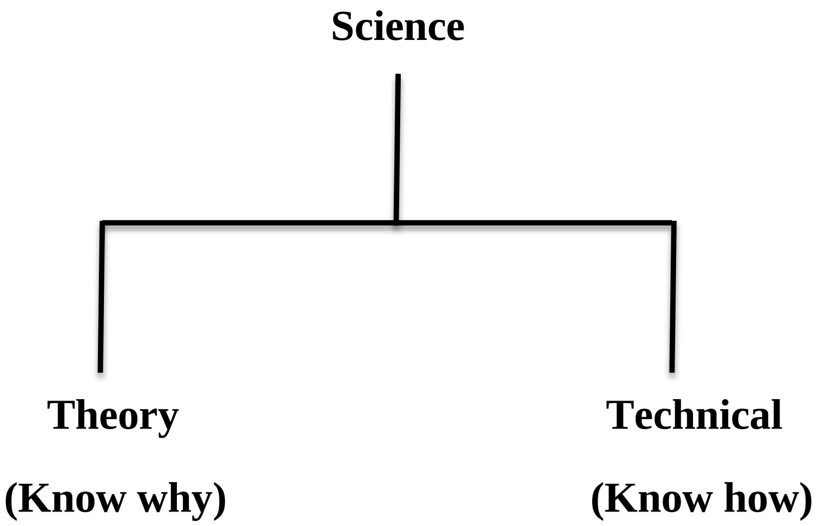
(Industrial chemistry))

Chapter (1)



Technology

A scientific and engineering a manner and methods used to transfer scientific theories and hypothesis and a mathematical equations to manufacture an important product needs for human living.

Chemical technology: it is the arrival to get the best methods to produce a material by choosing out the better chemical reactions and knowing the conditions for making them with regarding the importance of economy, humanness and the environment.

These conditions were studied in order to materialize the principles of higher and better production with lower cost.

The principles studies for this materialize are :

1) Choosing the right reaction. Depending on raw material availability and controlling on their working = for chemist .
2) Choosing the ideal design for production units, like the constructional materials and resisting the corrosion ,lower cost and their suitability for working condition.

Chemical industry

The most important factor for opening the chemical industry is the availability of the raw materials.

The general sources for the raw materials are: mines ,forest ,sea, wells, agricultural farms, air and water .

The chemical products can be classified into three classes :

1) Chemicals for commons chemical industry (primary product)
   e.g . acids and bases, organic solvent, starting materials for petrochemicals and polymers industry.
2) Intermediate for limited industries
   e.g. fabric fibers , rubbers, petrochemical derivatives, etc…..

   Those materials are used in other industries in order to produce the final product.
3) Final chemicals
   e.g. drugs , fertilizer, cleaners, so on…

Chapter (2)

Operations ,Apparatus and materials used in chemical technology

In chemical industry, the operations are of two types:

1) Physical or unit operations like: grinding, mixing, separation, distillation, drying, extraction, crystallization.
2) Chemically or unit processes

In this division the study includes doing the chemical reaction and the materials used to build the reactor (construction materials), like the metals and alloys, also perform the design of the chemical reactors with different shape.

Physical processes

1) Increasing the surface area of the reactants.

The surface area can be increased by decreasing the volume of the particles by using cracking and grinding. By this operation for the reaction will be decreased where by the number of the collected molecule increased , so the needed time for the reaction decreased so in the other word the time of reaction is inversely proportion with the surface area of the reactant particles.

There are two types of grinding:

1) Hard grinding (rough) used for solid materials like stone .
2) Soft grinding used for soft materials like organic substances, fruits, plants roots, animals horns…….

The unit used to measure the degree of mesh is micrometer μ_m,$1\mu_m=10^{-4}$cm or 10^{-6} m. The surface area of the liquid can be also increased by converting to a spray with very little volume drop.

The surface area of the gases can be increased by pushing the gas through a borer tube or through multiple fine tubes.

2) Increasing the particles volume

This is the opposite process of the last. The aim of this operation is to increase the resistance of the materials towards the physical factors like breaking up and fractionation some types of this operations are crystallization from saturated solution and using adhesive materials to accumulate the powder of charcoal to form a ball of charcoal.

3) Mixing

In order to get good reaction, the reactant must mix very well before and through the reaction .

The gaseous reactant mixed through diffusion and no need to use a mixer.

The liquid materials must be mixed very well in order to overcome the dead area that forms without the bulk of the reaction.

Type of mixer was in page 58 (Arabic).

Emulsifying :

It was a mixing of two immiscible liquids

The major liquid (A) called suspender body and the liquid (B) was suspended within A

The system of A and B called emulsion of B in A

e.g. Milk consist of water A and B in the fat so it was called emulsion of fat in water natural oils is emulsion of water in fat sequential emulsion like natural froth; it appears as an emulsion of water in animal fat , also the water droplet which was suspended in the fat is also a system of emulsion of fat in water , this fat is an emulsion of water in fat , and so on until to reach the molecular volume , where by there is molecule of water suspended with molecule of fat.

4.) Separation methods

It was the opposite process of mixing four divisions are the separation operations:

-Mechanical - electromagnetic – thermal –chemo physics.

A) Mechanical separation methods

This process depends on gravitation of earth and reducing the pressure , it was classified as follows:

1) Volumetric classification:

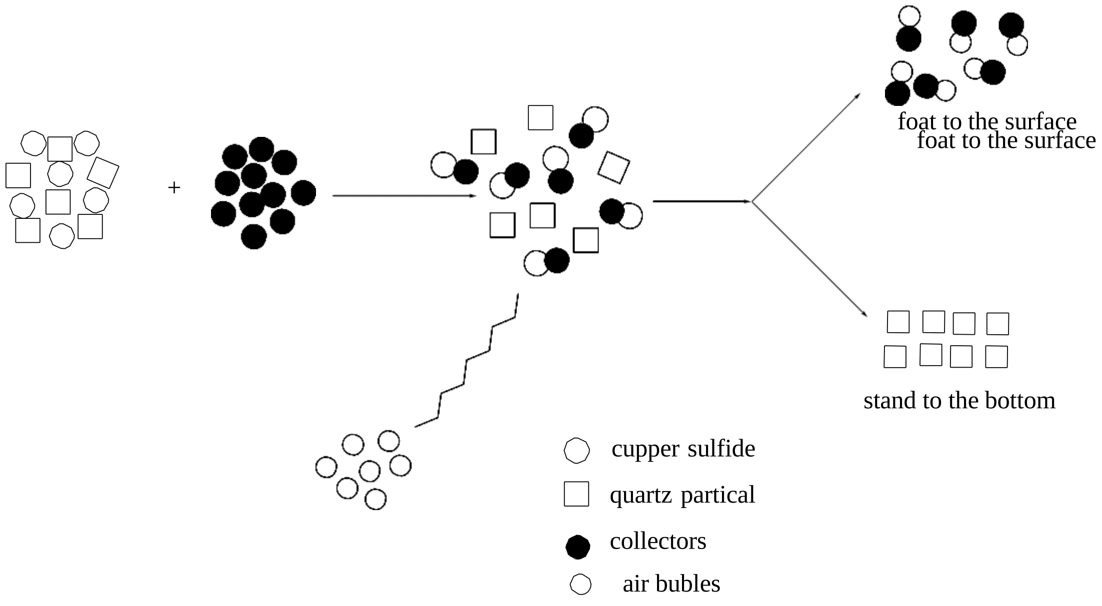
By using sieves or floatation by air in order to separate the small particles from the large one.

2) Floatation on water:

This operation was used to concentrate the metals and to separate them from the ores , by mixing the ores with the water and then bubbles the water from down the vessel with presence of materials called the collectors .

The collector will attach with the metal and float with the surface of the water by the action of the air bubbles.

e.g. Separation of cupper sulfide from the sand



Two types of collectors was used

1) Anionic collectors : used to separate the nonferrous or anti-ferric ores and are two types of the

a.) Collectors with OH group like Carboxylic acids and sulfonic acid

b.) Collectors with SH group like mercaptan and thio carbonates.

2) Cationic collectors for example , amines , used to separate the metal oxide , like Zink oxide , and the salt of alkali metals.

The amines used are in their hydrochloric forms.

3) Centrifugation

Used to separate small particles that cannot be settled down by gravitation.

4) Pressing

Used to separate the liquids from the solids (spongy solids), for example:

Extraction of fats from fruits, removing the water from industrial waste.

5) Filtration

Used to separate the solids from the liquids by using different types of filters like sand, cellulose, ceramic or cloth.

The types of the filter play the important role in the operation, where the extracted solids will accumulate on the filter as a layers.

In this operation no vibration must be done.

In order to increase the rate of this process, two ways can be followed , by using pressure in the mixture area or by using vacuum in the liquid area

In industry this method was used to separate the solid from gases by using sacks of cloth(vacuum cleaner),or used (dust collecters) to separate the dust from the cement factories.

B- Electrical and magnetic separation method

Electrical methods:

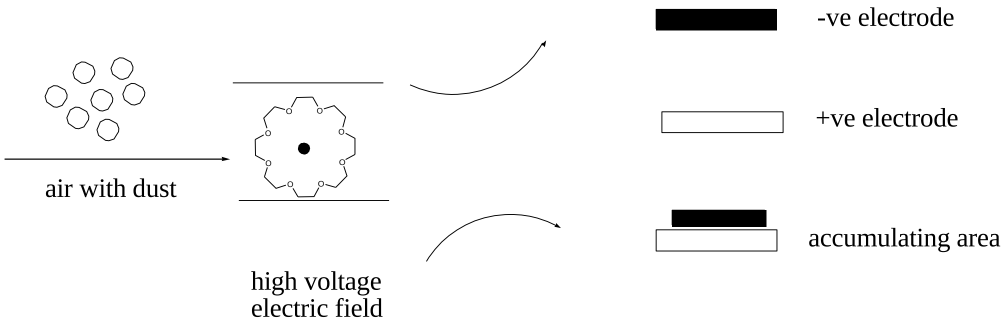
Used to remove the dust from the gases phase, or separate the solid from the gas or; liquid, by using electrical methods.

The aim of this process is to reclaim the dust and to overcome the pollution problem or to decrease the effect of dust on the metallic surfaces.

Also in the electricity generator unit which used some type of fuel that produce dust through the combustion.

The technique include passing the air with the dust through high voltage field which charged the dust particles with different charges , the this particles was passed through two electrodes (negative and positive charged).

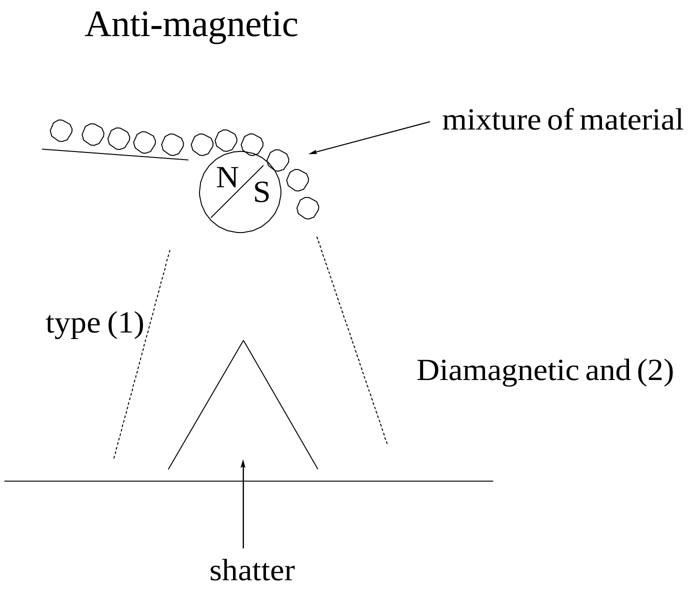
The charge of the dust will be naturalized and full down in the accumulating areas.



Magnetic methods

This methods are used when the mixture have different responding towards the magnet, where the material may be:

1) Have low ability to response (paramagnetic).
2) Have high ability to response (high magnetic).
   e.g. iron, nickel, cobalt, cupper
3) Diamagnetic (no response to magnet)



Magnetic method

C) Thermal methods

These methods include:

Evaporation-normal distillation –fractional distillation –drying

These methods depend on the absorption of the thermal energy by the mixed molecules, so their internal energy will increased by different degree according to their physical & chemical properties . by this phenomenon we can separate them.

The most important method is the fractional distillation, in this operation we used a fraction column which have many different shapes .

a- packed column

In this column an inert substance was filled the column, like glass or porcelain , fig (3-7), page 67.

b- plate column; which are of the types :

-Sieve
-Bubble-cap } fig (3-8) page 68

D) The chemo-physical methods:

Extraction-Crystallization

Adsorption-Absorption

Extraction:

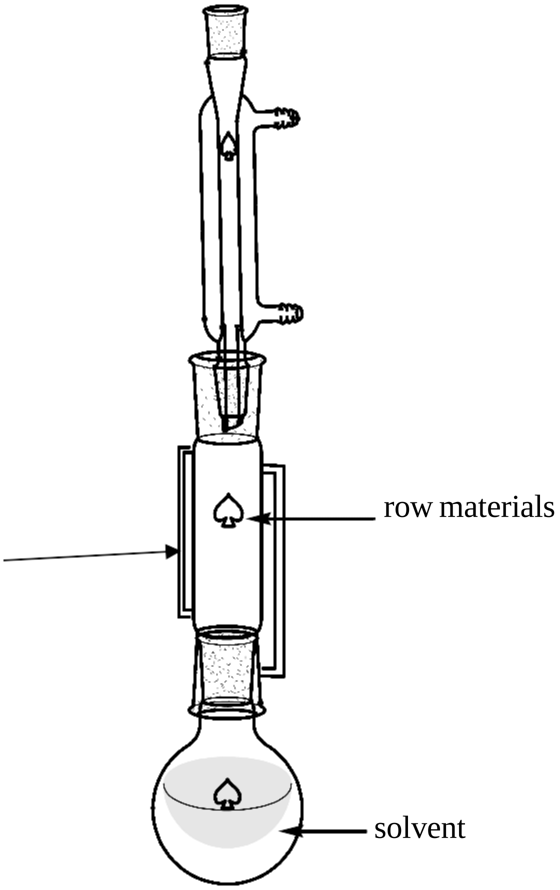
The methods include the using of appropriate solvent to isolate one of the constituent of the mixture from the other constituents, for example extraction of oils, sugar from beet, extra….

