

Industrial Chemistry

Industrial Aspects of Chemistry

Industrial Aspects of Inorganic Chemistry

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Metallurgical Operations , Physicochemical principles , Extraction of metals , Industrially important Inorganic materials.

Metallurgical Operations

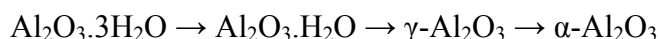
The process of extracting metals from their ores is called metallurgy. Ores as mined are hardly in a condition to be used directly for the extraction of metals. The ores are generally associated with non-metallic impurities of earth and rocks called gangue or matrix. The ore is therefore subjected to physical and chemical processes with a view to effect the concentration of the value mineral and minimizing the proportion of the gangue in ores. The process of metallurgy depends upon the nature of the ore and the impurities present in it. Hence, it is not possible to have a universal method which may be applicable to all the metals. Although the extraction of each metal involves an individual procedure, however, some common steps involved in the metallurgical operations are: (a). crushing and grinding of the ore, (b). concentration or beneficiation of the ore, (c). working of the concentrated ore and (d). purification or refining of the metal.

1. Crushing and grinding of the ore (Pulverization)

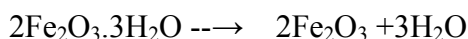
The ores occur in nature as huge lumps. They are broken to small pieces with the help of crushers or grinders. These pieces are then reduced to fine powder with the help of a ball mill or stamp mill. This process is called pulverization.

2. Calcination

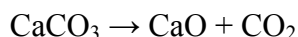
The concentrated ore is not directly used in the extraction of a metal but is subjected to thermal pretreatment to remove volatile products and to effect the conversion into a compound from which the metal may be extracted easily. Calcination is the thermal treatment of an ore in which a hydrated ore is dehydrated or a carbonate ore may be decomposed to give the corresponding oxide. In case of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, the following transformations occur upon heating to about 1200°C . In which a mixture of 70% $\gamma\text{-Al}_2\text{O}_3$ and 30% $\alpha\text{-Al}_2\text{O}_3$ is obtained as the final product.



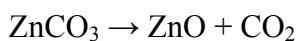
The water of hydration is removed from limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) at 800°C



For calcining CaCO_3 to give CaO and CO_2 , temperatures between $1000\text{--}1200^\circ\text{C}$ are required:



The MgCO_3 , MnCO_3 and FeCO_3 dissociate at 417°C , 377°C and 400°C respectively to their oxides. The carbonates of Cu and Pb decompose below 500°C . The zinc occurring as ZnCO_3 in calamine is calcinated i.e. heated strongly in the absence of air to convert it to zinc oxide with the expulsion of carbon dioxide as:

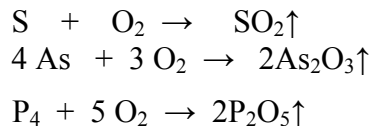


The calcination temperature should be such that the partial pressure of CO_2 in equilibrium with the carbonate exceeds the partial pressure of CO_2 in the atmosphere in contact with the carbonate. The same applies to the hydrates.

3. Roasting

Roasting is defined as the process to produce oxides or sulphates from sulphide ores. The phenomenon of roasting involves heating the concentrates of sulphide ore with controlled or excess quantities of air at temperatures between $500\text{--}1000^\circ\text{C}$. As a result of roasting, the moisture

and volatile impurities are removed and the ore is converted to oxide e.g impurities of sulphur, arsenic and phosphorus ore are removed as their volatile oxides, SO_2 , As_2O_3 , P_2O_5



The roasting to produce oxides is favoured by high temperatures (800-900°C) and low partial pressure of SO_2 in the furnace i.e a large excess of air. On the other hand, low temperatures (500-700°C) are required for sulphate formation, as high temperatures lead to the dissociation of sulphate into the metallic oxide and SO_3 . A restricted supply of air (high partial pressure of SO_2) and if necessary, recirculation of the SO_2 gas favours the formation of sulphate.

Another requisite for an appreciable rate of roasting is the large surface area of finely powdered ore, which ensures uniformity of temperature on account of efficient heat transfer and escape of gaseous products from the surface. However, the SO_2 liberated during the roasting operation as well as other volatile constituents must not be allowed to escape into the air in order to avoid air pollution. In modern roasters, the finely divided ore fed from the top of the roaster is allowed to fall from one hearth to the lower one by mechanical stirrers whereby the descending ore particles meet the ascending stream of preheated air.

Both calcinations and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open while in case of calcinations, the air holes are partially or completely closed.

4. Refining

The metals in the process of their extraction from ores by various metallurgical processes viz. crushing, grinding, concentration of the ore, working of the concentrated ore etc. are obtained in impure state known as crude metal. The impurities may be in the form of

- (i) unreduced oxides of the metals
- (ii) non-metals like C, Si, P, As, S, etc.
- (iii) foreign metals
- (iv) slag or flux

The process of purifying the crude metal is called refining. The refining of the impure metal is carried out either to obtain a pure metal or to give an impure product with the desirable qualities. The refining processes are also based on the ability of the impurities to get distributed between the different phases which can be separated by physical means. The following are the common methods of refining:

- (i) **Distillation:** This method is useful for metals having low boiling points. The metals like mercury (b.p. = 375°C); cadmium (b.p. = 765°C) and zinc (b.p. = 905°C) can be purified by distillation. The distillations are normally carried out at reduced pressures so as to work at lower temperatures. Zinc can be separated from lead and cadmium by fractional distillation.

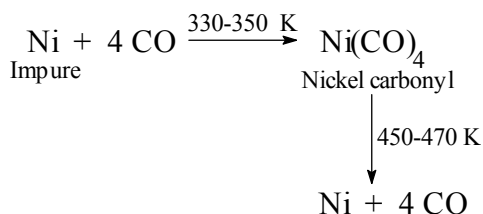
- (ii) **Liquation:** This method used for refining the metal having low melting points such as tin, lead, bismuth etc., whereby a readily fusible metal is separated from high melting impurities. In this method, the impure metal is placed on the sloping hearth of the reverberatory furnace and is gently heated in an inert atmosphere of carbon monoxide. The metal melts and flows down leaving the non-fusible impurities on the hearth. The pure metal is collected at the bottom of the sloping hearth in a receiver. The crude tin containing about 10% iron is refined by liquation. Tin melts and flows down.
- (iii) **Poling/Fire-refining:** This is based on the fact that the impurities in metals are more easily oxidized when air or oxygen is bubbled through the molten metal to be purified. This is used for refining Cu, Pb, Sn, pig iron, etc. This process is used to remove reducible oxides from the respective metal. Blister copper contains about 98%Cu and the impurities are Fe, Co, Ni, Pb, Zn, As, Sb, Ag, Au. The molten metal is stirred with the logs of green wood and any metal oxide present is reduced to metallic state. The carbon and the decomposition products of wood effect the deoxidation. The stirring action due to the evolution of the decomposition products of the wood promote the deoxidation in the bulk of the metal also. The impurities get removed either in the form of gases such as SO_2 , As_2O_3 , etc. or they form scum over the molten metal. The scum is skimmed off leaving behind pure metal. When air is bubbled into molten Cu at about 1200°C , it gets oxidized as Cu_2O . The Cu_2O is unstable above 1000°C . The Cu_2O formed dissolves in molten Cu and can be considered to be oxidizing the dissolved metallic impurities.
- (iv) **Cupellation:** This is an oxidation method for the refining of certain metals. This method is used for refining those metals in which the impurities have greater tendency to get oxidized than the metal itself.

Silver is refined by this method. The impure metal is fused in small boat-shaped dishes made of bone ash called cupels. The cupels are heated in a suitable furnace by a blast of air blown over cupels. The lead (impurity) is easily oxidized to lead monoxide (PbO) and is carried away by the blast, while pure silver is left behind.

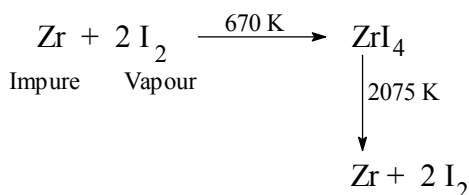
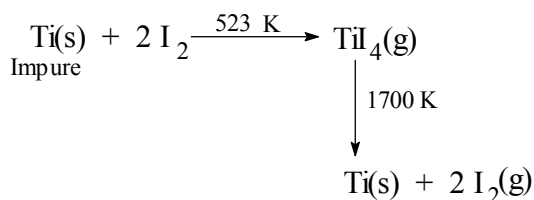
- (v) **Zone-refining:** This method is based on the principle of fractional crystallization that the impurities are more soluble in the melt than the pure metal and on allowing a molten mixture of metals to cool it is the less soluble one that crystallizes out first. The impurities being more soluble tend to remain in the liquid phase and crystals of pure metal get deposited. This method is used for metals, which are required in very high purity. Silicon, germanium, boron, gallium and indium are refined by this method. In this method, the impure metal is cast into a thin bar. The metal to be purified is heated by a circular mobile induction heater, which is slowly moved along the bar. As the heater moves, the molten zone of the metal also passes forward. The unheated portion on cooling crystallizes to give a solid, which contains much less impurity than before. Each operation of movement of the heating from one end to another is called a zone pass. After many zone passes, the one end is pure metal. This method is especially useful for producing semiconductors of very high purity. Germanium purified by this method contains impurities only upto 7-10 ppm.

- (vi) **Vapour phase refining:** This method is based on the fact that certain metals are converted to unstable compounds while the impurities are not affected during compound formation. The compound formed decomposes on heating to give pure metal. For example, nickel is refined by this technique and the method is known as Mond process. In this method, nickel is heated in a stream of carbon monoxide to form volatile nickel carbonyl $\text{Ni}(\text{CO})_4$.

