization leads to a sharp increase in farm crops. The great potenti-alities of chemistry must be utilized to raise crop yields and the productivity of animal husbandry so as to provide the population of the world with sufficient amounts of foodstuffs and industrial raw materials.

In the USSR plans envisage not only increasing the amounts of mineral fertilizers produced, but also improving their quality. The manufacture of concentrated and mixed fertilizers, of inexpensive liquid fertilizers (liquid ammonia, ammonia liquor, their solutions containing ammonium nitrate, urea and other nitrogen compounds) is being expanded. Production of three-component fertilizers containing phosphorus, nitrogen and potassium in ratios corresponding to agricultural requirements is being increased. Flotation processes for the separation of potassium chloride from sylvinite and carnallite, and the production of non-caking potassium chloride and no-chlorine potassium fertilizers (potassium nitrates and phosphates) will be used much more. New and efficient processes and equipment will be introduced; batch processes will be replaced by continuous, highly mechanized and automated processes.

The manufacture of mineral fertilizers involves the consumption of various mineral acids (sulphuric, nitric, phosphoric, etc.), alkalis (soda, ammonia, etc.), the use of high tempertures and pressures (in the production of phosphorus, carbamide, phosphate slags and fuse phosphates), release of harmful gases and vapours (fluorine gas, ammonia nitric acid vapours, etc.) into the workshop atmosphere is possible. Therefore, in operating fertilizer plants and in building new ones much attention should b given to problems of safety and improving working conditions.