There are four steps in this process:

1) Increase the surface area for the starting material by cutting up or grinding.
2) Dissolving as large as possible of the substance in solvent by using heat.
3) Filter the solution in order to remove the tarnishes (solid) from the mixture.
4) Separate the dissolved matter from the solvent by precipitation, crystallization or by evaporation the solvent.

In modern methods the soxhlet was used.

In this apparatus small amount of solvent can separate a very much amount of the substance as in the figure below.



Soxhlet extraction apparatus

Crystallization:

It was the separation of the crystal of the substance from its saturated solution. The process was accomplished by cooling the saturated solution or by evaporate part of the solvent.

The process can be accelerated by many ways; evaporate part of solvent under vacuum , freezing out part of the solvent and salting out.

Adsorption

Some solid materials can be bonded physically with liquid or gases. The solid matter must have a surface area more than 100 m^2/g. The desorbed matter can be removed by using another matter; for example activated carbon and silica gel.

The solid material (adsorbent) can be activated by using the heat or by using inert gases like CO_2 or N_2 in order to remove the adsorbate matters.

Absorption

In this methods a chemical bonds occurred between the solvent (absorbent) and the matter (absorbate) to be separated.

This chemical bond may be stable as in the absorption of CO_2 by NaOH

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

Or unstable as in the absorption of CO gas by CuCl. The process was carried out industrially by using absorption column contain solid filler like stone or chars, the solvent was run from the top of the column and the gas was run from down.

Materials used for the constructing of chemical technology tools:

In order to choose the suitable methods in chemical technology must be suitable for the temperature change, so the main factors that depends for designing the chemical react are:

1) Temperature of the reaction and the methods of heating.
2) The needed pressure, as the pressure increase the units are complicated.
3) The manner for doing the reaction, by continuous or by batch.
4) Types of tools used for feeding and discharging the reactor.
5) The chemical properties and the physical phase of the starting materials, solvent and the product.
6) If the reaction are catalyzed or not.

The constructional materials

The main factors that limit the type of material are:

1) Resistance the high temperature .
2) The requirements of rigidity (resisting the high weight and pressure).
3) Resist the corrosion and the friction.

Many metals that resist the corrosion and can be used in chemical technology like:

-Rubber-covered steel

-Resin-bonded carbon } resist hydrochloric acid

-Tantalum

-Stainless steel-resist diluted HNO_3, and the organic acids

-Nickle and the steel with nickel-resist the basic solution (hot or cooled).

-Polymeric materials-resist the corrosion.

Metals

The characteristic of metals that are useful in using as a construction materials in chemical technology are :

1) Are good thermal and electrical conductors.
2) Have high rigidity.
3) Resist the sudden charge in temperature.
4) Easy to welding.
5) Can formulized many different shapes or twisting because they have high flexibility .

The disadvantages of metals are undergoing corrosion with different degrees.

Iron

From long time the human have used the iron as a metal because of its natural abundance in the incrustation of earth

The iron is the most important metal that used as a construction materials in chemical technology, but the most important used is as an alloy.

There are many types of alloys can be used as:

1) Iron-carbon alloy
   a) If the proportion of carbon is lower than 1.7% called wrought iron
   b) If the proportion of carbon is higher than 1.7% the alloy called cast iron.
2) Stainless steel.
   Which contain different proportion of may metals like Ni, Mn, Cr, V, see table page 75.

The uses of apparatus make from iron:

1) Transfer of a mixture from HNO_3 and conc.H_2SO_4 with water content less than 20%.
2) Resist chlorine, bromine and SO_2 gas in absence of moisture, also resist PCl_3,$AlCl_3$,$SbCl_3$.
3) The storage tank make from cast iron can be used to store H_2SO_4 with concentration of (85-100)%.
4) The iron storage tank can be used to store alkali solution like NaOH,KOH,NH_4OH, but cannot resist the acids like HCl and chloro-acetic acid or chloro-sulfonic acid.
5) The concentrated alkali react with iron.

Alitizing process :

Is a process make by heating a mixture of iron and alumina (Al_2O_3) at 500-700 °C. The aluminum penetrates the surface of iron and form a protecting layer from iron-aluminum alloy. The alitized iron have lifetime 50 double order than the normal iron.

Aluminum

The characterization of this metal to be beneficial in chemical technology is :

1) Can be easily formalized to any shaped .
2) Have light weight.
3) Resist the corrosion upon exposing to moisture by forming a thin layer of Al_2O_3.
4) Resist the solutions of ammonia, chromate and dichromate and the concentrated solution of acetic acid.
5) The products from corrosion are not poisonous so it was favoring to be used in alimental industry.
6) Did not effect by strong acids (cooled) like H_2SO_4 and HNO_3.
7) The salt of chloride or nitrate well led to corrosion.
8) It must marketing as a pure substance, because if there are any trace of element was exist, like Fe, Cu or Zn with presence of moisture, an electrical cell was formed and the aluminum be an anode electrode and dissolve gradually.

Cupper

The general properties of this metal to be used in chemical technology are:

1) The thermal conductivity and the ductility is higher than that of steel, so it was more favorable than steel to be used in the chemical industries.
2) Have high resistivity toward moisture.
3) Absorbed almost all the heat fall on it and did not reflect it.
4) Corroded on exposing to chlorides and mineral acids, react with sulfur and ammonia.
5) Did not effect by organic acid except in the presence of air.

6) It must be knocked before it was processed in order to increase its rigidity.

Zinc:

It was used as a metallic film to protect the iron from corrosion, moisture and oxidation reagent.

Nickel

1) Easily formalized
2) Used as alloy with iron and steel.
3) Used as a receptacles for fusing KOH and NaOH because it resist the hydroxides.
4) Stable in air.
5) React with dilute acids.
6) It must be pure because the impurities like sulfur and oxygenated compound effect on its properties.

Platinum

It was very expensive, so its uses are very limited as:

- Used for making electrodes in electrical cells.
- Used as an alloy with rhodium in making a thermocouple to measure a temperature higher than 2100 °C.

Tantalum

-Resist hydrochloric acid even at high temperature.

Silver

-Resist water, acids and basis

- used in cooling coils, in medical and food industries, and used as a catalyst for oxidation processes at high temperature.

Lead

A ductile and soft metal, in order to rigid it, it must be mixed with antimony.

Resist sulfuric and phosphoric acid affect by impurities like Se , Te and water contain SO2 and have low resistivity towards bases.

Catalysis in chemical technology:

The catalysis is the increasing of rate reaction with facilitating and increasing the period for initiation the reaction.

The catalyst is a materials that did not change its chemical structure through the reaction.

There are two types of catalysis processes:

1) Homogeneous ; when the catalyst was dissolved in reaction medium.
2) Heterogeneous; when there are two different phases, one for the catalyst and the other for the reactions.

The stability of the catalyst can be increased through loading the catalyst on another materials, as in the preparation of ammonia from H_2 and N_2 gases by using the catalyst iron loaded on alumina Al_2O_3, where the alumina protect the active centers of the iron catalyst, this type of catalysis called mixed catalysis.

In these process we must pay attention that the presence of some tarnishes will poisoning the catalyst, so that the H_2 and N_2 gas must be pure.

Steps of catalysis process:

1) Adsorption of the catalyst molecules on the loading material.
2) The dissolution of the reactant molecules in the active centers of the catalyst. In this step the forces between the molecules decrease by changing the distances between them(increasing or decreasing).
3) Because of these change in distances, the energy content the system increased and the system become ready to change its formulary and formed new architecture depending on type of the used catalyst.

Generally the rate of the chemical reaction will increase by the presence of the catalyst by decreasing the activation energy of this reaction

$$\text{Rate of reaction} = \frac{\text{Driving forces}}{\text{Resistance}}$$

The driving forces depends on the chemical nature of the reactants, while the resistance have many types like structural resistance or as called steric effects so the molecule need energy to overcome this resistance. This energy called activation energy, which is the energy needed to make the bond force in molecule weak and make it ready to react. The catyst reduce this energy, so the reaction rate be increased example

$$CO + H_2\text{-}36.8\ \text{Kcal} \rightleftharpoons -(CH_2)- + H_2O$$

In case of using catalyst. Energy will liberate when the reactant molecule adsorbed on the surface of the catalyst. The liberated energy recover large amount of energy needed in this reaction. The energy of the reaction can be written as :

$\Delta W = Wg - Wk$

Wg = activation energy without catalyst.

Wk= the liberated energy through the adsorption of reactant on catalyst surface.

ΔW= the actual activation energy in presence of the catalyst.

Properties of catalysts

Increase the reaction rate but did not effect on the equilibrium constant for reversible reactions, or increase the reaction in both sides.

Example: reaction of alcohol with acid to form ester and water.

The general properties of catalyst are:

1) High efficiency and selectivity
2) Large surface area.
3) Have high structural stability and durability .
4) Easy regenerate

In order to increase the surface area many methods can be applied as:

1) Mixed and pressed the catalyst pellets with the appropriate holder.
2) Reduced the oxide structure.
3) Dissociating the nitrate metal by heating.
4) Chemical precipitating of the catalyst from solution on the holder.
5) Preparation of structural catalyst, as by preparation alloy from two metals, then one metal is removed from the alloy, by this process we get a porous metal.
6) Chemical dissociation of the compounds of catalyst. e.g. dissociation of Ferro cyanide to prepare the iron catalyst.

Contact catalysis

The catalyst used in industry by contact catalysis technology. This type of processes need special design for reactors, in order to get the best reaction conditions with lowest temperature and easy to control the reaction by removing the excess energy through the reaction or addition of thermal energy in the beginning.

In some cases the mixture of the gases interring the reactor was partially heated by the lifted hot gases (product), this was done by using heat exchanger which was putted in the reactor or out the reactor on the wall.

Chapter (3)

Corrosion

Corrosion is defined as the deterioration or destruction of metal (alloys) by an unwanted chemical or electrochemical reaction with its environment, starting at its surface.

Note: Corrosion refers only to metals and alloys. Rotting of wood, paper is not corrosion. It is erosion. Also it refers to chemical or electrochemical attack and not physical or mechanical wearing of metals.

The most familiar example of corrosion is rusting of iron.
The process of corrosion is slow, but the losses incurred are enormous.

Some of the social and economic consequences of corrosion include:

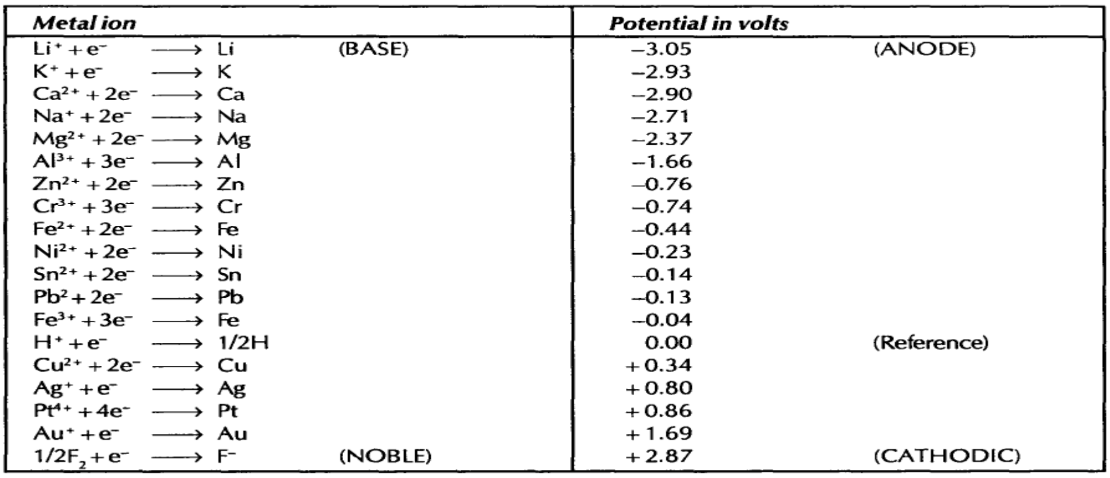
- Plant failure and subsequent shutdown
- Replacement of corroded equipment
- Loss of efficiency
- Contamination or loss of the product (e.g., from corroded container)
- Preventive maintenance

It is estimated that annual loss due to corrosion runs into several billion dollars per annum all over the world. It is therefore necessary that an engineer must understand the mechanism of corrosion, if its effects are to be minimized. Also it is more prudent to avoid 'severe corrosion conditions and provide simultaneous protection against corrosion.

When metals are arranged in the order of their standard electrode potentials, it is called electrochemical series.

Table 1.1 gives the standard oxidation potential of some of the elements. A metal will normally displace any other meral below it in the series from solutions of its salts and precipitate it as metal. Thus Mg will displace Al, Zn will displace Fe, Fe will displace Cu and so on from solution of its salts.

Table 1.1: Standard electrode potentials (reduction) at 25°C.



Metal ion		Potential in volts	
$Li^+ + e^- \longrightarrow Li$	(BASE)	−3.05	(ANODE)
$K^+ + e^- \longrightarrow K$		−2.93	
$Ca^{2+} + 2e^- \longrightarrow Ca$		−2.90	
$Na^+ + 2e^- \longrightarrow Na$		−2.71	
$Mg^{2+} + 2e^- \longrightarrow Mg$		−2.37	
$Al^{3+} + 3e^- \longrightarrow Al$		−1.66	
$Zn^{2+} + 2e^- \longrightarrow Zn$		−0.76	
$Cr^{3+} + 3e^- \longrightarrow Cr$		−0.74	
$Fe^{2+} + 2e^- \longrightarrow Fe$		−0.44	
$Ni^{2+} + 2e^- \longrightarrow Ni$		−0.23	
$Sn^{2+} + 2e^- \longrightarrow Sn$		−0.14	
$Pb^{2} + 2e^- \longrightarrow Pb$		−0.13	
$Fe^{3+} + 3e^- \longrightarrow Fe$		−0.04	
$H^+ + e^- \longrightarrow 1/2H$		0.00	(Reference)
$Cu^{2+} + 2e^- \longrightarrow Cu$		+0.34	
$Ag^+ + e^- \longrightarrow Ag$		+0.80	
$Pt^{4+} + 4e^- \longrightarrow Pt$		+0.86	
$Au^+ + e^- \longrightarrow Au$		+1.69	
$1/2F_2 + e^- \longrightarrow F^-$	(NOBLE)	+2.87	(CATHODIC)

Galvanic series

Although electrochemical series gives very useful information regarding chemical reactivity of metals, it may not provide sufficient information in predicting corrosion behavior in a particular set of environmental conditions because-

(i) in practical situations many side reactions may take place which influence the corrosion reactions.