The carbonyl vapours when subjected to still higher temperature (470K) undergo thermal decomposition giving pure nickel.



- (vii) **Van Arkel method:** This method is similar to vapour phase refining method and used for getting ultra pure metals. In this method, the metal is converted to a volatile unstable compound (e.g iodide) taking care that the impurities are not affected during compound formation. The compound thus obtained is decomposed to get the pure metal. This method is used for the purification of metals like titanium and zirconium.



Physiochemical principles of extraction

Extraction of iron: Iron is the fourth most abundant element in the earth's crust after oxygen, silicon and aluminium. Iron is used in quite larger quantities than any other metal and steel making is of immense importance throughout the world. The largest sources of iron are USSR (26%), China (17%), Brazil (15%), Australia (10%), USA (6%), Canada (4%) and India (5%). In India, iron ores are found mainly in the states of Bihar, Orissa and west Bengal. India ranks 5th in the world iron resources and is 3rd largest producer and exporter of iron in world only after Brazil and Australia. Bihar and Orissa have 43% of the total Indian iron ore reserves.

Only a few of iron minerals are important for extraction of iron. The iron mineral deposit is called iron ore only if it is possible to produce iron from it economically. Iron ores, in terms of their appearance are classified as:

- (i) Black ore – Magnetite Fe_3O_4 (magnetic oxide of iron)
- (ii) Red or reddish black ore – Haematite Fe_2O_3
- (iii) Brown ore – Limonite $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- (iv) Grey or whitish ore – Siderite FeCO_3
- (v) Greenish or brownish black ore – Pyrites FeS_2

Though iron pyrite (FeS_2) is common ore of iron, but because of its higher sulphur content, it is not used for the production of iron.

Iron ores may also be classified according to the quantity of gangue associated with them as:

<u>Nature of ore</u>	<u>Characteristics of associated gangue</u>
Siliceous	Predominantly silica
Aluminous	Largely alumina
Argillaceous	Chiefly clayey matter
Calcareous	Predominantly lime
Bituminous matter	Large amounts of bituminous or coaly
Titaniferous	Large amounts of ilmenite ($\text{FeO} \cdot \text{TiO}_2$)

The raw materials required for the production of iron are: iron ore , coking coal or coke, limestone, dolomite, manganese ore (or its substitute).

The extraction of iron ore has played an important role in the development of modern civilization. The Iron age began when man found how to use the charcoal formed by burning wood to extract iron from iron ores. The industrial revolution began when Abraham Darby developed a process using coke instead of charcoal at Coalbrookdale in Shropshire, England in 1773. The production of coke from coal is not only easier, relative to than making charcoal by burning wood but is also much cheaper. The greater mechanical strength of coke made it possible to blow air through a mixture of coke and iron ore in a blast furnace and thus extract iron ore on a much larger scale. These two factors increased the production of iron at reduced price.

Iron is extracted from its oxide ore (hematite) and requires a number of treatments to render it acceptable as a blast furnace feed

(i) Crushing and sizing: The ore is crushed in jaw or gyratory crushers except for sticky and clayey ore, for which double roll crushers are commonly adopted. The ore is broken to small pieces of 25-55 mm (1-2.5 inch). The crushed ore is then concentrated by anyone or more of the methods viz. magnetic separation at either high or low intensity magnetic fields, gravity separation using either a heavy fluid medium or by jigging (a bed of ore particles placed on a perforated bottom is subjected to periodic impulses of water flow through the perforations whereby the heavier particles move downwards and are removed as the concentrate) tabling (sandy feed moves over an inclined shaking table and is washed with a cross-stream of water)

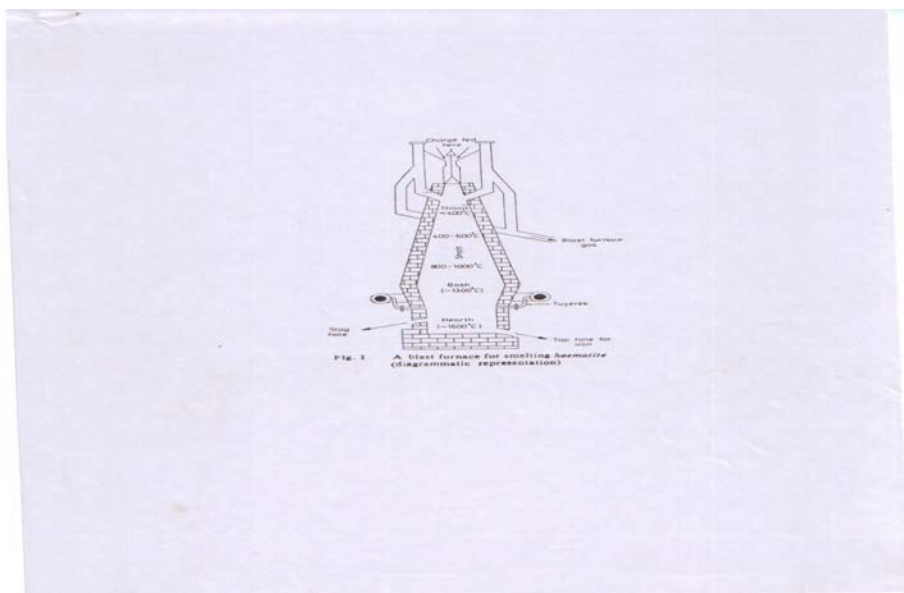
floatation, electrostatic separation, etc. Some degree of concentration is achieved by washing to remove clay, sand etc.

(ii) Calcination: The concentrated ore is then calcined (heated strongly in the presence of a limited supply of air) in a reverberatory furnace. During this process the moisture gets removed and the impurities such as sulphur, phosphorus and arsenic are converted to their gaseous oxides which being volatile escape. The ferrous carbonate if present changes to oxide.

(iii) Smelting: The calcined ore is reduced with carbon i.e smelted with coke in a blast 'furnace' in the presence of limestone (CaCO_3) as a flux. The amount of CaCO_3 is varied depending on the amount of silicate materials in the ore. The blast furnace plant consists of the following important sections:

- (i) Blast furnace proper
- (ii) Hot blast supply equipments
- (iii) Gas cleaning system and gas storage
- (iv) Raw material storage and handling
- (v) Liquid products disposal
- (vi) Process control equipments

The schematic arrangement of the various sections in a modern blast furnace plant is shown as in Fig. 1.

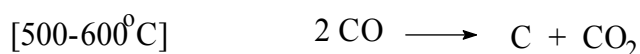
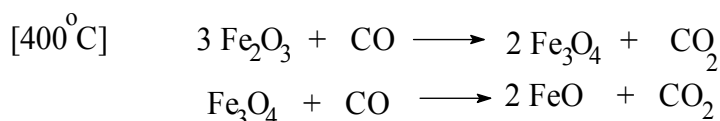


The furnace consists of an almost cylindrical shaft 20 to 30 m high, made of steel lines with fire bricks with a cross-sectional area of varying sizes at different level. The cross-sectional area increases from the top or throat downwards, a maximum being at the bosh level (mantle) and it decreases thereafter. The structure essentially consists of the foundation, the hearth, the bosh, the mantle and columns, the stack, the raw material hauling and charging facilities and the top.

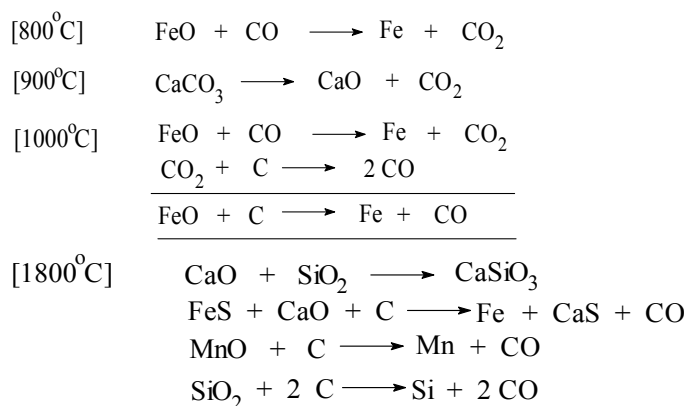
In the blast furnace solid charge materials like iron ore (1 part), coke (0.4 parts) and limestone (calcium carbonate) (0.2 parts) are fed at the top of the furnace through a “double bell” system. This allows the charging of the ore while maintaining a gas seal. A blast of preheated air is blown upwards with the help of tuyeres (a form of blow pipe) arrangement). The burning of coke to carbon monoxide supplies most of the heat required for the working temperature of the furnace. The temperature of the furnace is nearly 2000°C (Hearth region) at the point where the air enters, but is about 1500°C (Shaft region) at the bottom and 400°C (Throat region) at the top. The iron oxide is reduced to iron mainly by CO (though some reduction by C takes place). The molten/crude iron is called pig iron and contains about 4-5% carbon, 2% Si, traces of S,P etc. The melting point of iron is 1535°C while the impurities in pig iron lower the melting point possibly to as low as 1015°C. Molten iron collects in the hearth at the bottom of the blast furnace. The temperature of the furnace decomposes CaCO_3 to CaO , which then reacts with any silicate impurities present (such as sand or clay) forming molten iron silicate or slag. The slag floats on the molten iron, thus protecting it from oxidation. Molten slag and molten iron are drawn off through separate openings at intervals. The molten iron is run into moulds made of sand and is allowed to solidify into ingots called ‘pigs’. Pig iron or cast iron is hard but is very brittle. The non metallic element must be removed to reduce brittleness.