(ii) electrochemical series does not shed light about alloys.

1. Theories of Corrosion

Corrosion occurs in 2 ways-

(1) Dry or Chemical corrosion

(2) Wet or Electro-Chemical or Immersed corrosion.

1.1. Dry or Chemical Corrosion

It occurs mainly through:

(i) Direct chemical attack of atmospheric gases like O_2, H_2, H_2S, NO_2, etc., on metals.

(ii) Action of anhydrous inorganic liquid with the metal surfaces.

O_2: At ordinary temperature, metals, in general, are very slightly attacked. However, alkali and alkaline earth metals are attacked by 02 even at low temperatures. At high temperatures, all metals (except Ag, Au and Pt) are oxidized.

$$2M + n/2O_2 \longrightarrow M_2O_n$$

The oxidation first occurs at the surface of the metal and the resulting metal oxide forms a barrier, that tends to restrict further oxidation. Further oxidation then depends upon the nature of the oxidized product-

(i) Stable- If the oxide film is stable and finely grained in structure, it gets tightly adhered to the parent metal surface protecting the metal eg., oxide films on Al, Sn, Pb, Cu, Pt. etc.

(ii) Volatile- If the oxide layer volatalises as soon as it is formed it leaves the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, eg., molybdenum oxide, MoO_3.

(iii) Porous-If the oxide layer is porous or has cracks the oxygen has access to the underlying metal surface and the corrosion continues unobstructed, eg., oxides of alkali and alkaline earth metals.

(iv) Unstable- The oxide layer decomposes back into the metal and oxygen and consequently, oxidation corrosion is not possible in such a case, eg., Ag, Au and Pt do not undergo oxidation corrosion.

$$\text{Metal oxide} \rightleftharpoons \text{Metal} + \text{oxygen}$$

Corrosion by other gases like SO_2, CO_2, Cl_2, H_2S, etc : Like oxidation, the degree of attack depends on the formation of protective or non-protective films on the metal surface-:

(i) Protective film or non-porous film - e.g. AgCl film, resulting from the attack of Cl_2 on Ag. The AgCl film protects the metal from further attack.

(ii) Non-protective or porous film - e.g. $SnCl_2$ film formed when dry Cl_2 gas attacks Sn.

The film is volatile leaving fresh metal surface for further attack. FeS film is porous and exposes iron or steel to further attack by H_2S.

1.2. Wet or Electrochemical Corrosion

This type of corrosion occurs in presence of:

i) a conducting liquid
ii) a single metal/ alloy

is exposed to this liquid or two dissimilar metals/alloys in electrical contact are exposed to this liquid.
In either case separate anode and cathode areas are formed on the metal surface, between which the current flows through the conducting solution.
At anode, oxidation takes place, i.e., the metal dissolves in the surrounding electrolyte to form metal ions.

$$M \longrightarrow M^{+n} + ne^-$$

The electrons liberated at the anode migrate to the cathode through the metal. At the cathode, the electrons are consumed. Usually, the cathode reactions do not affect the cathode part of the metal, since most metals are already reduced and cannot be reduced further. So, usually at cathodic part, dissolved constituents in the conducting medium accepts the electrons.

Hence, corrosion always occur at anodic areas and the cathode areas usually remains free
from corrosion.

Cathode reactions:

(i) Acidic environment-In presence of acids the cathodic reactions proceeds with evolution
of H_2 gas.

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

For e.g. Consider a metal like Fe, the anodic reaction is dissolution or iron as ferrous ions with liberation of electrons.

$$Fe \longrightarrow Fe^{+2} + 2e^-$$

These electrons flow through the metal from anode to cathode, where H^+ ions from the electrolyte and get liberated as hydrogen gas.

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

The overall reaction is: $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2\uparrow$

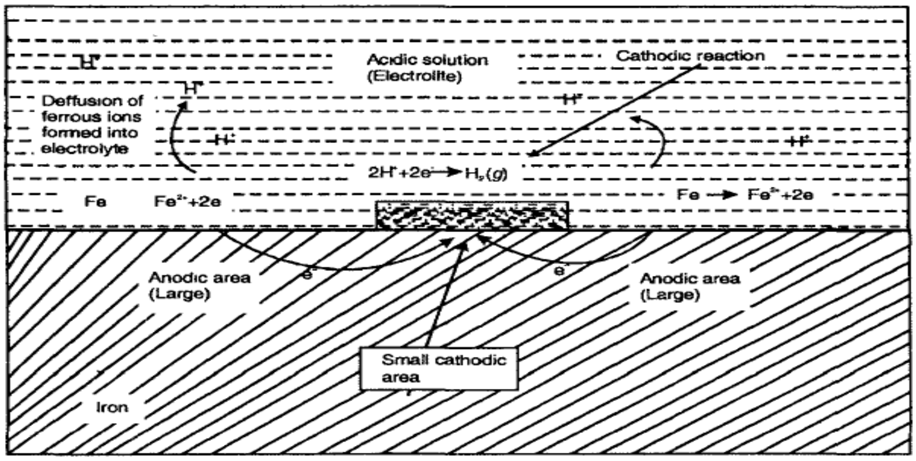


Fig. 1.1 Mechanism of wet corrosion by hydrogen evolution

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in the acidic solutions with simultaneous evolution of H_2 gas.

(ii) Neutral or alkaline environment- In neutral or alkaline environment, the electrons are accepted by the dissolved oxygen, to form OH- ions.

$$H_2O + \frac{1}{2} O_2 + 2e^- \longrightarrow 2OH^-$$

For e.g. Consider the corrosion of iron in neutral aqueous solution. At the anodic areas, iron metal dissolves as ferrous ions with liberation of electrons.

$$Fe \longrightarrow Fe^{+2} + 2e^-$$

Electrons liberated at the anode, migrate to the cathode through the iron metal and are intercepted by the dissolved oxygen and forms OH- ions.

$$H_2O + \frac{1}{2} O_2 + 2e^- \longrightarrow 2OH^-$$

The metal ions, Fe^{+2} ions, formed at the anode and the OH^- ions formed at the cathode diffuse towards each other and the corrosion product, ferrous hydroxide is precipitated.

$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2\downarrow$$

If there is enough oxygen present, ferrous hydroxide is easily oxidized to ferric hydroxide,
i.e., rust.

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \downarrow \quad \text{or } 2Fe_2O_3.2H_2O \quad \text{Rust}$$

The corrosion product is formed more commonly near or at the cathode because the smaller Fe^{+2} diffuse more rapidly than the larger OH^- ions.

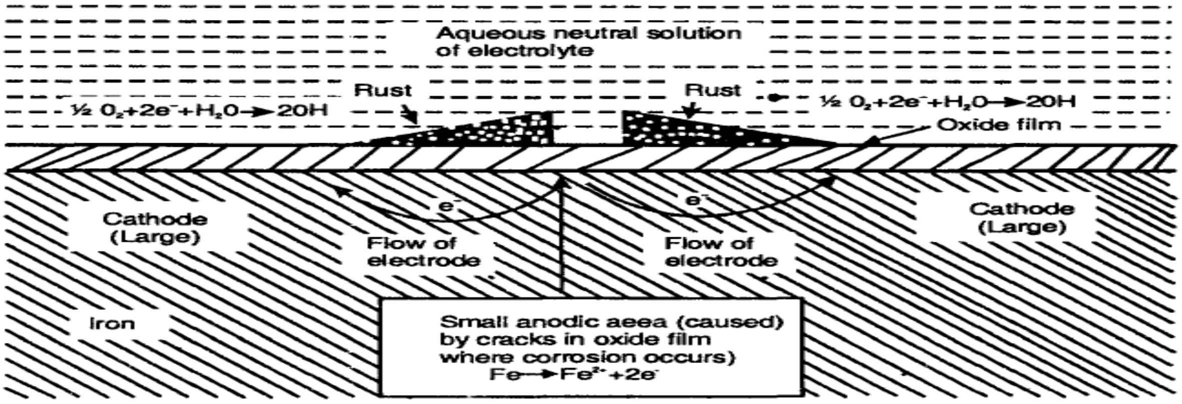


Fig. 1.2 Mechnism of wet corrosion by oxygen absorption

Types of Electro-Chemical Corrosion

1.Galvanic cell corrosion

Galvanic corrosion occurs when two dissimilar metals or alloys, e.g., Zinc and Copper, in electrical contact are exposed to an electrolyte. The metal or alloy higher in the galvanic series forms the anode and suffers corrosion while the metal or alloy placed below remains free from corrosion. Hence, in the above example, zinc, placed higher in the galvanic series, forms the anode and suffers corrosion whereas copper placed below forms cathode and remains free from corrosion.

Anode:

$Zn \longrightarrow Zn^{+2} + 2e^-$ ……………(oxidation)

Cathode:

In acidic solution. The corrosion occurs by the hydrogen evolution process.

$2H^+ + 2e^- \longrightarrow H_2$

In neutral or slightly alkaline solution, oxygen absorption occurs resulting in the formation of OH^- ions.

$$H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^- \quad \text{...............(reduction)}$$

The larger the potential difference between the two metals, the greater will be the rate of corrosion.
Some common examples of galvanic corrosion-
(i) Steel screws in a brass marine hardware.
(ii) Lead-antimony solder around copper wire.
(iii) A steel propeller shaft in a bronze bearing.
(iv) Steel pipe connected to copper plumbing.

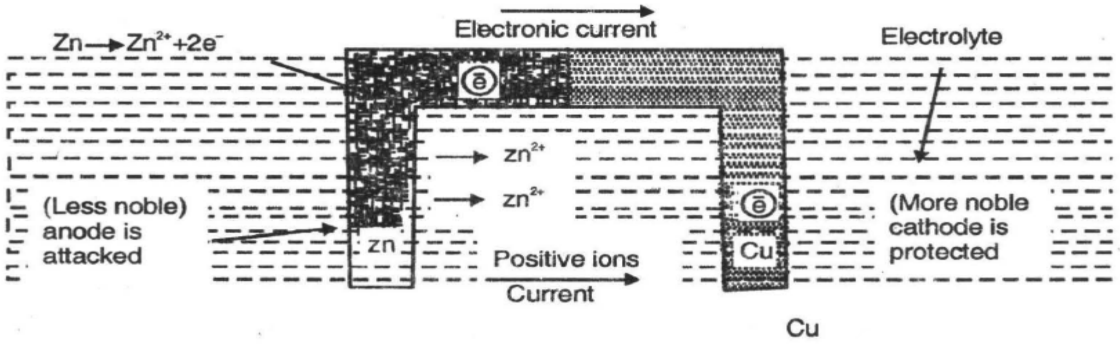


Fig. 1.3 Galvanic corrosion

2.Concentration cell corrosion

This type of corrosion is due to electrochemical attack on the metal surface, exposed to
(a) an electrolyte of varying concentrations, e.g., storage tank of a solution or
(b) an electrolyte of varying aeration or differential aeration.

(a) Metal in contact with solution of varying concentrations - This may be the result of local difference in metal ion concentrations, caused by local temperature differences or inadequate agitation or slow diffusion of metal-ions, produced by corrosion.

(b) Differential aeration - This is the most common type of concentration cell corrosion. It occurs when one part of the metal is exposed to higher concentration of air compared to the other part. This causes a difference in potential between differently aerated areas. The metal surface exposed

to higher concentration of oxygen, becomes cathodic, as oxygen helps in the consumption of electrons.
The metal surface which is exposed to lower concentration of air becomes anodic.
Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline. For e.g., consider a metal plate like Zn partially immersed in dilute solution of a neutral salt like NaCl. The parts above and closely adjacent to the waterline are more strongly aerated and hence become cathodic.

On the other hand, parts immersed to greater depth have less access to oxygen become anodic.
Thus a difference in potential is created, which causes a flow of current between the two differentially aerated areas of the same metal.
At anode, Zinc will dissolve to form Zinc ions.

$$Zn \longrightarrow Zn^{+2} + 2e^-$$

The electrons liberated at the anode, is accepted at the cathode by the oxygen to form hydroxyl ions.

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

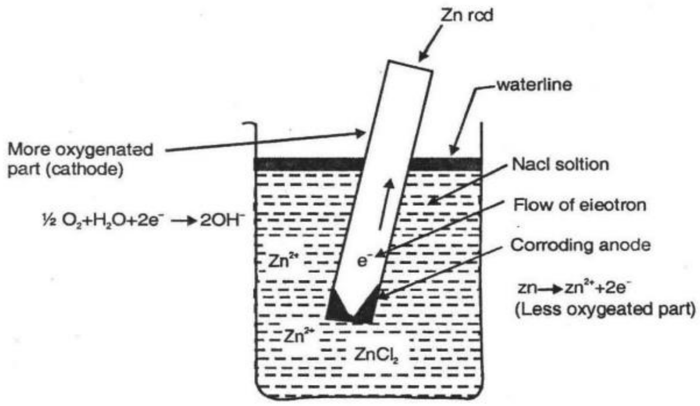


Fig. 1.4 Mechanism of differential aeration attack caused by partial immersion of a metal

Similarly, iron corrodes away under a drop of water or salt solution.
Areas underneath the drop, are less aerated and forms anode compared to

the areas at the periphery of the drop and the remaining areas, which are freely exposed to air and forms cathode. Metal dissolves at the anodic areas while the OH- ions are formed at the cathode and the corrosion product, i.e., rust is deposited at the cathodic areas.