All Fe/C alloys containing less than 2% carbon are called steel which is ductile and can be rolled into shape. With increasing carbon content the hardness and strength increases. The most common forms are mild steel (soft steel or low carbon steel) and hard steel (high carbon steel).

The reactions involved in the extraction of iron proceed in several stages at different temperatures:



The carbon is deposited as soot and reduces FeO to Fe but it also reacts with refractory lining of the furnace and is harmful.



Preparation of steel: The composition of pig iron varies as follows:

Carbon	3.5-4.2%
Silicon	0.5-2.5%
Manganese	0.5-1.5%
Phosphorus	0.04-2.0%
Sulphur	0.04-0.15%

Steel is made by removing most of the carbon and other impurities from pig iron by melting and oxidizing, so that the impurities are given off as gases or converted into slag. The mixing of molten pig iron with haemetite Fe_2O_3 gives wrought iron, which is malleable and ductile and can be converted into steel.

The following are the methods for the production of steel:

- (i) Bessemer and Thomas Process
- (ii) Siemens open hearth process
- (iii) Siemens electric arc furnace process
- (iv) Basic oxygen process (BOP)

(i). Bessemer and Thomas Process: The process is named after H.Bessemer a Frenchman, who in 1855 patented the process. It involves Bessemer converter, which is a large pear shaped furnace, made of steel and lined with silica. The converter is mounted on horizontal pivots around which it can be tilted. In horizontal position molten pig iron is poured in and is then tilted to vertical position and a blast of compressed air is blown through holes in the bottom of the furnace and through the molten metal. This burns the impurities such as Si, Mn and C to give SiO_2 , MnO and CO or CO_2 , which upon combining form manganese silicate slag, MnSiO_3 . When whole of C is oxidized, observed by the colour or spectrum of the flame produced, the air blast is cut off and the converter is tipped to pour the molten steel into cast iron moulds. The process is rapid and inexpensive but the steel obtained is not of very fine quality. Therefore, the process has been modified and replaced by new processes.

For the preparation of steel based on phosphorus ores, Thomas and Gilchrist process patented by S.G.Thomas in 1879, also called as 'Bessemer process' is used instead. Thomas converter lined with a basic material such as calcined (strongly heated) dolomite or limestone is used. This reduces reaction between iron phosphate slag and the lining of the converter, which prolongs the life of the converter lining. Limestone CaCO_3 or lime CaO are added as slag formers. These being basic react with P_4O_{10} forming 'basic slag' $\text{Ca}_3(\text{PO}_4)_3$ thus removing P form the steel. Basic slag is a valuable by-product and is finely ground and sold as a phosphate fertilizer.

(ii). Electric Arc Furnace: This process was invented by Sir William Siemens soon after the Bessemer process was invented. Molten pig iron was put in a shallow hearth and the impurities are oxidized by air. The furnace requires external heating by burning gas or oil in air. The lining of the furnace was acidic or basic depending on the impurities in the pig iron. This process though replaced Bessemer process in many places, it is slow and hence has largely been replaced by the basic oxygen process.

(iii). Siemens oxygen process: In this process an electric arc furnace patented by Siemens in 1878 were used to supply heat either by having an electric arc just above the metal or by passing an electric current through the metal. This process is still used to produce steel alloys and other high quality steel.

(iv). Basic oxygen process: This process was originated in 1952 as the Kaldo and LD processes which use pure O_2 instead of air to oxidize the pig iron as the older Bessemer and Thomas process took up small amounts of nitrogen which makes steel brittle and nitriding of the surface makes the metal more difficult to weld.

In LD process strong convection currents were set up in the melt to obtain an effective reaction, whilst in Klado process the converter was rotated to ensure mixing and hence an effective reaction. The furnace is initially charged with molten pig iron and lime and pure O_2 is blown onto the surface of the liquid metal at great speed. The O_2 by penetrating into the melt oxidizes the impurities rapidly. The heat evolved in oxidizing the impurities keeps the contents of the furnace in molten state and no external heat is required. The molten steel is then poured either into moulds to give steel castings or into ingots, which may then be passed to rolling mills. The advantages of using O_2 rather than air are that there is a faster conversion of steel so that not only larger quantities can be handled but the production is also large in a day. A purer product, free from nitrides is obtained.

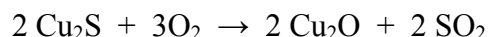
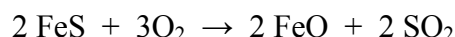
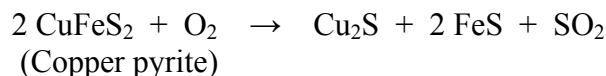
Extraction of copper: Copper does not occur abundantly in nature. It occurs as native copper as well as in the combined state. Native copper (in extremely pure form) is found only near Lake Superior in America. The main copper producing countries are China, Mexico, USA and Russia. In India, copper belts are located at Singhbhum (Bihar) and Khetri (Rajasthan). The main ores of copper are:

(i) Copper glance or chalcocite, dark grey coloured	Cu_2S
(ii) Copper pyrites (chalcopyrites)	$CuFeS_2$
(iii) Malachite (basic copper carbonate, green)	$Cu(OH)_2.CuCO_3$
(iv) Cuprite (Rubby copper, red)	Cu_2O
(v) Azurite	$2 CuCO_3.Cu(OH)_2$
(vi) Bornite or peacock ore as it has a mixture of colours like peacock feathers (blue, red, brown and purple) (popular gemstones)	Cu_5FeS_4
(vii) Turquoise (blue colour)	$CuAl_6(OH)_8.4H_2O$

It is mainly extracted from copper pyrites ($CuFeS_2$). The sulphide ore is usually of very low grade and contains iron sulphide, gangue and smaller quantities of arsenic, antimony, selenium, tellurium, silver, gold and platinum. The various steps involved in the extraction are:

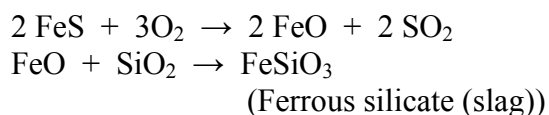
(i) Crushing and concentration. The ore is crushed in jaw crushers and then finely powdered. It is concentrated by froth floatation process. In this process, the finely powdered ore is mixed with water and some pine oil in a tank. The mixture is agitated by blowing compressed air into it. The particles are preferentially wetted by oil and rise to the surface of the tank in the form of a froth from where these are skimmed off. The siliceous and earthy impurities preferentially wetted by water sink to the bottom of the tank.

(ii) Roasting. The concentrated ore is roasted i.e heated strongly in the presence of excess air in a reverberatory furnace. During roasting moisture is removed from the ore and it becomes dry. The impurities of sulphur, arsenic, antimony and phosphorus are removed as their volatile oxides. Copper pyrite is converted to ferrous sulphide (FeS) and cuprous sulphide (Cu₂S) which are partially oxidized as;



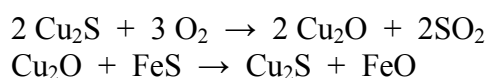
(iii) Smelting. The roasted ore is mixed with some powdered coke and sand and is heated strongly in a blast furnace. The blast furnace is made up of steel and is lined inside with fire bricks. A blast of hot air is introduced at the lower part of the furnace. The following changes occur during smelting:

(a) Most of the ferrous sulphide gets oxidized to ferrous oxide which combines with silica (flux) to form fusible slag.

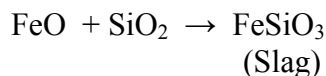


The slag being lighter floats and forms the upper layer. It is removed through the slag hole from time to time.

(b) During roasting or in the blast furnace if any oxide of copper is formed, it combines with FeS and is changed back into its sulphide.



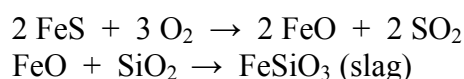
Ferrous oxide thus formed again combines with silica to form more slag.



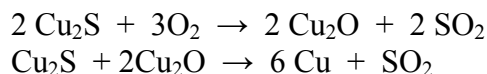
As a result of smelting, two separate layers are formed at the bottom of the furnace. The upper layer consists of slag and is removed as a waste. The lower layer of molten mass contains mostly cuprous sulphide and some traces of ferrous sulphide. It is called matte and is taken out from the tapping hole at the bottom.

(iv) Bessemerisation. The molten matte from the blast furnace is transferred into a Bessemer converter (Fig. 2). The vessel is made of steel and is lined inside with lime or magnesium oxide. A hot blast of air mixed with sand, is blown into the molten matte. During this process:

(i) traces of ferrous sulphide present in the matte are oxidized to FeO which combine with silica to form slag.



(ii) copper sulphide is partially oxidized to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.

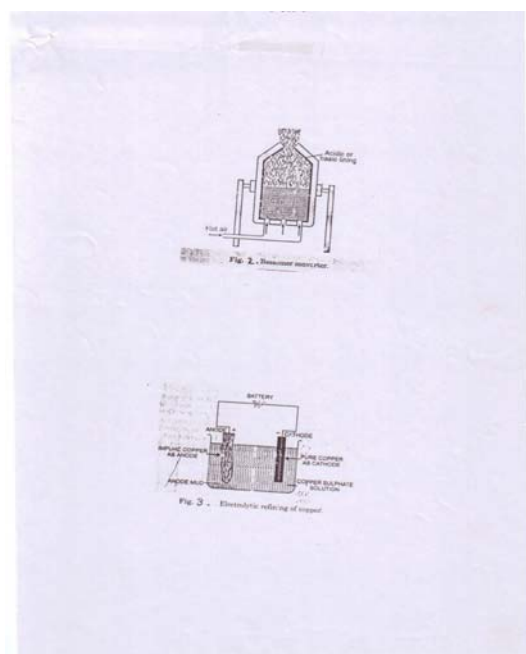


After the reaction has been completed, the converter is tilted and the molten copper is poured into sand moulds. On cooling, sulphur dioxide, nitrogen and oxygen escape from the metal. The copper thus, obtained is about 99% pure and is known as blister copper. The name blister comes from the fact that as the metal solidifies, the dissolved SO_2 escapes producing blisters on the metal surface.

(v) Refining. The blister copper is purified as follows:

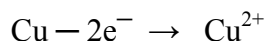
(i) Poling. The blister copper is purified by heating it strongly in a reverberatory furnace in the presence of excess of air. The impurities are either removed as volatile oxides or converted into slag. Some of the copper also changes to cuprous oxide. This is reduced back to copper by stirring the molten metal with green poles of wood. The hydrocarbons present in these freshly cut poles reduce cuprous oxide to copper which is about 99.5% pure. Further purification is done by electrolytic refining.

(ii) Electrolytic refining. The crude copper is further purified by electrolytic method. In this method, a thin sheet of metal is made as cathode and the block of crude metal is made as anode. Both the electrodes are placed in an acidified copper sulphate solution (Fig. 3).

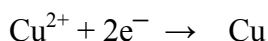


When electric current is passed through the solution, impure copper from anode goes into the solution and pure copper from the solution gets deposited at cathode.

At anode



At cathode



The impurities of zinc, nickel, iron etc. gets collected below the anode as anode mud.

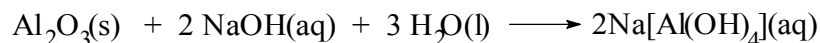
Alternatively, prolonged exposure of copper pyrites to air and rain leads to the formation of dilute solution of copper sulphate. Copper can be precipitated from this solution by the addition of scrap iron. It is then refined electrolytically.

Extraction of Aluminium: Aluminium is the third most abundant element (after oxygen and silicon) by weight in the earth's crust. Though aluminium occurs extensively as aluminosilicates (Feldspar, KAlSi_3O_8 ; Mica, $\text{KAlSi}_2\text{O}_{10}(\text{OH})_2$), the only ore from which its extraction is profitable is bauxite $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The largest sources are Australia 36%, Guinea 17%, Brazil 8%, Jamaica 7% and the USSR 6%.

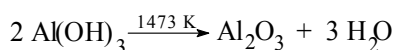
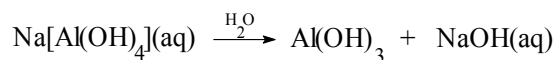
The extraction involves two steps:

- (i) Purification of bauxite ore
- (ii) Electrolysis of alumina

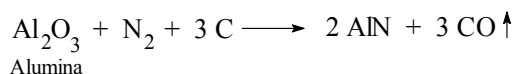
(i) Purification of bauxite ore : Bauxite ore is of two types. If the main impurities are oxides of iron, it is called red bauxite. On the other hand, if the main impurities are due to oxides of silicon, the bauxite is called white bauxite. Red bauxite ore also contains SiO_2 and TiO_2 as impurities. The purification of red bauxite ore is done by Bayer Process whereby waste materials are removed because these would spoil the properties of the product. The powdered bauxite is treated with hot concentrated (45%) solution of sodium hydroxide at 473-523 K and 35-36 bar pressure. As aluminium is amphoteric, it dissolves forming sodium aluminate. SiO_2 also dissolves to form sodium silicate leaving behind iron oxide and TiO_2 which are filtered off.



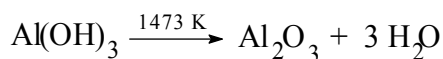
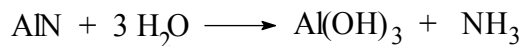
This process is called leaching. The filtrate containing sodium aluminate and sodium silicate is diluted and seeded with Al_2O_3 or some CO_2 (an acidic oxide which lowers the pH) is bubbled whereby the silicate ions remain in solution and the $\text{Al}(\text{OH})_3$ precipitates are formed. These are removed by filtration and are dried. These are then heated strongly which get converted to pure Al_2O_3 as:



The white bauxite is purified by Serpeck's process. In this process, the ore is powdered, mixed with coke and heated to 2073 K in an atmosphere of nitrogen. Alumina changes to aluminium nitride while silica gets reduced to silicon which being volatile is removed as vapours.



Aluminium nitride obtained is hydrolysed with water to get the precipitates of aluminium hydroxide. The precipitates are filtered, dried and ignited to get pure alumina.

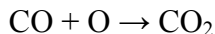
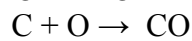


(ii) Electrolytic / Hall-Heroult Process: The purified alumina obtained from Bayer or Serpeck's process is melted with molten cryolite $\text{Na}_3[\text{AlF}_6]$. Other impurities such as CaF_2 and AlF_3 may also be added. A typical electrolytic mixture is $\text{Na}_3[\text{AlF}_6]$ (85%), CaF_2 (5%), AlF_3 (5%) and Al_2O_3 (5%). Some cryolite is mined as a mineral in Greenland, but this is insufficient to meet the demand for it, and hence is made synthetically.



The cryolite serves as an added impurity and lowers the melting point of the mixture to about 1173 K and also improves the electrical conductivity, as Al_2O_3 is a poor conductor.

The process of electrolysis is carried out in an iron tank having a lining of carbon (graphite lined steel tank), which serves as the cathode. The anodes are also made of graphite and may consist of a number of carbon rods, which dip, in fused electrolyte. The electrolyte is covered with a layer of powdered coke. On passing electric current, electrolysis occurs as:



The aluminium liberated at cathode gets collected at the bottom of tank, from where it is removed periodically. The oxygen evolved at the anode combines with the carbon of the anode to produce carbon monoxide. CO either burns to CO_2 or escapes out. For each kg of aluminium produced, about 0.5 kg of the carbon anode is burnt away. Therefore anodes need to be replaced periodically. The traces of fluorine formed cause serious corrosion hence, large amounts of Li_2CO_3 are now used as an alternative impurity, because this reduces corrosion. As the energy consumption is very high, the process is only economic if there is a source of cheap electricity, usually hydroelectric power.

Refining of Aluminium: The aluminium metal obtained by the electrolysis of alumina is 99% pure. It can be further refined by Hoop's electrolytic method. The process is carried out in an iron tank lined inside with carbon. It has three layers of molten liquids having different densities:

- (i) The top layer consists of pure aluminium having carbon electrodes dipped in it which serve as cathode.
- (ii) The middle layer consisting of mixture of fluorides of sodium, barium and aluminium in the molten state acts as an electrolyte.
- (iii) The bottom layer consisting of impure aluminium alongwith the carbon lining acts as the anode.

On passing current, aluminium ions from the middle layer are discharged at the cathode as pure aluminium. The pure aluminium is removed from the tapping hole. An equivalent amount of

aluminium from the bottom layer moves into the middle layer leaving behind the impurities. Thus, this method gives completely pure aluminium.

It may be noted that aluminium oxide, Al_2O_3 exists in several different modifications. For example, dehydration of $\text{Al}(\text{OH})_3$ below 1173 K gives γ -alumina. It is polycrystalline having large surface area. It is used in chromatography and as catalyst support. On heating above 1300 K, high temperature form is produced known as α -alumina or corundum. It is very hard and refractory material which is used as an abrasive. Many gemstones such as ruby, sapphire, topaz, emerald consist of Al_2O_3 with trace metal ion impurities of Cr, Fe, Ti which impart colour to the mineral.

Composition of β -alumina approximates to $\text{NaAl}_{11}\text{O}_{17}$, $\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3$ or $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ with a very complicated structure. Its essential character may be described as chunks of close-packed structure separated by relatively empty planes containing only Na^+ and an equal number of O^{2-} anions: within these planes the Na^+ ions can move easily and the structure is a two-dimensional ionic conductor used in sodium sulphur battery.

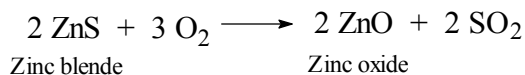
Extraction of Zinc: Zinc does not occur in native form as a reactive metal. The main regions where it is mined are Canada (19%), USSR (13.5%), Australia (11%), China and Peru (7%) and Spain, Mexico and USA (4% each). In India, zinc blende is mined in Zawar mines located near Udaipur (Rajasthan). The main ores of zinc are

- (i) ZnS - Sphaelerite (In USA called Sphalerite as it almost always contains iron and the formula may be written as $(\text{ZnFe})\text{S}$. This commonly occurs with PbS .
 - Zinc blende (called in Europe)
- (ii) ZnCO_3 - called as Smithsonite in USA
 - calamine in Europe
- (iii) $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ - Franklinite
- (v) Zn_2SiO_4 - Willemite
- (vi) $\text{Zn}_4(\text{OH})_2(\text{Si}_2\text{O}_7) \cdot \text{H}_2\text{O}$ - Hemimorphite

The principal ore of zinc is zinc blende. Zinc can be extracted from zinc blende by the following steps:

(1). Concentration – The ore is concentrated by froth floatation process. In this process the finely powdered ore is mixed with water and some pine oil in a tank. The contents are agitated vigorously by blowing air. As a result, the particles are preferentially wetted by oil and rise to the surface of the tank in the form of froth from where these are skimmed off. The impurities are preferentially wetted by water and thus sink to the bottom of the tank.

(2). Roasting – The concentrated ore is roasted in the presence of air at about 1200 K to convert zinc sulphide into zinc oxide.