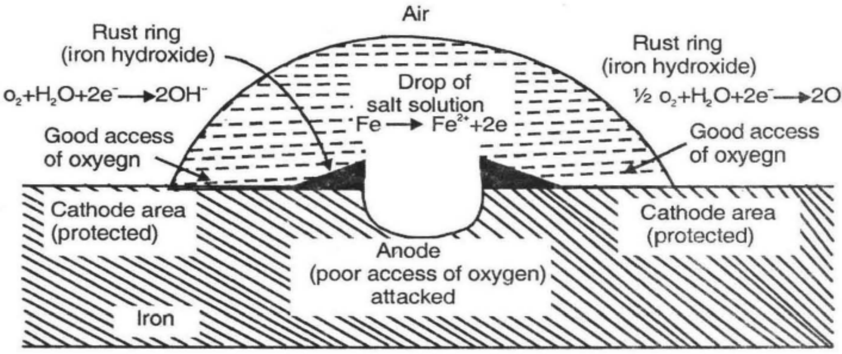


Fig. 1.5 Mechanism of differential aeration attack, caused by the presence of drops of salt solution on the iron surface. metal dissolves at the less-aerate anodic areas; whereas corrrodsion product (iron hydroxide) is deposited at the cathodic areas.

Some more examples of differential aeration corrosion:
(i) Corrosion of metal in cracks or crevices are accelerated, as these areas are deficient in oxygen concentration and consequently behave as anode while the rest of the plain surface of the metal behaves as the cathode.

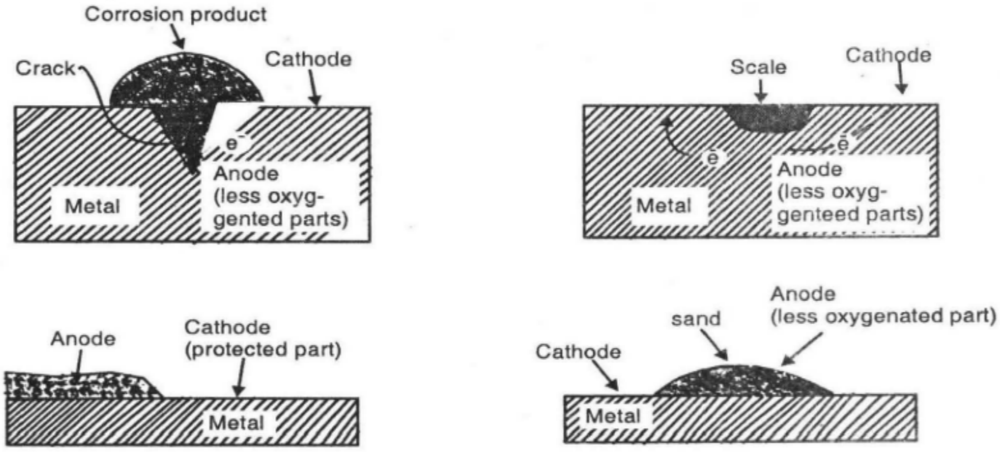


Fig. 1.6 Oxygen concentration corrsion. Anode is formed at inaccessible location, where oxygen is less available. The cathode forms, where oxygen is freely available

Corrosion of metal is accelerated under the accumulation of dirt, sand, scale or other contamination. This is because accumulation or rust, scale or sand, etc. restricts the access of oxygen. The portion of the metal under these areas thus behave as anode and the remaining areas that are clean and free from the impurities form the cathode.

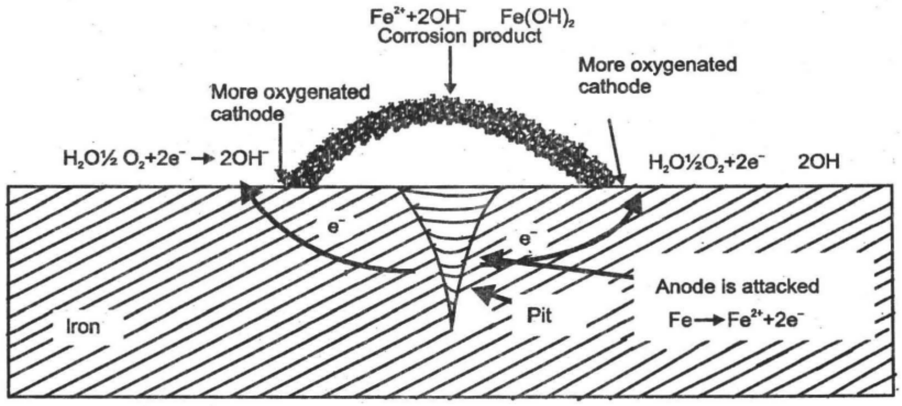


Fig. 1.8 Pitting corrosion at the surface of iron

(ii) Metals under block of wood or pieces of glass, which screen that portion of metal from oxygen access form anode when exposed to a suitable electrolyte.

3. Intergranular corrosion

This type of corrosion occurs along grain boundaries in metal alloys. Metal alloys are finely grained in structure.
This type of corrosion occurs because of an alloy concentration gradient between the grains and the grain boundaries and the presence of an electrolyte which possess the selective character of attacking only at the grain boundaries. This concentration gradient occurs due to precipitation of certain compounds at' the grain boundaries, thereby leaving the solid metal solution (alloy) adjacent to the grain boundary, deficient in one constituent. The grain boundary acts as an anode with respect to the grain centre which becomes the cathode. The precipitated compound also becomes cathodic.

For e.g., During the welding of stainless steel (alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries. Thus the region just adjacent to the grain boundaries become deficient in chromium and is therefore more anodic with respect to the grain centre which is richer in chromium. It is also anodic to the particles of chromium carbide so precipitated.
This type of corrosion occurs on a microscopic scale without any external signs of any intensive attack. On account of this sudden failure of material occurs (without any pre-warnings) due to loss of cohesion between grains.

The remedy for such corrosion of alloys is heat treatment followed by rapid quenching to avoid heterogeneous precipitation, that usually occurs due to slow cooling.

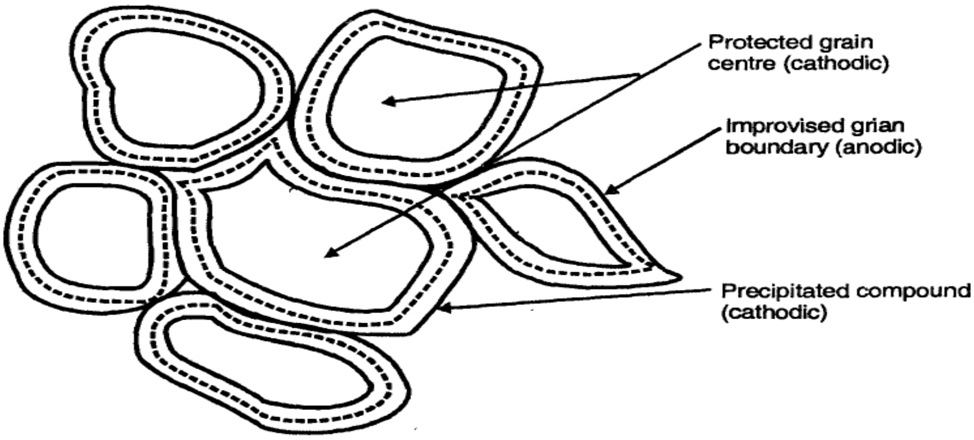


Fig. 1.9 General intergranular attack

4. Stress corrosion

Stress corrosion is the combined effect of static tensile stresses and the corrosive environment on a metal. Stress corrosion is characterized by a highly localized attack when overall corrosion is negligible. For stress corrosion to occur –

(i) the presence of tensile stress and

(ii) presence of specific corrosive environment is necessary. The corrosive agents are highly specific and selective such as acid chloride solution for stainless steel.

The stress may have been produced during manufacture or fabrication or heat treatment. The external stress is due to the service condition.

FACTORS AFFECTING RATE OF CORROSION

The rate and extent of corrosion, depends on the following factors:

- Nature of the metal
- Nature of the environment

1.Nature of the metal:

(i) Position of metal in the galvanic series: When two different metal or alloys in electrical contact is exposed to an electrolyte, the metal which is placed above in the galvanic series forms the anode and suffers corrosion while the metal which is placed below forms cathode and remains free from corrosion.

Greater the difference in the position in the galvanic series, faster is the rate of corrosion.
(ii) Overvoltage: Reduction in the overvoltage of the corroding metal/alloy accelerates the corrosion rate.
(iii) Relative areas of anode and cathode: Rate of corrosion is directly proportional to the ratio of the areas of the cathodic part to the anodic part.

Corrosion is more localized and accelerated, if the anodic area is much smaller than the cathodic area because the demand for electrons by the large cathode is very high and can be satisfied only by undergoing corrosion more rapidly, eg., a small steel pipe fitted in a large copper vessel.

(iv) Purity of metal: The rate of corrosion increases with increase in the impurities in the metal.

Impurities in a metal, form tiny galvanic cells with the base metal and the anodic part gets corroded.

(v) Physical state of the metal: The rate of corrosion is influenced by the physical state of the metal (such as grain size, orientation of the crystal, presence of stress, etc.).

The smaller the grain size of the metal or alloy, the greater will be its corrosion. Areas under stress, even in a pure metal tend to be anodic and corrosion takes place at these areas.

(vi) Nature of the surface film: In aerated atmosphere, practically all metals get covered by a thin film, a few Angstroms in thickness, of metal oxide. The ratio of the volumes of the metal oxide to the metal, is known as specific volume ratio.
(vii) Solubility of the corrosion products: If the corrosion product is soluble in the surrounding medium, then corrosion proceeds at a faster rate. On the other hand, if the corrosion product is insoluble or it forms an insoluble product on reacting with the medium, then it forms a physical barrier, and protects the metal from further attack by the medium, eg., PbS04 formed when Pb reacts with H2S04 medium.
(viii) Passive character of metal: Metals like AI, Cr, Ni, Co are passive and exhibits a much higher resistance to corrosion than expected from their positions in galvanic series.

This occurs due to the formation of a highly stable, but very thin film of the corresponding metal oxide on the metal surface. Also, the film is self-healing, i.e., if the film is broken, it repairs itself, on re-exposure to oxidizing conditions. The exceptional corrosion resistance of stainless steel is due to the presence of a passive chromium oxide film on its surface.

2.Nature of the environment

(i) Humidity: Iron does not corrode in dry air but undergoes rapid corrosion, when exposed to moist air. In fact, the corrosion of all metals become faster in humid atmosphere.
Gases (C02, 02' etc.) and vapors dissolve in the moisture, providing the electrolyte, necessary for setting up of an electrochemical corrosion cell. Also, rain water, helps to wash away a good part of oxide film from the metal surface, leading to enhanced atmospheric attack, unless the oxide film is exceptionally adherent (eg., Cr, Al)

(ii) Temperature: The rate of any reaction as well as diffusion reactions, increases with increase in temperature. Hence the rate of corrosion reaction also increase with increase in temperature.

(iii) pH: Corrosion reactions involve H+ and OH- ions, hence rate of corrosion reactions are affected by the pH of the medium.

(iv) Presence of impurities in the atmosphere: Atmosphere in the vicinity of industrial areas, contains corrosive gases like CO2, H_2S, SO_2 and fumes of HCl, H_2SO_4, etc. In the presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases resulting in increased corrosion.

Corrosion is also a severe problem in marine atmosphere due to the presence of chloride ions in the environment.
(v) Nature of the ions present: Ions can enhance the rate of corrosion or depress the rate of corrosion.
Presence of anions like silicate in the medium leads to the formation of insoluble reaction products which inhibit further corrosion. Chloride ions, on the other hand, destroy the protective and passive surface film, thereby exposing the metal or alloy surface for fresh corrosion. Many metals, including iron, undergo corrosion rapidly, if the corroding medium contains ammonium salts. Presence of even traces of copper or other noble metals in mine waters, accelerates the corrosion of iron pipes carrying such waters.

(vi) Conductance of the medium: The conductance of the medium plays a great role in the corrosion of underground or submerged structures. Conductance of clay or mineralized soils is higher than that of dry sandy soils. So, stray currents from power leakages will damage the metal structures buried under soils of higher
conductance to a greater extent than those under dry sandy soils.

(vii) Concentration of oxygen and formation of oxygen concentration cells: The rate of corrosion increases with increasing concentration of oxygen. Differential aeration also promotes corrosion by the formation of oxygen concentration
cell. Corrosion often takes place under metal washers where oxygen cannot diffuse easily.

METHODS TO DECREASE RATE OF REACTION

1.Cathodic protection

It is based on the principle that the metal to be protected is forced to behave as a cathode, and thereby avoid corrosion.

The two types of cathodic protection are:

(i) Sacrificial anode method - The metallic structure, to be protected, is connected by a metallic wire to a more anodic metal called the sacrificial anode SQ that all the corrosion is concentrated on this more anodic metal.

When sacrificial anode is corroded completely it is replaced by a fresh one. Examples of sacrificial anode metals- Mg, Zn, 'AI and their alloys.

Uses - This method is used for the protection of buried pipelines, underground cables, marine structures, ship hulls, water tanks, etc.

(ii) Impressed current cathodic protection - An impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The impressed current is derived from a direct current source like battery with an insoluble anode like graphite, high silica iron, scrap iron, stainless steel, platinum black fill (coke).

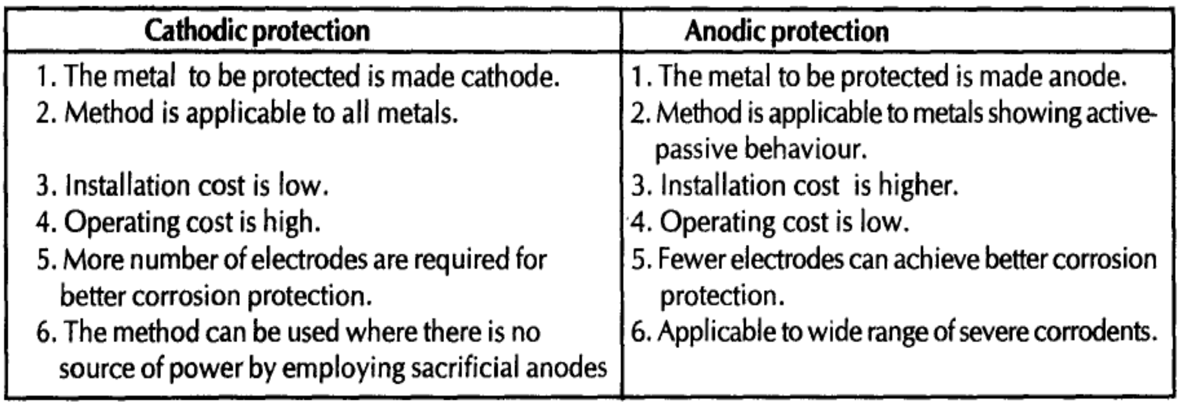
Uses - This type of protection has been applied to open water-box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine pliers, laid up ships, etc.

2.Anodic protection

Certain metals exhibit active-passive behavior depending on the pH of the medium and the potential developed in contact with a liquid.

For e.g., iron can be active as well as passive to corrosion in contact with water under the influence of pH and electric potential. Thus for any given condition, X, of the metal, we can achieve corrosion protection by cathodic protection, by neutralization or by anodic protection. Thus anodic protection of iron can be achieved by applying a potential more than 0.1 V (pH = 7) through an external circuit. This protection method is generally applied in iron, steel, stainless steel, aluminum, titanium, chromium.

The cathode material used must be such that it does not suffer much corrosion. Platinum clad metals or some corrosion resistant alloys are often used.



Cathodic protection	Anodic protection
1. The metal to be protected is made cathode.	1. The metal to be protected is made anode.
2. Method is applicable to all metals.	2. Method is applicable to metals showing active-passive behaviour.
3. Installation cost is low.	3. Installation cost is higher.
4. Operating cost is high.	4. Operating cost is low.
5. More number of electrodes are required for better corrosion protection.	5. Fewer electrodes can achieve better corrosion protection.
6. The method can be used where there is no source of power by employing sacrificial anodes	6. Applicable to wide range of severe corrodents.

3.Advanced coatings

A coated surface isolates the underlying metal from the corroding environment. It can be metallic, inorganic or organic.

3.1. METALLIC COATINGS:

A coating of one metal or alloy over another metal or alloy is called metallic coating.
It can be divided into-
(i) Anodic coatings.
(ii) Cathodic coatings.

(i) Anodic coatings: These coatings are produced from metals which are anodic to the base metal to be protected, i.e., metals which lie above in the galvanic series, e.g., Zn, AI, Cd coatings on steel.

If any pores or breaks occur in such coatings, a galvanic cell is formed between the coating and the exposed part of the base metal. In such a case, since the coating metal is anodic, it corrodes, leaving the underlying metal unprotected.

Thus the anodic coatings act as 'sacrificial anode'. The corrosion is more uniform and less severe as the anode surface area is much larger compared to the cathode.
These coatings can be applied by hot dipping, spraying, etc.

(ii) Cathodic coatings: These coatings are produced from metals' which- are cathodic to the base metal to be protected i.e., metals which lie below in the galvanic series, e.g., Sn, Ni, Cr coatings on steel.

If any pores or breaks occur in such a coating, a galvanic cell is formed between the coating a galvanic cell is formed between the coating and the exposed part of the base metal. In such a case, the base metal being more anodic corrodes.
As the surface area of the anode is much less compared to the cathode, intense corrosion occurs resulting in severe pitting and perforation of the base metal.

3.2. ORGANIC COATINGS

Organic coatings are inert organic barriers (like paints, varnishes, lacquers, enamels) applied on metallic surfaces and other constructional materials for both corrosion protection and decoration.

a) Paints

Paint is a mechanical dispersion of one or more pigments in a vehicle. Vehicle is a liquid, consisting of non-volatile film-forming material, drying oil and a highly volatile solvent, thinner.

b) Varnishes

Varnish is a homogenous colloidal dispersion-solution of natural or synthetic resin in oil or thinner or both.

c) Enamels

Enamel is a pigmented-varnish. On drying enamels give a lustrous, hard and glossy finish.

d) Lacquers

A lacquer is a colloidal dispersion of solution of cellulose derivative, resin, plasticizer insolvent and diluents. Lacquers on drying yield a transparent, hard and water-proof film.

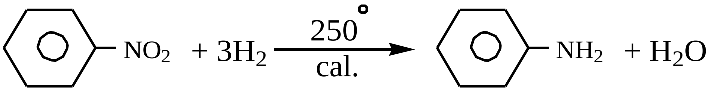
Chapter (4)

Fundamental of choosing the chemical reactions and the technology to transfer them to industrial level.

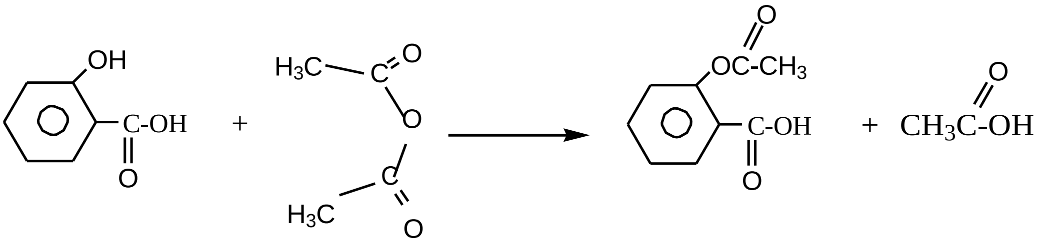
In general there are different methods to prepare any chemical, the methods are differ from each others in the starting materials or solvents or the conditions of the reaction , and so on….

In order to transfer the reaction from the laboratory to the industry, the economic must be studied first, also the control of the reaction and the dangerous on the workers and on the environmental.

Some reactions are very simple and can be used directly on the industrial level without any modulations for examples:



Preparation of aspirin, production of magnesium preparation of soda lime limestone, as the side products of all these reactions is agas. So it was favored in chemical industries



$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

There are another reaction need some modulation to converted it from laboratory level to industrial level like oxidation of olifins. See types of reactions on page 103.

The general observations for these reactions are:

1) All the reactions used oxygen instead of $KMnO_4$
2) The catalyst used in laboratory is the some used in industry.
3) The reactions need high pressure and temperature that can not be found in the simple laboratories.

Another example, the preparation of ethyl amine there are eight methods,page 104. In order to choose the suitable reaction to be used as industrial one, many factors must be known as:

1) Choosing the simplest reaction that produce the product directly.
2) The conditions of the reaction must be simple (heat, pressure, catalyst).
3) The available of the solvent with high qualitative and quantitative.
4) Choose the reaction with high conversion .
5) In case choosing the low conversion reaction, it must be used another technique to rolate the unreacted starting materials (recycling) .
6) Choosing the lowest pollutant method.

The industrial conversion technology

It is a process that convert the row natural materials or the halfed made to industrial products. This process include three steps:

1) Carrying the reactants from its sources to the factory.
2) Made the reaction and provide all the tools for controlling.
3) Separate the main products and pared it and recycle the unreacted materials and solvent, also separate the side products.

The industrial conversion process in a complete system includes all the chemical physical and mechanical operations which are correlated with each other by high accuracy. This was done to get lower cost and work.

The chemical processes include reactors, burning chamber, so on…

All the units of production are contacts with each others by using a map, this map called flow diagram or flow sheet (flow chart) . the flow diagram is a universal language with known symbols to elucidate the way of flowing of the materials through the process. This diagram provide a main information's about:

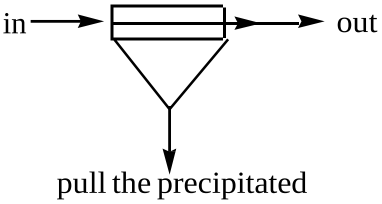
1) The starting materials and its interning points to the chemical process.
2) The needed energy and its interning points.
3) The different chemical, physical and mechanical operations with the recycling processes.
4) The points of pulling up the products.
5) The points of pulling up the important side products.

There are two ways to draw the flow diagram

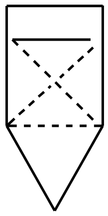
1) Detailed diagram
2) Blocked diagram

In detailed diagram the unit can be represented by some symbols like

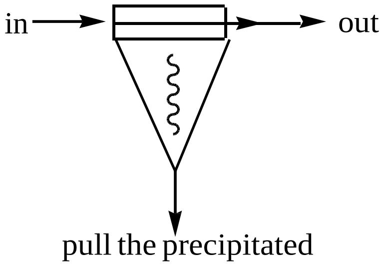
- The way of fllowing → ↑ ↓ ← arrows
- Pumps
- Clarifiers



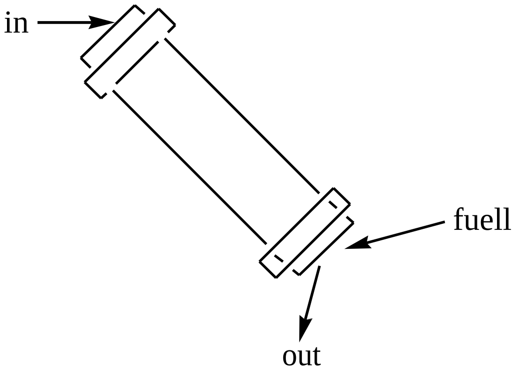
- Reactors



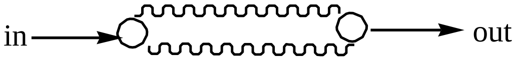
- Cyclone (separating by centerfuge)



- Kilm, mixer



- Coverter belt

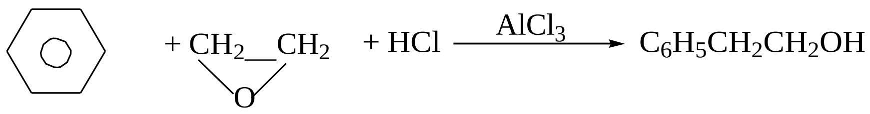


In this diagram many important information must be written like the energy needed, temp. amount of rotation , etc….

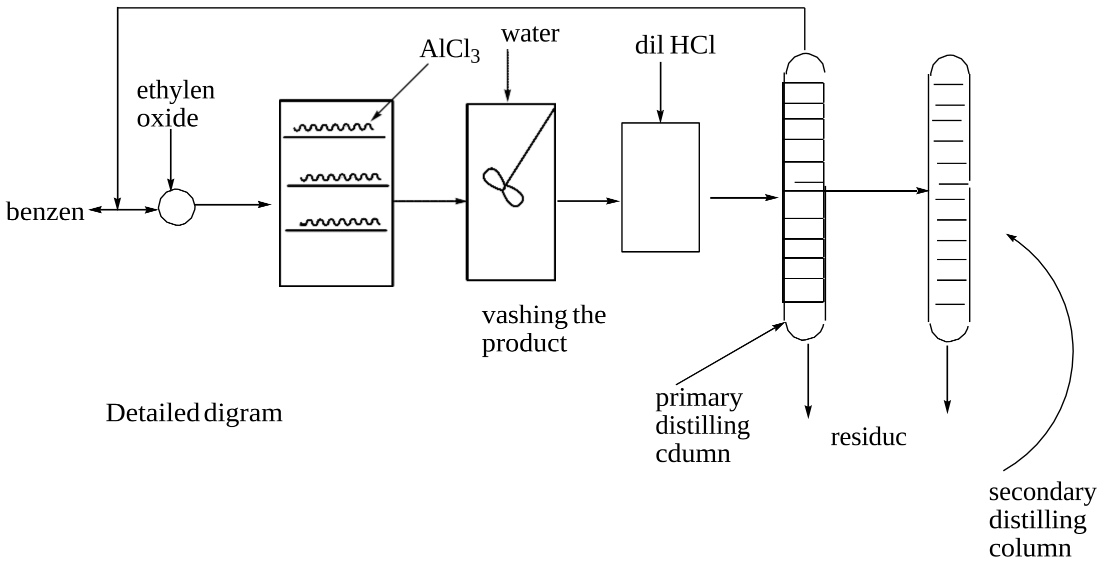
While in the blocking diagram , is so simple, only the name of the process was written in a rectangle without any details.

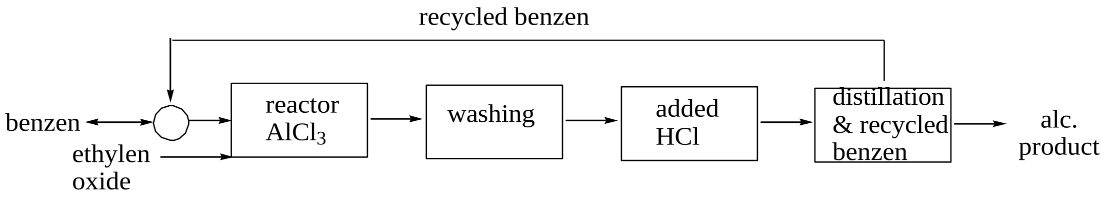
Examples:

Preparation of phenylethylacohole by the reaction of ethylene oxide with benzene in an acidic medium by using aluminum chloride as a catalyst.