(3). Reduction – ZnO may be reduced by carbon monoxide at 1473 K in a smelter. The reaction is reversible, hence the high temperature is required to move the equilibrium to the right. At this temperature the Zn is gaseous. If the gaseous mixture of Zn and CO₂ are simply removed from furnace and cooled, then some reoxidation of zinc may occur. Thus the zinc powder obtained contains large amounts of ZnO. Modern smelters minimize the reoxidation by following phenomenon:

- (i) by heating ZnO with excess carbon so that the CO₂ formed is converted to CO.
- (ii) by shock cooling the gases leaving the smelter so they do not have time to attain equilibrium. This rapid cooling is achieved by spraying the hot gas with droplets of molten lead, which give 99% pure zinc.

In an alternative method, ZnS is heated in air at a lower temperature, yielding ZnO and ZnSO₄. These are dissolved in H₂SO₄. Zinc dust (prepared by melting zinc and then atomizing it with blast of air) is then added to precipitate Cd and then ZnSO₄ solution is electrolyzed to give pure Zn.

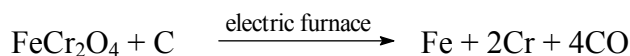
(4). Refining – The impure metal is refined by fractional distillation or by electrolytic method.

(i) Fractional distillation: Impure zinc contains impurities of cadmium (b.p. = 1073 K), lead (b.p. = 2024 K) and iron (b.p. = 3273 K). The boiling point of zinc is 1183 K. The impure metal is distilled when zinc and cadmium with low boiling points distil over leaving behind lead and iron. The boiling points of zinc and cadmium are again subjected to fractional distillation when low boiling cadmium distils leaving behind zinc metal in the distillation flask.

(iii). Electrolytic method: In this process, the impure zinc is made anode while a plate of pure zinc is made the cathode. The electrolyte is zinc sulphate containing a small amount of dilute sulphuric acid. On passing current, zinc from the electrolyte is deposited at the cathode while an equivalent amount of zinc from anode goes into the electrolyte. Therefore, pure zinc is obtained at cathode.

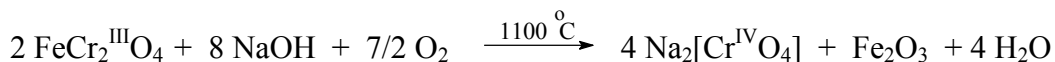
Extraction of chromium: Chromium is never found in nature in the free state and the only commercially important ore of chromium is chromite (FeCr₂O₄). This ore corresponds ideally to the formula FeO·Cr₂O₃ containing 68% Cr₂O₃ and 32% FeO. The true composition of higher grade ores varies between 42-56% Cr₂O₃ and 10-26% FeO with varying amounts of magnesia, alumina and silica. Chromite is a black to brownish black brittle powder, chemically neutral, slightly magnetic and an insoluble mineral. Chromite is chromium analogue of magnetite Fe₃O₄ which is written as Fe^{II}Fe^{III}₂O₄. Chromite has a spinel structure, in which the oxygen atoms are arranged in a cubic-close packed lattice with Fe^{II} in one eighth of the available tetrahedral holes and Cr^{III} in one quarter of the octahedral holes. The largest sources of chromite ore are South Africa 36%, USSR 28%, Turkey 7%, India 6.5%, Albania 6% and Finland and Zimbabwe 5% each. Small amounts of crocoite PbCrO₄ and chrome ochre Cr₂O₃ are also mined

Chromium is produced in two forms (A) ferrochrome and (B) pure chromium metal depending on what it is to be used for. Ferrochrome is an alloy containing Fe, Cr₄ and C. It is used to produce stainless steel and hard chromium steel. Ferrochrome (Fe + 2Cr) is prepared by reducing chromite with carbon.



Production of chromium metal: Chromium metal may be produced either by the reduction of chromium compounds or employing the electrolytical methods.

(i). Reduction methods: For the preparation of pure chromium, chromite is fused with NaOH in air when the Cr^{III} is oxidized to $\text{Cr}^{\text{IV}}\text{O}_4^{2-}$



The Fe_2O_3 formed is insoluble but sodium chromate is soluble. Hence the melt is dissolved in water to remove Fe_2O_3 and the $\text{Na}_2[\text{CrO}_4]$ formed is extracted with water. The aqueous extract is concentrated and then acidified with sulphuric acid to convert sodium chromate into sodium dichromate.



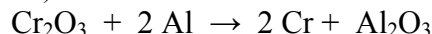
which is less soluble and can be precipitated out. The sodium dichromate is then reduced to Cr_2O_3 by heating with carbon.



Alternatively, sodium dichromate is heated with ammonium chloride to form Cr_2O_3 .

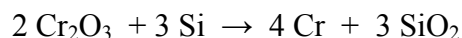


From chromium sesquioxide (Cr_2O_3), chromium is prepared commercially by reduction with aluminium (thermite process)

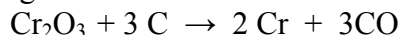


Wherein the chromium oxide and aluminium powder are mixed and placed in a refractory-lined vessel and ignited with barium peroxide and magnesium powder. The reaction is exothermic and self-sustaining. A 97-99% chromium metal is thus obtained alongwith aluminium, iron and silicon as impurities. The contents of carbon, sulphur and nitrogen are about 0.03, 0.02 and 0.045% respectively.

The commercial metal may also be produced from the oxide reducing with silicon as



and also reducing the oxide with carbon at low pressure



(ii). Electrolytic methods: For the deposition of chromium on the surface of a metal in order to protect the metal from corrosion and to give it a shiny appearance, chrome alum electrolyte $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and chromic acid electrolyte CrO_3 are used.

Alumina (Aluminium oxide): The oxides and hydroxides of aluminium owing to the very diversity of their forms and properties find utility in a wide variety of fields. Three crystalline modifications of the trihydrate of alumina $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and two modifications of the monohydrate $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ are known. There is no dihydrate. The nomenclature of the crystallized alumina hydrates is given as:

<u>Composition</u>	<u>Aluminium Company of America (Alcoa)</u>	<u>Minerological</u>
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	α -aluminatrichydrate β -aluminatrichydrate new-aluminatrichydrate	hydrargillite or gibbsite baycrite nordstrandite
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	α -alumina monohydrate β -alumina monohydrate	boehmite diaspore

The use of Greek letters in the naming of aluminium hydrates introduced by Alcoa is conventional designations. The letter α being always associated with those hydrates, which occur more abundant in nature.

The α -trichydrate when heated begins to lose its water of constitution at about 140°C . The dehydration sequence characteristic of the α -trichydrate leads successively to the transition aluminas and then to α - Al_2O_3 as the final term. α - Al_2O_3 can be prepared by heating γ - Al_2O_3 or any hydrous oxide above 1000°C . α - Al_2O_3 is hard and is resistant to hydration and to attack by acids. In its mineral form it is known as corundum. An impure form of corundum contaminated with iron oxide and silica is called emery, which is used to make emery paper (sand-paper used to polish metals). Alumina has a high melting point of over 2000°C . It is used as a refractory material to line furnaces and to make containers for high temperature reactions. The structure of α -alumina consists of an hcp array of O^{2-} ions with the Al^{3+} ions occupying two-thirds of the octahedral holes in an ordered array. Alumina is white, but it can be coloured by the addition of Cr_2O_3 or Fe_2O_3 . The white sapphires are gem quality corundum. The synthetic rubies can be made by strongly heating a mixture of Al_2O_3 and Cr_2O_3 in an oxy-hydrogen flame. Rubies are very hard and are used for jewellery and to make bearings in watches and instruments. Thus ruby is a mixed oxide. Blue sapphire is another mixed oxide containing traces of Fe^{2+} , Fe^{3+} and Ti^{4+} . The mixed oxides containing macroscopic proportions of other elements include the minerals spinel, MgAl_2O_4 and crysoberyl, BeAl_2O_4 . The spinel structure is important as a prototype for many other $\text{M}^{\text{II}}\text{M}^{\text{III}}\text{O}_4$ type compounds. Compound of composition NaAlO_2 , made by heating Al_2O_3 with sodium oxalate at 1000°C is also ionic mixed oxide.

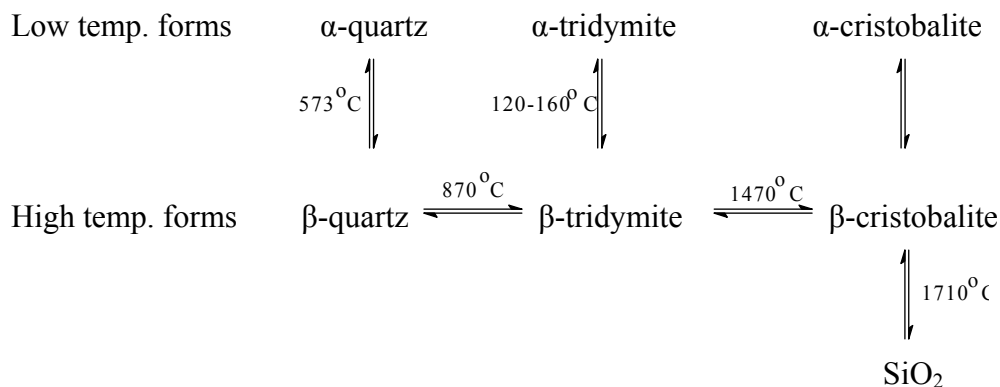
The dehydration of aluminium hydroxide at temperatures below 900°C leads to the formation of γ -alumina, a metastable polycrystalline form with very high surface area. On account of its surface area and bare sites, this material is used as a solid phase in chromatography and as a heterogeneous catalyst and catalyst support. The γ - Al_2O_3 structure is sometimes regarded as a defect spinel structure i.e the structure of spinel with deficit of cations.