In this process the benzene was added with excess amount, this amount must be recycled





Preparation of sulfur element by clauss process

The chemical equation of the reactions are:

$H_2S_{(g)} + 3/2\ O_{2(g)} \xrightarrow{\quad\quad} SO_{2(g)} + H_2O \quad \Delta H = -123.9\ Kcal$

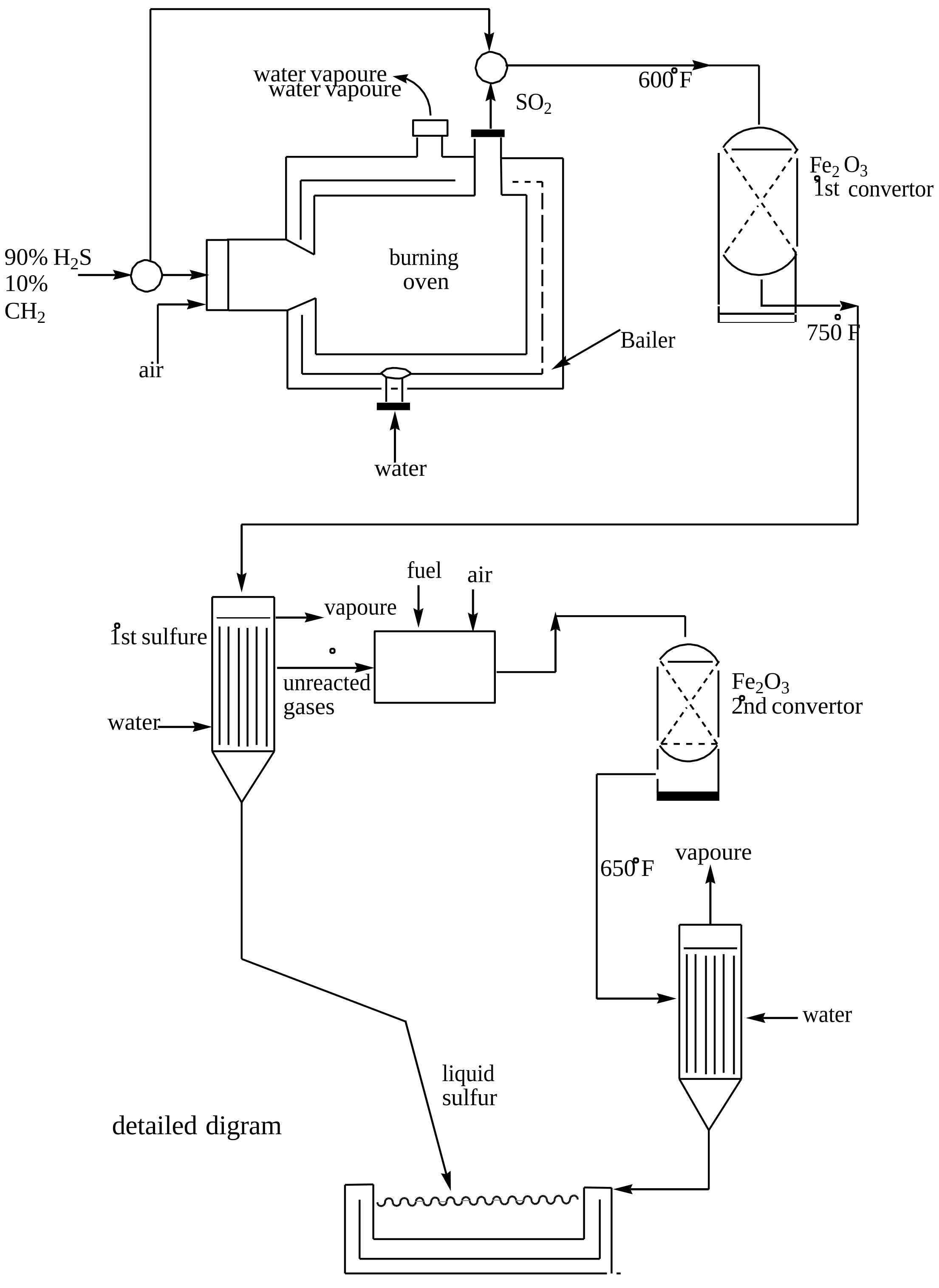
Strong exothermic

$SO2 + H_2S \xrightarrow[Cat.]{Fe_2O_3} 3S + 2H2O(g) \quad \Delta H = -34.2\ Kcal$

exothermic

the reaction include burning part of H_2S gas , the resulted SO_2 reacls with the another part of H_2S to produce a free sulfure in presence of a catalyst. The two reactions are exothermic, the excess heat can be used in another placeses.

The diagram in page 117 Arabic.


water vapoure
water vapoure
SO$_2$
600°F
Fe$_2$O$_3$
1st convertor
90% H$_2$S
10%
CH$_2$
air
burning
oven
Bailer
750 F
water
fuel
air
vapoure
1st sulfure
unreacted
gases
water
Fe$_2$O$_3$
2nd convertor
650°F
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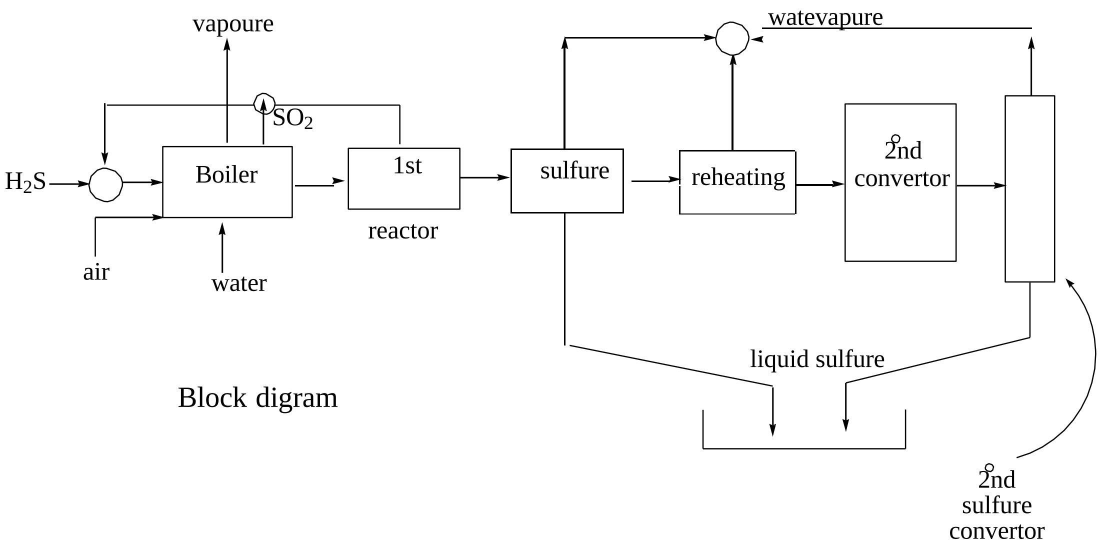
water
liquid
sulfur
detailed digram



Block digram

Application the chemical processes in industry

Two types of application in in production

1) Batch system (batch processing).
2) Continuous system (continuous processing).

In the batch system the process was done as in the laboratory, where the reactor was and stay with appropriate time in the conditions of the reaction until the time is spent, then the reactor was poured from the product and recharged again with the reactants.

Batch process

1) Stimulation as in a laboratory
2) The degree of reaction proceeding is a fuction of time.
3) There is a loss in time and energy where by the reactor must be powred and recharged.

But the batch processes is necessary in the following case.

1) Need the sufty especially in manufacturing of explosives and poisonous materials .
2) In slow reactions or that have low conversion.
3) In initial steps of new industrial process.

Continuous processing

The properties are:

1) No loss of time or energy.
2) Need a pollutant equipment for controlling the reaction (temperature, prossure,…..) .
3) The factory was self controlled by compouters.

Chemical reactors

It was the most important unit in chemical technology because it represent the part in which the reaction was carried out. Also it represent the main economic area to open any industrial project.

The properties of any reactors must be:

1) Have high production power, this depends on many factors like velocity of lowing and concentration factors like velocity of flowing and concentration.

$$\text{Power of production} = \frac{V_m\text{-}C}{V}$$

V_m = velocity of flowing of reactants in m^3/hr.

C= concentration of products in the output point.

V= volume of the reactant.

2) Have high yield and selectivity, this can be obtained through accurate controlling on the reactions conditions (temperature ,pressure, and concentration of reactants and products).

3) Low spending of energy, also the liberated energy can be used in another places.
4) Easy to control the reaction
5) Low cost and low degree of repairing.

From these properties, we can noticed that the reactor in batch process in differe from continuous process, since the power of production for batch is lower that the continuous, and the contents in batch reactors were changed with time but does not changed in continues system (or does not depends on time with the continues system).

The main fundamental factors to design the reactors are:

1) Rate of the chemical reactions.
2) The phase of reaction.
3) Homogenely of the reaction.
4) If the reaction are catalyzed or not.

1) Tubular reactor

Some characterstics of these reactors are

-the reactants have one direction in flow.

- generally the flowing is from up to down.

- there are no stopping of flowing through the reaction proceeding.

- the uses are in gaseous reactions and some aqueous or liquid reactions

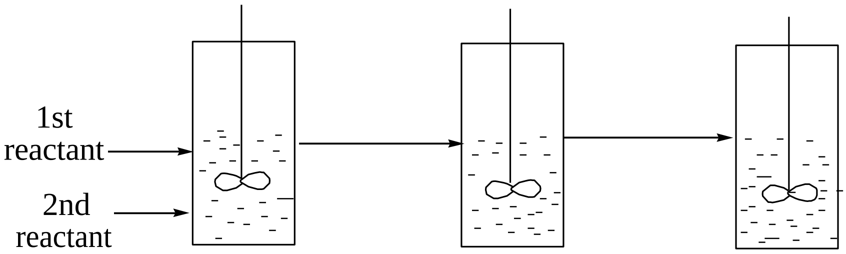
- some types of reactions in gas phase are thermal craking of hydrocarbons to produce ethylene-oxidation of NO to NO2 in nitric acid industry-sulfonation of olefins.

All these reactions are of homogeneous type.

- Can be used in catalytic reactions, where as the reactors are filled with the catalyst (solid catalyst) this types of reactors called Fixed-bed reactors, it was used in; preparation of ammonia from the reaction of H_2 with N_2-preparation of methanol by the reaction of CO with H_2.

- The reactor consist of one large tube or multiple fine tubes

2) Continuous stirred tank reactor
   - This tank have efficient stirrer.
   - The reactants inter continuously and transfer from unit to another continuously also.
   - The design is a wide cylinder, have widish equal to its depth with efficient mixer. The general characteristics are
   1) easy in designing and low cast.
   2) Ease in controlling on temperature.
   3) Ease in cleaning and conserving.
   - The types of reactions can be do in this reactors;sulfonation-nitration-polymerization .



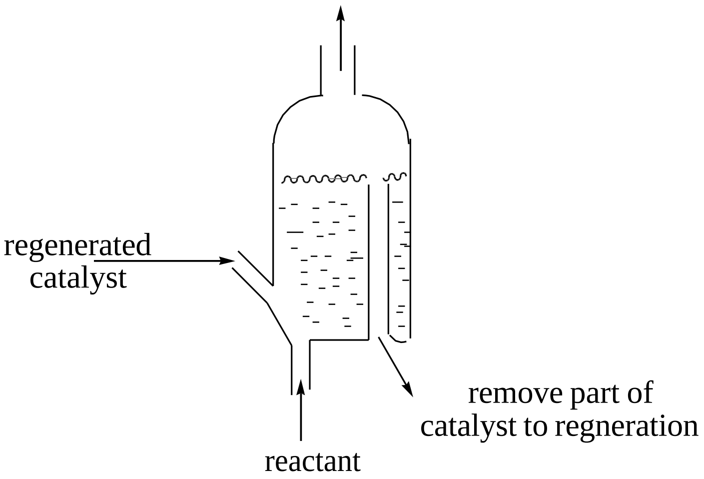
3) fluidized-bed reactor

   Fluidized materials: are materials with very fine powdered, it behaves as a liquid in flowing.
   - The using in reaction between gas material with fluidized solid. It can be used in catalytic cracker reactions, whereas the fluidized matter is the catalysis to creake the vapours of hydrocarbons, another reactions; oxidation of solid naphthalene by air to phthalic anhydride- reduction of uraniumtrioxide to uranium dioxide by using hydrogen and to tetrafloro uranium.

$$UO_3 \xrightarrow{H_2} UO_2 \xrightarrow{HF} UF_4$$

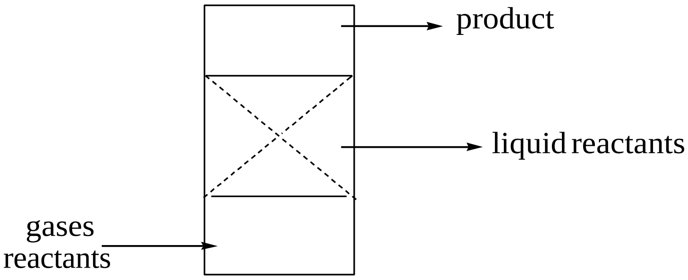
- In this reactor the fluidized matter was filled in a cylinder and the gases are bubbled from down by a rate enough to push the solid another up only, this make the gas bubble leave the surface of the solid with operation like a boiling. This continuous movement in the solid matter led to a homogenous distribution of heat in the reaction.

In catalytic cracking of hydrocarbons, the surface of the catalyst is gradualy coated with char, and this char will decrease the activity of the catalyst. The best solution for this problem is to remove part of this catalyst (fluidized matter) continuously to regenerate it and then return it to the reaclor. The two process can flow in the same time continuously with out need to another reactor.



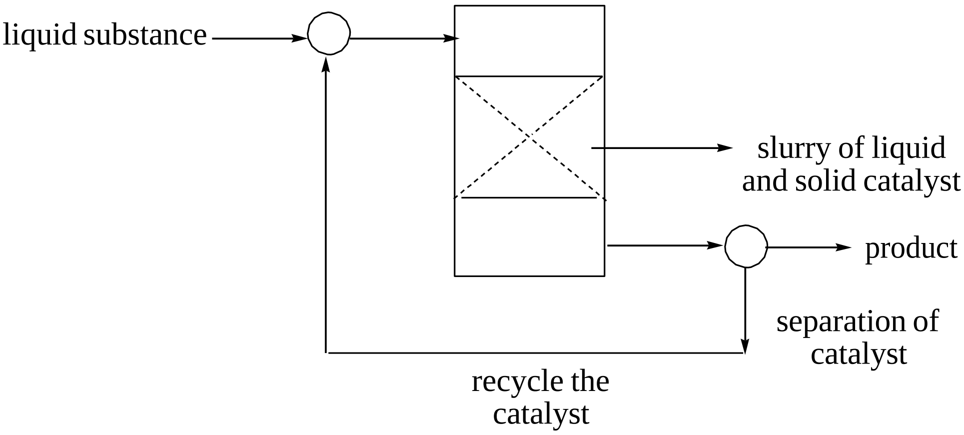
4) Some special reactors
- Bubble-phase reactor

The reactant was pushed as bubbled gas through another liquid reactant, e.g. oxidation of ethylene to acetaldehyde.



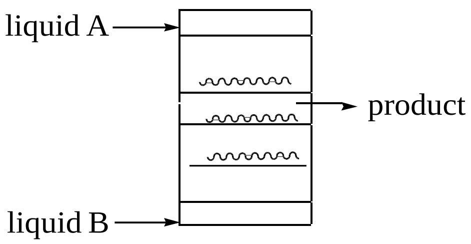
- Slurry-phase reactor

The reactants are slurry liquid with solid catalyst, e.g. oxidation of hydrocarbons to alcohols.

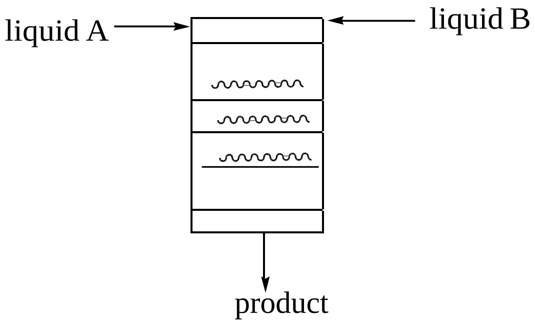


- Trickle-bed reactor

The liquid reactant was passed through stable solid catalyst either by concurrent (in one direction) or by counter current (two opposite direction).



concurrent

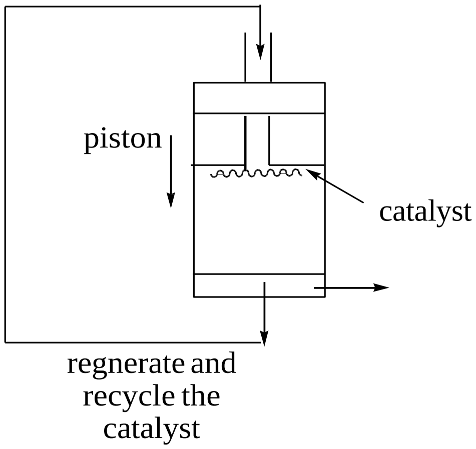


counter current

- Moving burden –bed reactors

The solid catalyst was moved by using a piston from up the reaction through the liquid reactants the catalyst was drawen from down the reactor, regenerate and recycled to the reactor.

e.g. isomerization of xylenes, continuous removing of hardness from water by ion exchange.



Pilot plant

It was small production unit, it produce small amount of products in the same design of the main unit. All the computational processes was accomplished within this unit in order to calculate the needed energy and the elucidate the amount of matters needed.

The benefit of this unit is to:

1) Identified the problems that may be seen in the big unit, and repair it.
2) Continue the development and the factory and to design the new generation of the industrial technology.

Chapter (5)

Water in industry and for human usage

The needed for water in chemical technology is in the following areas:

1) Is a main reactant in some reactions, like production of alcohols from olefins, production of hydrogen gas, manufacturing of soaps.
2) Used as a solvent
3) Used in cooling system
4) Used in converting the energy of heat to another energy.

Sources of water in nature

In water cycle, the underground water stay for several periods until the people digging it out, it contains different concentration of salts, according to where it is.

In industry only the sweet water can be used, the sources of water are:

1.) Superficial water: it was as
a.) Sweet, b.) Salty
2.) Underground water.

All the types of water must be treated before used.

The reasons for treatment the water to be used in chemical industry are:

1.) Preparing for different application, for example the cooling water must be soft , the water used in chemical reaction must be very pure.
2.) The used water must be recycle to be used again the main purpose is rationalization in using the sweet water.

    Some recycling process are cooling the hot water or removing the impurities from the expended water.
3.) Separation the side product from the used water this step is very economical step.
4.) Protection from pollution.

The material in water must be treated:

a- Hardness causative -b- inorganic mutters -c- organic mutters -d- suspended materials -e- soluble gases.

a.) Hardness causative:

The hard water is the water that the lather of soap cannot be formed.

This causes different in cleaning process.

The reason is the presence of some salts, these salt leave some solid precipitate after boiling the water in the surface of metal flasks.

In the other hand the soft water is the water that didn't consist these salts.The reason of no lather of soap can be formed in the hard water is the converting of the sodium soap to calcium of magnesium soap. Which will not dissolve in water and precipitate on clothes.

$$\begin{array}{cccc} \mathrm{RCOONa} & +\mathrm{Ca}^{+2} & \xrightarrow{\hspace{2cm}} & (\mathrm{RCOO})_2\mathrm{Ca} \\ \text{soup} & \mathrm{Mg}^{+2} & & (\mathrm{RCOO})_2\mathrm{Mg} \end{array}$$

Types of hardness:

1) Temporary hardness which can be caused by the presence of calcium or magnesium bicarbonate $Mg(HCO_3)_2$ or $Ca(HCO_3)_2$
2) Permanent hardness, the reason is the salt of coliseum or magnesium of chloride of sulfate

The first one known as carbonated hardness and can be removed by heating only. The second one known as non carbonated hardness and cannot be removed by heating.

The degree of hardness can be expressed by the contains in water that cause hardness, the content of Calcium or Magnesium salt is expressed by ppm as equate to $CaCO_3$

Example

Sample of water contains 70 ppm of permanent hardness as $MgSO_4$.The degree of hardness can be expressed as $CaCO_3$ as below:

$$\frac{\text{M.t of } MgSO_4}{\text{M.t of } CaCO_3} = \frac{120}{100} = 1.2$$

Degree of hardness = 70×1.2 =84 ppm.

Classification of water according to hardness

Water	**Degree of hardness /ppm**
Very soft water	0-1.5
Soft water	1.5-3.0
Moderate softening	3.0-6.0
Hard	6-10
Very hard	>10

Another system of hardness expressing in English system is b) gram/gallon where gram/gallon =17.1 ppm

b- Soluble inorganic matters

It is a matter other than hardness causative, as Al_2O_3, S_1O_2, Sodium silicate.

The contents concentration of these matters depends on the source of water, and can be removed according to the needed.

c- Soluble organic matters

This can be produced by the decomposition of organic materials or the dead living.

This matter causes a change in the test and the odor of water.

d- E.g.mud, slami and sand which can produce by human action.

These materials can be removed by settle sown and filtration.

e- Soluble gases

e.g. N_2 or CO_2, O_2, H_2S which causes a corrosion.

The stagnant water contain another harmful gases like NH3, CH_4 and Phosphine (PH_3) which can be produced by decomposition of the dead beings

Basic process to prepare the industrial water

Generally there are no specifications of industrial water, as every industry need specific water , any way there are two types of water can be used:

1.) Pure water:

It doesn't contain organic material or microscopic beings.

2.) Soft water: doesn't contain hardness

The water may be pure but hard or vers versa (soft but un pure)

.

1) Purification and sterilizing

To purify the water from the flotant partical, the filtration process can be used.

The small organic solube partical can be removed by using the aerobic or chemical oxidation

$$\text{Organic} + O_2 \longrightarrow CO_2 + H_2O \qquad \text{aerobic}$$

$$\text{Organic} + \text{oxidizing agent} \longrightarrow CO_2 + H_2O \qquad \text{chemical}$$

The sterilizing process is by using chlorine or the fresh chloramines (NH_2Cl)

$$2NH_3 + Cl_2 \longrightarrow NH_2Cl + NH_4Cl$$

The chloramines is more favouvable because it was more stable and give better test to water.

2) Hardness elimination process

A) Jon exchange process

The material used in this process called ion exchanger resins.It was a solid polymeric materials have ability to exchange ions in its surface with ion in the solution (ions causing the hardness) like Calcium and Magnesium

$$y^+ + R^-X^+ \longrightarrow R^-y^+ + X^+$$

y^+= harmful ion in water
X^+= un harmful ion holded on the surface of ion exchanger
R^-=resin

The most popular resin called zeolite, it was a natural matter have Sodium ion can be exchanged.

The process include passing the hard water through the zeolite which was put in a columa from up to down.

There are another synthesised polymeric material used as ion exchanger as styrene-divinly benzene polymer which have SO_3H function al group.This matter used hydrogen ion to be exchanged.

The removal of hardness by using zeolite is according to the equation

$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$$

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$$

The expended zeolite can be regenerated by washing with concentrated solution of Sodium chloride at pH=6-8.

$$CaZ + \underset{\text{excess}}{2NaCl} \xrightarrow{pH=6-8} Na_2Z + CaCl_2$$

Types of ion exchangers

a) Cataionic exchangers (acidic)

Which are two types

i. Strong acidic ion exchanger contains SO_3H or SO_3Na as function group.The exchange processes are according to the following equations:

Temp. $Ca(HCO_3)_2 \longrightarrow Ca(SO_3R)_2 + 2CO_2 + 2H_2O$

Permanent $CaSO_4$ $nRSO_3H \longrightarrow Ca(SO_3R)_2 + H_2SO_4$

$+$

$CaSO_4$ $n=1,2 \longrightarrow Ca(SO_3R)_2 + 2HCl$

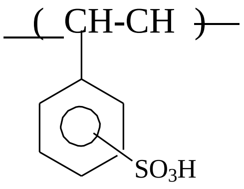
No hardness $NaCl \longrightarrow \underline{NaSO_3R} + \underline{HCl}$

stay on column soluble in water

The regeneration process of these types is by washing the expended coloum by H_2SO_4

$$\underset{\text{excess}}{Ca(SO_3R)_2 + H_2SO_4} \longrightarrow 2RSO_3H + CaSO_4$$

$$2NaSO_3R + H_2SO_4 \longrightarrow \underset{\text{Regenerated coloum}}{2RSO_3H} + \underset{\text{remove and pullout}}{NaSO_4}$$

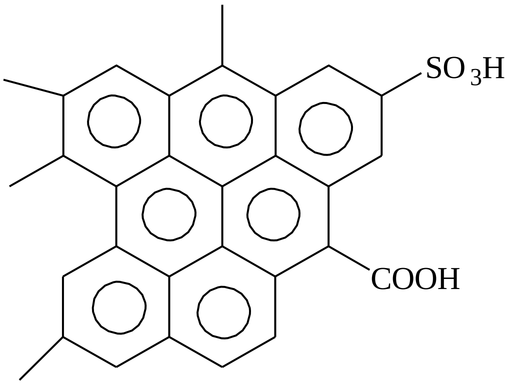


Sulfonuted polystyrene is a type of this one

ii. Weak acidic ion exchanger: Contain -COOH as a functional group.

a) type of good ion exchanger,

Cationic exchanger with alcohol base contain both type of functional groups have high efficiency exchanging.



a) organic anionic exchanger (basic) two types:

i) Strong basic

Used to eliminate weak acids like oxalic, salcilik and carbonic and strong acids also.

The functional group of this exchangers is –OH group as hydroxylamine R_4NOH. The equation of exchanging process is below:

$$R_4NOH + H_2SO_4 \longrightarrow (R_4N)_2SO_4 + 2H_2O$$

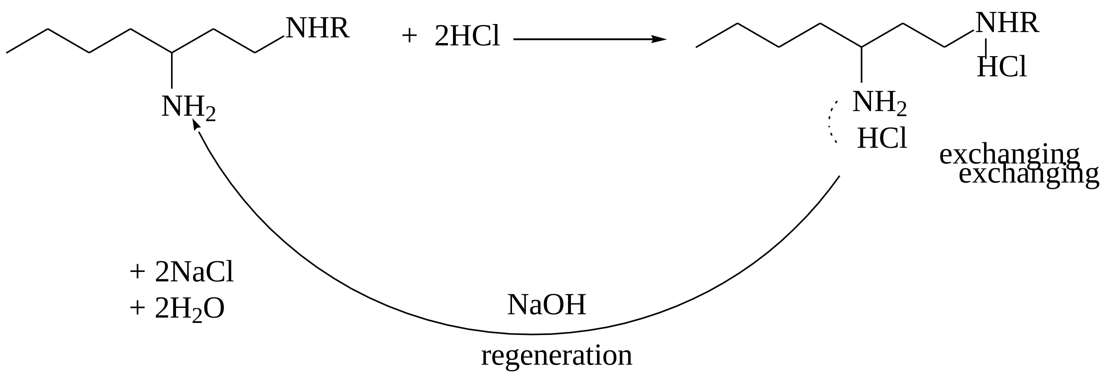
The regeneration process is

$$(R_4N)_2SO_4 + NaOH \longrightarrow 2R_4NOH + Na_2SO_4$$

ii) Weak basic

Is used only to remove the strong acid.The functional group is amine.

The process equation is



B-) Removal of hardness by precipitating methods

The Calcium and Magnesium ions from two types of hardness can be precipitate by using lime and soda

i) The lime was used to remove the temporary hardness

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3$$

ii) Non carbonated hardness was removed by using the lime and the soda.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + \underline{CaCl_2}$$

Causing hardness

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3 + Na_2SO_4$$

The application of this method is by two ways:

1.) Cold soda-lime method :used at room temperature and used in the case
    - i-) Partial removing of hardness to about 35 ppm by using lime only.
    - ii-) Removing the hardness from domestic water, cooling water and the paper industry water.
2.) Hot soda-lime method: used at 80-90 °C in the cases of:
    - i-) Accelerating the precipitation
    - ii-) Extruding the harmful gases (O_2, CO_2) this way reduced the hardness to 20 ppm

Complete removal of Calcium ion by phosphotizing treatment

The method depends on the formation of a precipitate with very low solubility product like phosphate.

The precipitating reagent used is sodium phosphate (Na_3PO_4)

$$3Ca^{2+} + 2PO_4^{3-} \longrightarrow Ca_3(PO_4)_2$$

The method was used in the case of:

i.) Steam boilers
ii.) In using the water as a reactant
iii.) In cooling water

Silicate removing

The silicate cannot be removed by any above methods, The silicate from solid crusts on the inner walls of reactors and boilers.