Silica: Silicon dioxide SiO_2 , the most common binary compound of silicon and oxygen commercially called silica constitutes ~60% by weight of the earth's crust. It occurs either alone or in combination with other oxides in the silicates. Silica is the basic material of glass and ceramic industries and an important raw material for the production of soluble silicates, silicon and its alloys. Silicon based chemicals and the silicones. Silica itself is used in large quantities as a constituent of building materials in concrete, bricks and building stones and its various amorphous forms as a desiccant, adsorbent, reinforcing agent and catalyst. It finds numerous specialized applications as piezoelectric crystals and vitreous- silica optical elements and glassware.

Silica is a high melting solid. The basic structural unit of most of the forms of silica and of the silicate materials is a tetrahedral arrangement of four oxygen atoms surrounding a central silicon

atom. In terms of covalent bonding model, the silicon atoms forms bonds to oxygen utilizing four equivalent sp^3 hybrid orbitals with possible participation of $p\pi-d\pi$ bonding. Structurally silica represents a limiting case in which an infinite three-dimensional network is formed by the sharing of all oxygen atoms of a given tetrahedron with neighboring groupings.

Silica exists in a variety of polymorphic crystalline forms as well as in amorphous modifications and as a liquid. The main forms are quartz, tridymite and cristobalite, each of which has different structures at high and low temperatures. The difference between these structures is the way in which the tetrahedral SiO_4 units are arranged.



At atmospheric pressure, the stable crystalline phases are quartz ($867^\circ C$), tridymite (from 867 to $1470^\circ C$) and cristobalite ($1470^\circ C$ to $1710^\circ C$). All the varieties of silica melt at $1710^\circ C$ to give a viscous liquid, which on cooling does not crystallize, but super cools forming silica or quartz glass.

Quartz is important as a piezoelectric material for the crystals in gramophone pickups, for cigarette and gas lighters and for making crystal oscillators for radios and computers. There is insufficient natural quartz of high purity, and so it is made synthetically by hydrothermal growth of seed crystals from aq. NaOH and vitreous silica at $400^\circ C$ under pressure. In α -quartz, tetrahedra forms interlinked helical chains. Since the helix may be left or right handed, they can't be superimposed, so it exists as d and l optical isomers. Individual crystals can be separated by hand.

The structure of tridymite is more open than that of quartz and is similar to that of cristobalite i.e the Si atoms have the same arrangements as the C atoms in diamond, with O atoms midway between them. The oxygen atoms of the SiO_4 tetrahedra of tridymite and cristobalite have the relationship of hexagonal close packing to cubic close packing, the difference between the structures being like the difference in the wurtzite and zinc blende structures. The idealized tridymite structure thus involves two-layer sequence of SiO_4 tetrahedra, and the idealized cristobalite structures, three-layer sequences.

The interconversion quartz and cristobalite on heating requires breaking and re-forming of bands, and the activation energy is high. However the rate of conversion are profoundly affected by the presence of impurities, or by the introduction of alkali-metal oxides or other "mineralizers". The studies of the system have shown that what was believed to be another form of quartz, tridymite, is a solid solution of mineralizer and silica.

The dense forms of SiO_2 , called coesite and stishovite, were first prepared under drastic conditions (250-1300°C at 35-120 atm) but they were subsequently identified in meteor craters where the impact conditions were presumably similar. Stishovite has the rutile structure. Both are chemically more inert than normal SiO_2 to which they revert on heating.

Amorphous forms: High cristobalite melts slowly at 1723°C to the liquid form. Because of the slowness of the tridymite-cristobalite conversion, it is possible to observe the melting point of the metastable form at 1680°C. Similarly quartz melts at a temperature lower than that of either cristobalite or tridymite, probably about 1470°C, but the rate of fusion is comparable to the rate at which cristobalite is formed. On cooling the liquid vitreous silica is formed. Vitreous silica is a glass composed essentially of SiO_2 . It has a low coefficient of expansion, is quite resistant to shock and is very transparent to visible and ultraviolet light. It is used for laboratory glassware, for optical components such as lenses and prisms and cells to hold samples in UV-visible spectrophotometers.

Amorphous silica is dehydrated, polymerized silica which may be considered as a condensation polymer of silicic acid. Amorphous silicas are usually further categorized as silica gel, colloidal silica, precipitated silica, or fumed silica. These sub classifications are related to the method of preparation in each case.

Silica gel is widely used as a drying agent, a catalyst and in chromatography. When the solution of a silicate is acidified, a gel-like mass results. On heating, the water molecules contained in the gel are driven off and the shrunken product that results is called silica gel. The mineral opal, used as a white or pearl like gem stone, is hard (amorphous) silica gel. Various minerals, cut and polished as gemstones display ordered structures viz. agate (banded colors), onyx (often white and black bands) carnelian (yellow or red), jasper (usually red or brown but sometimes green blue or yellow) flint (colourless or black if carbon present). These are best written as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

Kieselguhn is another form of SiO_2 . It is a fine white powder and is used in filtration plants, as an abrasive and as inert filler. The mixture of the explosive nitrobenzene (liquid) and inert kieselguhr (solid) is called Gelignite.

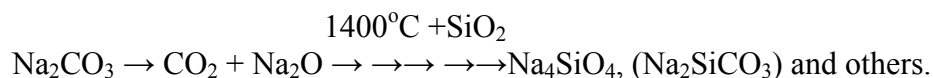
Colloidal silica finds use in cellophane films, blueprint and other photosensitive papers. In textile industry the applications of colloidal silica reduces the slippage of rayon and lowers the surface luster of filament yarns. The incorporation of colloidal silica into floor wax imparts increased skid resistance.

Precipitated silicas find use in rubber industry as fillers and in paper industry both as filler and in coating formulations.

Silicates: The high affinity of silicon for oxygen accounts for the existence of a vast array of silicate minerals and synthetic silicon oxygen compounds. Silicates are extremely important because the cement, ceramic and glass industries are based on their chemistry. The metallurgical extraction processes often produce silicates as waste products or slag. The difference in electro negativity between Si and O being quite appreciable (1.7) suggests that Si–O bonds are almost 50% ionic and 50% covalent. The structural features can be explained by considering that Si^{4+} and O^{2-} ions are present. The radius ratio being 0.3, it is reasonable to expect a tetrahedral

arrangement of oxide ions around Si^{4+} ion, i.e. $[\text{SiO}_4]^{4-}$. In general, these tetrahedra share vertices and (much more rarely) edges or faces. Each terminal oxygen atom contributes -1 to the charge of the SiO_4 unit, but each shared oxygen atom contributes zero. The SiO_4 tetrahedra may occur singly or may share oxygen atoms with other tetrahedra.

The majority of silicate minerals are very insoluble, because they have an infinite ionic structure and great strength of the $\text{Si}-\text{O}$ bond. The water soluble silicates with low molecular weights can be prepared by fusing an alkali metal carbonate with sand in an electric furnace at about 1400°C .



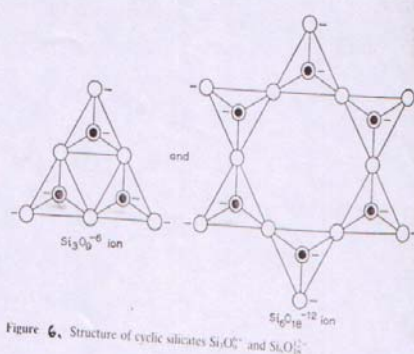
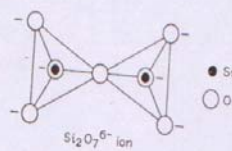
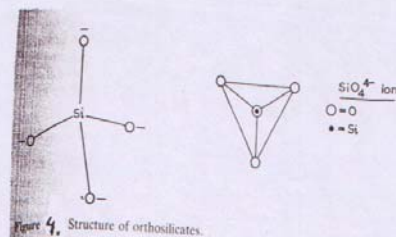
The soluble sodium silicates find use in liquid detergent preparations to keep the pH high, so that grease and fat can be dissolved by forming a soap. Sodium silicate is also used as an adhesive for pasting paper, in asbestos roof tiles, in fire proof paint and putty and in making silica gel. The way in which these are linked, provide a convenient basis for the classification of silicates:

- (i) Orthosilicates (neso-silicates)
- (ii) Pyrosilicates (soro-silicates, disilicates)
- (iii) Cyclic silicates
- (iv) Chain silicates
- (v) Sheet silicates
- (vi) Three-dimensional silicates

(i) Orthosilicates: A wide variety of minerals contain discrete SiO_4^{4-} units i.e no oxygen atoms are shared between adjacent tetrahedra Fig. 4. These have the general formula $\text{M}_2^{\text{II}}[\text{SiO}_4]$, where M may be Be, Mg, Fe, Mn or Zn or $\text{M}^{\text{IV}}[\text{SiO}_4]$ e.g. $[\text{ZrSiO}_4]$. The minerals phenacite $\text{Be}_2[\text{SiO}_4]$, forsterite $\text{Mg}_2[\text{SiO}_4]$, olivine $(\text{Mg}, \text{Fe})_2[\text{SiO}_4]$ and $(\text{Mg}, \text{Fe}, \text{Mn})_2[\text{SiO}_4]$, willemite $\text{Zn}_2[\text{SiO}_4]$ are a few representative examples.

The structure can be regarded as hexagonal close packed arrangement of oxide ions, and the Si^{4+} or other ions occupy the tetrahedral or octahedral voids. Small ions ($r < 0.30\text{\AA}$) like Be^{2+} , Si^{4+} occupy tetrahedral voids. Al^{3+} ($r = 0.42\text{\AA}$) may occupy either an octahedral or tetrahedral void and ions like Mg^{2+} , Fe^{2+} , Zn^{2+} ($r < 0.7\text{\AA}$) occupy octahedral voids.