The types of silicates can be found in the water are:

Na_4SiO_4, $Na_4(SiO_3)4$, Na_2SiO_5

The use reagent in this method is activated magnesia which was produced freshly.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

$$Si^{4+} + MgO_4 \longrightarrow \left.\begin{array}{l} MgSiO_4 \\ MgSiO_3 \end{array}\right\} \text{Precipitated complexes}$$

Extruding Oxygen from water

The most saturation (higher concentration) oxygen in water is at 8° C. The concentration is about 8 cm^3/l. The oxygen will accelerate the corrosion of iron as it present in water according to the following equations:

$$2Fe(s) \longrightarrow 2Fe^{+2}(aq) + 4e$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)(aq.)$$

$$2Fe^{2+}(aq.) + 4(OH^-)(aq.) \longrightarrow 2Fe(OH)_2(s)$$

$$2Fe(s) + O_2(g) + 2H_2O \longrightarrow 2Fe(OH)_2(s)$$

The solid $Fe(OH)_2$ partially dissolved in the water, and the corrosion will continue, so that the dissolved oxygen must be extruded from the water used in boilers. The method includes:

i) Using preservative salt (oxidation preventer) like chromate, silicate and phosphate. These materials react with the dissolved oxygen more rapid than the reaction of iron, or it behave as anode electrode in the oxidation reduction reaction on the metal surface.

ii) Adding strong reduction agent (Sodium sulfate) which can react with the oxygen very rapidly.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

Preparation of water

Domestic water

Properties of domestic water:

1) Does not contain microbes.
2) Does not contain suspended matters.
3) It is best to be soft.

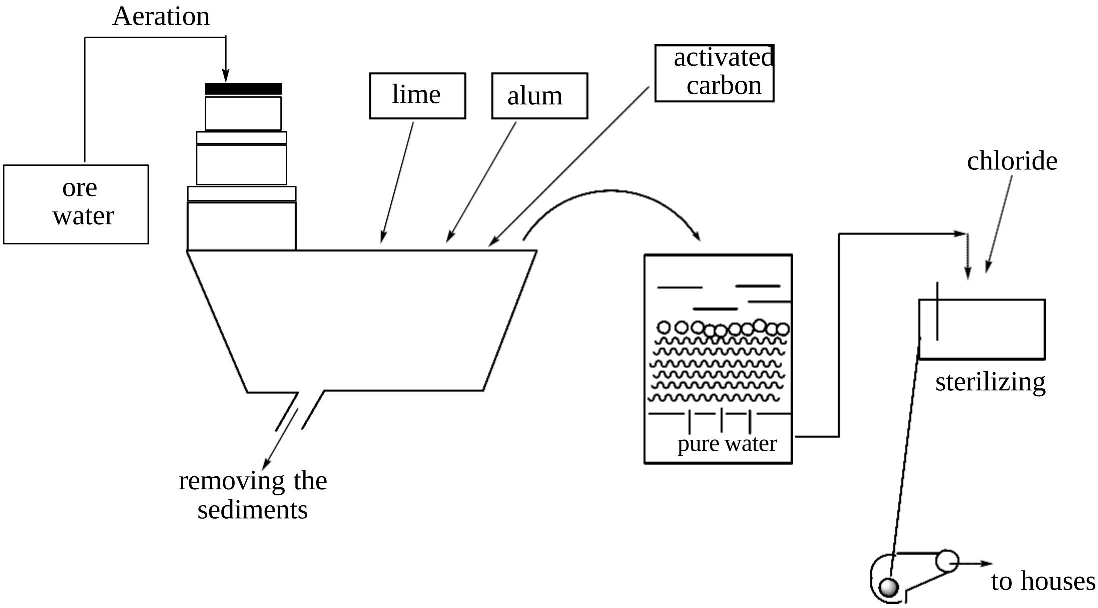
Fundamental operation to prepare the domestic water

1) Aeration

The aim of this method is to remove the dissolved iron, so the odor and the test improved

$$2Fe(OH)_2 + 1/2O_2 + H_2O \longrightarrow 2Fe(OH)_3$$

2) Partial removing of hardness by lime.
3) Using activated carbon to remove the color and to improve the test and odor.
4) Adding chlorine or chloramines.



For producing 750,000 gallon of water in a day contain 4.5 grain/gallon in needs the following:

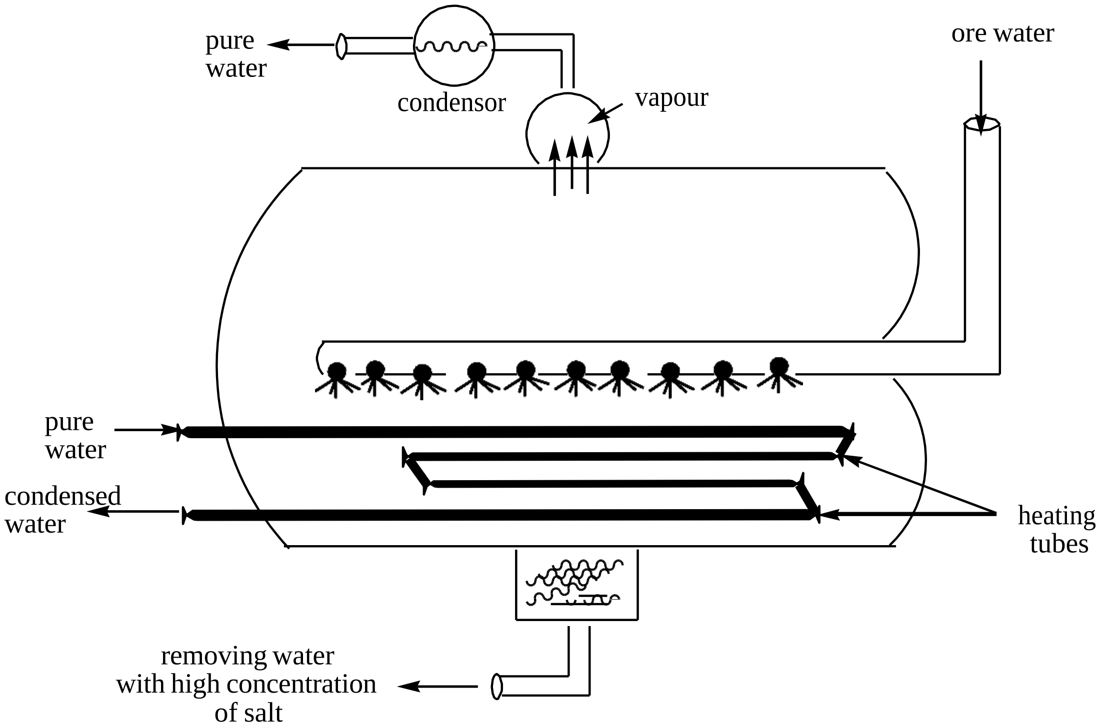
2145 pounds of lime
110 pounds of alum (aluminum sulfate)
5 pounds of activated carbon
5 pounds of chlorine

Preparing the industrial water

To prepare the water for industrial uses it needs some preparation according to the type of industry, for example:

- Water for boilers must be soft and without oxygen.

- Water in cooling system with partial hardness
- Some industries need deionized water which can be prepared by distillation many times. Because the exploding increase of population, the sea water need to be used after sweating it. The sea water contain salt concentration of about 35000 ppm to be suitable for drinking uses the concentration must be decreased to 500 ppm, where to be used in boilers the salt must be removed at all. The figure below indicates the vaporization method to prepare sea water .



Repairing the waters crap

1) Domestic water

The domestic water contains high concentrations of organic craps, which can be removed by using aerobic bacteria and dissolved oxygen

$$C, H + O_2 \xrightarrow{\text{Aerobic bacteria}} CO_2 + H_2O + \text{energy}$$

This process will cause the consumption of the dissolved oxygen in water and starting the anaerobic oxidation process.

The amount of oxygen needed to oxidation the organic materials in water called (BOD), biological oxygen demand.

Types of process in this field are:

Mechanical – Chemical - Activated sludge.

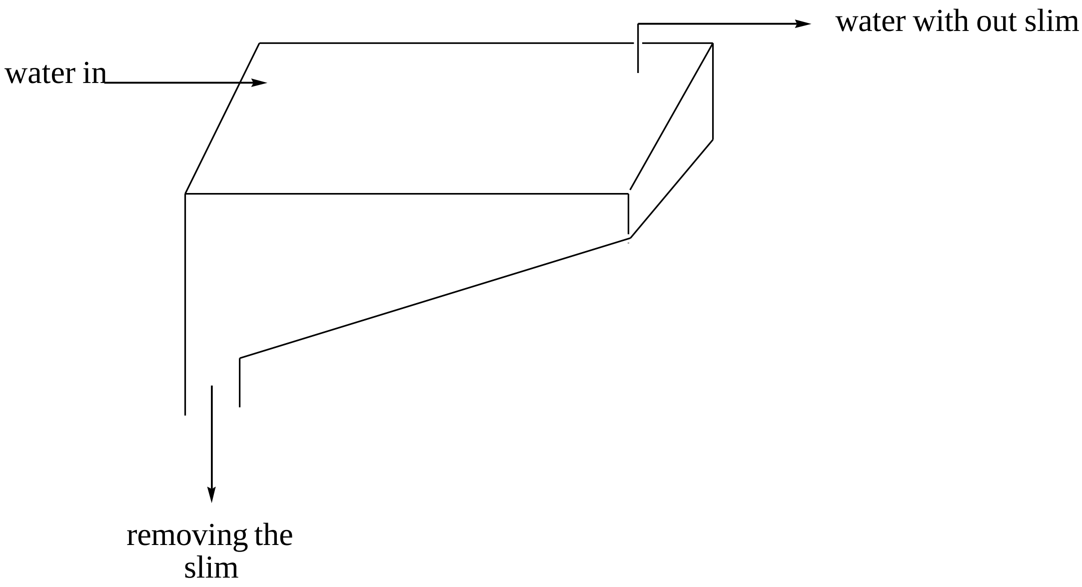
Mechanical treatment methods:

These methods include:

1) Removing the big particals (suspended and floating) by using some mineral or plastic networks.

2) Settling out process:

By using depthless tanks, where by the water stay for long periods, the slime was settled in the downward of the tank which was sloped in order to facile the slime to slipping.



3) Filtration:

This method was used to separate the suspended matters that cannot be removed by sitting method. The process used some filters with different volume and design.

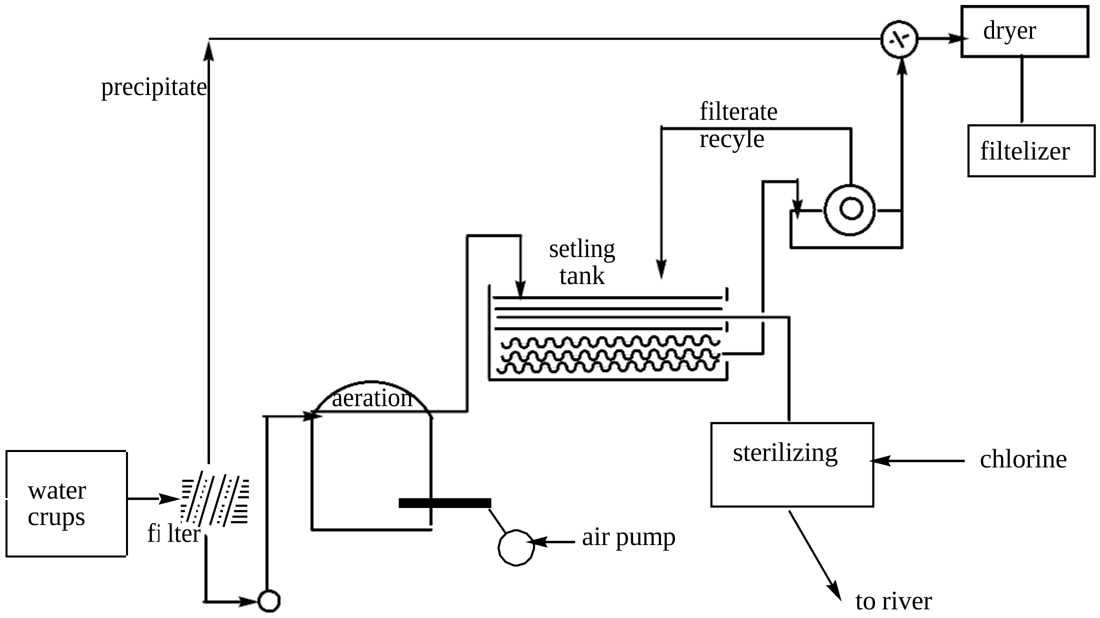
Chemical treatment methods:

These methods were used by adding some chemicals, for example alum used to precipitate the suspended matters, and lime to precipitate the dissolved matters.

Activated sludge treatment methods:

These methods used to remove the dissolved and suspended organics.

Some aerobic bacteria's are grown in slims .These bacteria digest the organic materials as a food and burns it by respiration process.



-The extruded gases in aeration parts are ammonia, H_2S, CH_4, RSH, CO_2, and others, which were produced by anaerobic degeneration

-The sterilizing to kill many numbers of bacteria

-The solid participated was used in many places as a fuel- a fertilizers

4) Industrial water

The most important source of pollutants is the industrial water because it contains craps of organic and inorganic as a solute or suspended.

These materials are very poisons even they are in very low concentration, because it can be accumulated in the body. The level of these materials are shown in table page 155. So these water must be treated before inflecting there. The treatment includes using a tank called lagoons, which was used to treat the water with high concentration of organics.

These lagoons consist of pelvis with high area and low depth in order to allow the sunlight to penetrate. The distances of these pelvis are 300m×300m with 1-2m depth.

In some cases many pelvis can be used and the water can be convert from one to another.

There are many advantages of this pelvis :

1) Neutralizing the acids or bases.
2) Decreasing the suspended materials by settling or through the neutralizing.
3) Decrease the body BOD by removing the organics.
4) The growing of plants and the presence of sunlight will increase the dissolved oxygen by photo synthesis process. This oxygen is very important for aerobic bacteria. In some cases the water treated with chlorine before in fleeting.