It is quite noteworthy that different structures are formed depending upon the coordination number adopted by the metal. In phenacite $\text{Be}_2[\text{SiO}_4]$ and willemite $\text{Zn}_2[\text{SiO}_4]$, the Zn and Be atoms have a coordination number of four, occupy tetrahedral holes and are surrounded by a tetrahedrally arranged set of four oxygen atoms. In forsterite $\text{Mg}_2[\text{SiO}_4]$, the Mg has a coordination number of six and occupies octahedral holes. When octahedral sites are occupied, it is quite common to get isomorphous replacement of one divalent metal ion by another of similar size, without changing the structure. The mineral olivine $(\text{Mg}, \text{Fe})_2[\text{SiO}_4]$ has the same structure as forsterite, but about 1/10th of Mg^{2+} ions in forsterite are replaced by Fe^{2+} ions. The ions have the same charge and similar radii ($\text{Mg}^{2+} 0.72\text{\AA}$, $\text{Fe}^{2+} 0.78\text{\AA}$) and occupy the same type of hole. The substitution of one metal for another does not change the structure. This mineral may also have Mn^{II} in some octahedral sites, thus giving $(\text{Mg}, \text{Fe}, \text{Mn})_2[\text{SiO}_4]$. These structures are all related to hexagonal close packing. (Figure 3). In Zircon ZrSiO_4 , Zr has a coordination number of eight, although not all Zr-O distances are equal. It is used as a gemstone. It is cheaper and much softer than diamond.



(ii). Pyrosilicates (disilicates): In pyrosilicates, two tetrahedral units are joined by sharing the one corner oxygen atom thus giving the unit $[\text{Si}_2\text{O}_7]^{6-}$. This is the simplest of the condensed silicate ions. The name pyro comes from the similarity in structure with pyrophosphate such as $\text{Na}_4\text{P}_2\text{O}_7$. The minerals containing the disilicate anion $\text{Si}_2\text{O}_7^{6-}$ are not common. The thortveitite $\text{Sc}_2[\text{Si}_2\text{O}_7]$, hemimorphite, $\text{Zn}_4(\text{OH})_2[\text{Si}_2\text{O}_7]$ (does not contain discrete $\text{Si}_2\text{O}_7^{6-}$ ions) and barysilite, $\text{MnPb}_8[\text{Si}_2\text{O}_7]_3$ are a few examples of pyrosilicates. A number of lanthanide disilicates of composition $\text{Ln}_2[\text{Si}_2\text{O}_7]$ are known, but these are not similar to thortveitite, as the Si–O–Si angle is not 180° as in the Sc compound, but varies down to 133° and the coordination number of the metal changes from 6 to 7 and then to 8 as the size of the metal increases (Fig. 5).

(iii). Cyclic silicates: Two oxygen atoms of each tetrahedra can be shared between adjacent tetrahedra to give ring structure of formula $(\text{SiO}_3)^{2n-}$ (Fig. 6). The cyclic ion $\text{Si}_3\text{O}_9^{6-}$ occurs in wollastonite, $\text{Ca}_3[\text{Si}_3\text{O}_9]$ and in bentonite $\text{BaTi}[\text{Si}_3\text{O}_9]$. The $\text{Si}_6\text{O}_{18}^{12-}$ unit occurs in mineral beryl $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$. In beryl, the Si_6O_{18} units are stacked one above the other leaving channels, owing to which the mineral is permeable to gases consisting of small atoms or molecules such as helium. Na^+ , Li^+ and Cs^+ ions are also found in these channels. Beryl is found with granite and usually forms pale green crystals, which are six-sided prisms. (Figure 6)

(iv). Chain Silicates: These are of two main types, the pyroxene, which contain single strand chains of composition $(\text{SiO}_3^{2-})_n$ (Fig. 7) and the amphiboles which contain double strand, cross-linked chains or bands of composition $(\text{Si}_4\text{O}_{11}^{6-})_n$.

The various examples of pyroxenes are enstatite, MgSiO_3 ; diopside, $\text{CaMg}(\text{SiO}_3)_2$ and spodumene, $\text{LiAl}(\text{SiO}_3)_2$. The typical amphiboles are tremolite $\text{CaMg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$ and crocidolite $\text{Na}_2\text{Fe}_3^{\text{II}}\text{Fe}_2^{\text{III}}[(\text{Si}_4\text{O}_{11})_2](\text{OH})_2$. Amphiboles apparently always contain some hydroxyl groups attached to the cations. Because of the strength of the $(\text{SiO}_3)_n$ and $(\text{Si}_4\text{O}_{11})_n$ chains in pyroxenes and amphiboles and also because of the relative weakness and lack of strong directional properties in the essentially electrostatic forces between them via the metal ions one might expect such substances to cleave most readily in directions parallel to the chains.

(v). Sheet Silicates (Phyllosilicates): If all the SiO_4 tetrahedra units share three corners (oxygen atoms) an infinite two-dimensional sheet structure of formula $[\text{Si}_2\text{O}_5]_n^{2n-}$ results (Fig. 8). In this silicate sheet, the oxygen atoms which are shaded are above the plane of the paper while the other three O atoms are in the plane of the paper. There are strong bonds within the Si–O sheet, but much weaker forces hold each sheet to the next one. Thus these minerals tend to cleave into thin sheets. A large number of sheet silicates are important and well known. These have slightly more complicated structures and are made up of either two or three layers joined together by the cation which lie between them. The minerals which have this type of silicate structure include

- (i) Clays (aluminosilicates: kaolinite pyrophyllite, talc)
- (ii) White asbestos (chrysotile, biotite)
- (iii) Micas (muscovite & margarite)
- (iv) Montmorillonites (fullers earth, bentonite & vermiculite)

In kaolinite, $\text{Al}_2(\text{OH})_4[\text{Si}_2\text{O}_5]$ a third layer of OH groups is also present. Pyrophyllite, $\text{Al}_2(\text{OH})_2[(\text{Si}_2\text{O}_5)_2]$ has three layer structure. The brucite $\text{Mg}(\text{OH})_2$ combined with two Si_2O_5 layers forms a triple sheet structure called talc or soapstone $\text{Mg}_3(\text{OH})_2[(\text{Si}_2\text{O}_5)_2]$.

The mineral chrysotile $\text{Mg}(\text{OH})_2[\text{Si}_2\text{O}_5]$ (white asbestos) is of considerable commercial importance. The biotite or black mica has the formula $\text{K}(\text{MgFe}^{\text{II}})(\text{OH})_2[\text{Si}_3\text{AlO}_{10}]$.

In muscovite, $\text{Al}_2\text{K}(\text{OH})_2[\text{Si}_3\text{AlO}_{10}]$, AlO_4 tetrahedra are also present along with the SiO_4 tetrahedra. The K^+ ions required for making up the deficit positive charge are responsible for holding the two identical units in a repeat unit. Margesite has the formula $\text{CaAl}_2(\text{OH})_2[\text{Si}_3\text{O}_{10}]$.

A typical formula for vermiculites is $\text{Na}_x(\text{Mg, Al, Fe})_3(\text{OH})_2[(\text{Si, Al})_2\text{O}_5]_2 \cdot \text{H}_2\text{O}$. If vermiculite are heated they dehydrate in an unusual way by extruding little worms, hence the name. The

vermiculates are formed if in talc, $\text{Mg}_3(\text{OH})_2[(\text{Si}_2\text{O}_5)_2]$ the substitution of Mg^{2+} in brucite sheet and of Si^{4+} with Al^{3+} occurs in the silicate sheet.

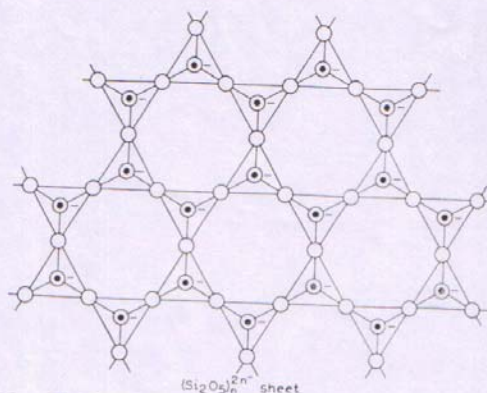
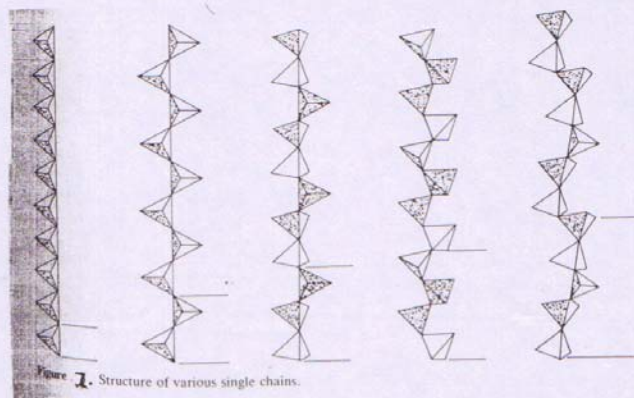


Figure 8. Structure of sheet silicates (Si_2O_5) $_n^{2-}$.

(vi). Three-dimensional Silicates: Three dimensional framework structures result when all the four oxygen atoms of each SiO_4 tetrahedra is shared with adjacent tetrahedral. The empirical formula of such a silicate framework consisting only of Si and O is $(\text{SiO}_2)_n$ (e.g quartz, tridymite or cristobalite). These contain no metal ions but if there is isomorphous replacement of some of the Si^{4+} by Al^{3+} plus an additional metal ion, three groups of aluminosilicate minerals occur as:

- (i) feldspars
- (ii) zeolites
- (iii) ultramarines

The feldspars are the major constituents of igneous rocks like granite. Feldspars are divided into two classes:

1. orthoclase feldspars (orthoclase, $K[AlSi_3O_8]$; celsian $Ba[Al_2Si]$
2. plagioclase feldspars (albite, $Na[AlSi_3O_8]$, anorthite, $Ca[Al_2Si_2O_8]$

The orthoclases are more symmetrical than are plagioclases as K^+ and Ba^{2+} are just the right size to fit into the lattice whilst Na^+ and Ca^{2+} being smaller allow distortion.

Zeolites are the most important among the three dimensional silicates and have a much open structure than feldspars. Zeolites are often used as ion-exchange materials and as molecular sieves. Natrolite, $Na_2[Al_2Si_3O_{10}].2H_2O$ is a natural ion exchanger. Permutit water softeners use sodium zeolites. Zeolites also act as molecular sieves by absorbing molecules which are small enough to enter the cavities. Molecular sieves can be made with pores of appropriate size to remove small molecules selectively.

The ultramarines are a group of related compounds, which contain no water, but do contain anions such as Cl^- , SO_4^{2-} and S_2^{2-} . The examples of ultramarines include:

Ultramarine	$Na_8[(AlSiO_4)_6]S_2$
Sodalite	$Na_8[AlSiO_4)_6]Cl_2$
Nosean	$Na_8[AlSiO_4)_6]SO_4$

The blue colour ultramarine mineral lapis lazuli used for oil paintings contains $Na_8[(AlSiO_4)_6]S_2$, in which the colour is produced by the polysulphide ion.

Clays: Clays are characterized by extreme fineness of particles (often colloidal in size having diameter of $1/256$ mm or smaller) and by wide variations in physical and thermal (ceramic) properties and in mineral and chemical compositions. Clay is also defined as disperse system of the colloidal products of weathering in which secondary mineral particles of smaller dimensions than 2μ predominate. The composition of clay minerals corresponds to that of an aluminosilicic acid usually mixed with an indefinite amount of sand and minerals and compounds producing a mass which both crystalline and amorphous become plastic when mixed with a suitable quantity of water. Clay minerals are platy in shape less commonly lath like and tubular (or scroll shaped). Owing to the extreme fineness of individual clay particles and some clays possessing relatively open crystal lattices, these exhibit surface and internal surface colloidal effects. Other minerals and rock particles which are not hydrous aluminosilicates but show colloidal dimensions and characteristics may occur intimately intermixed with the clay minerals displaying an essential role in the material.

Thus, a clay is a naturally occurring sediment or sedimentary rock composed of one or more minerals and accessory compounds, rich in hydrated silicates of Al, Fe or Mg, hydrated alumina, or iron oxide, predominating in particles of colloidal or near colloidal size and commonly developing plasticity* (the property of the material which permits it to be deformed under stress without rupturing and to retain the shape produced after the stress is removed) when sufficiently pulverized and wetted.

The commercial valuable deposits of clay constitute numerous forms viz. glacial, ball, fire, slip, adobe, flint, kaolins, bentonite etc. and are widely distributed. The deposits of kaolin and bauxitic clays are produced in abundance from Hungary, Missouri, Colorado, Texas, Ohio, Indiana, Oregon and Pennsylvania. Kaolin reserves of high quality in the Carlsbad and adjacent region of Czechoslovakia are enormous. Chile, Argentina and Brazil hold deposits of refractory clays. Fireclays in Scotland are the basis of refractories industry. Loess used primarily for brick making occur in great volume along the Missouri, Mississippi and Ohio rivers and their tributaries.

Clay minerals may originate through several processes:

1. by hydrolysis and hydration of a silicate (alkali silicate + water $\rightarrow$ hydrated aluminosilicate clay + alkali hydroxide).
2. by the solution of a limestone or other soluble rock containing relatively insoluble clay impurities that are left behind.
3. by the shaking and weathering of shales (clay rich sedimentary rocks).
4. by the replacement of a preexisting host rock by invading guest clay whose constituents are carried in part or wholly by solution.
5. by deposition of clay in cavities or veins from solution .
6. by bacterial and other organic activity including the extraction of metal cations as nutrients by plants.
7. by the action of acid clays, humus and inorganic acids on primary silicates.
8. by the laboratory synthesis.

The clay minerals are essentially hydrous aluminosilicates, with Fe or Mg proxying wholly and impart for the Al in some minerals and with alkalies and alkaline earths also present as essential constituents in some of them. In addition to the clay minerals, some clays contain varying amount of so called nonclay minerals, such as quartz, calcite, feldspar and pyrites. Clay materials are used in the manufacture of a large number and variety of products – ceramic, paper, rubber, catalysts etc.

Clay minerals have been classified into an amorphous (to X ray) and the crystalline forms:

- Amorphous: allophane and evansite
- Crystalline: kaolins groups including polymorphs of individual mineral species and magnesium analogs such as serpentine etc.
- Montmorillonite group
- Illite, or mica clay mineral group
- Chlorite group and vermiculite group
- Palygorskite group (attapulgitite and sepiolite)

Allophane and Evansite: Allophane is an amorphous clay that is essentially an amorphous solid solution of silica, alumina and water. It may be associated with halloysite and it may occur as a

homogeneous mixture with evansite, an amorphous solid solution of phosphorus, alumina and water. It is versatile in composition, hydration and properties.

Kaolins and Serpentine Minerals: Kaolinite mineral has the formula $\text{Al}_2(\text{OH})_4[\text{Si}_2\text{O}_5]$. It is a white solid and is formed by the decomposition of granite. Large amounts are used for filling paper and is a refractory. China clay or kaolin is a high grade of kaolinite and when small amounts of SiO_2 and mica are removed it can be mixed with water to give white or nearly white plastic clay. Small amounts are used for making porcelain, china cups and plates, sanitary ware and other ceramics for chromatography and as treatment for indigestion.

The kaolinite lattice is interpreted as consisting of one sheet of tetrahedrally coordinated Si with oxygen i.e simple silicate sheet, one side of the sheet contains all the unshared (singly bond) O atoms and one sheet of octahedrally coordinated Al with oxygen and OH^- (the pure $\text{Al}(\text{OH})_3$ crystallizes out with layer structure when Al is six coordinate and occupies octahedral sites). The unshared O in a silicate sheet have almost the same relative positions as two thirds of the OH groups on each side of these hydroxide layers. If a Si_2O_5 layer is placed alongside a layer of γ -gibbsite $\text{Al}(\text{OH})_3$, then many of the O atoms will coincide. The OH groups in $\text{Al}(\text{OH})_3$ can be removed and an electrically neutral two layer structure is formed. Hence a 1:1 or double layers stacked parallel give the mineral kaolinite. The serpentine minerals (chrysotile) $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (white asbestos) result wherein the kaolin structure, $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$, two Al are substituted by three Mg. The two layer structure may be considered to be formed from the combination of brucite $\text{Mg}(\text{OH})_2$ with a Si_2O_5 layer. In serpentine, all three possible octahedral cation sites are filled, yielding a trioctahedral group carrying a +6 charge whereas in kaolinite, only $\frac{2}{3}$ rd of the sites are occupied by Al yielding a dioctahedral group also carrying +6 charge. The serpentines are analogs of kaoline minerals, although they depart from aluminous clays in certain other properties. The pyrophyllite of composition $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ or $\text{Al}_2(\text{OH})_2[(\text{Si}_2\text{O}_5)]$ has three layer structure made up of two Si_2O_5 sheets combined with both sides of $\text{Al}(\text{OH})_3$.

Illite or Mica – Clay – mineral group: Illite is defined as a general term for the clay mineral constituents of argillaceous sediments belonging to the mica group. Its origin has been attributed to alteration of silicate minerals by weathering and hydrothermal solutions, reconstitution, wetting and drying of soil clays. Illite is the most abundant clay mineral in Paleozoic shales and is widespread in many other sedimentary rocks. Illite has the formula $(\text{OH})_4\text{K}_y(\text{Al}_4\text{Fe}_4\text{Mg}_4\text{Mg}_6)(\text{Si}_{8-y}\text{Al}_y)\text{O}_{20}$, where y refers to the K^+ ions that satisfy the excess charges when about 15% of the Si^{4+} positions are replaced by Al^{3+} . A representative chemical analysis of illite is: 51.22% SiO_2 , 25.91% Al_2O_3 , 4.59% Fe_2O_3 , 1.70% FeO , 2.84% MgO , 0.16% CaO , 0.17% Na_2O , 6.09% K_2O , 0.53% TiO_2 7.49% ignition loss above 110°C ; 100.7% total. The cation exchange capacity of illite is 20-30 meq/100g of dry clay.

Montmorillonite Minerals: This Group of minerals is well known as the main component of bentonite clays. Montmorillonites are derived structurally from pyrophyllite, $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4$ or talc, $\text{Si}_8\text{Mg}_6\text{O}_{20}(\text{OH})_4$ by substitution mainly in the octahedral layer. Some substitution may occur for Si in the tetrahedral layer and by F for OH in the structure. When substitutions occur between elements (ions) of unlike charge, deficit or excess charge develops on corresponding parts of the structure. The deficit charges in montmorillonite are compensated by cations (commonly Na, Ca, K) sorbed between the three layered (two tetrahedral and one octahedral,

hence 2:1) clay-mineral sandwiches. These are relatively loosely (although stoichiometrically) held and give rise to major cation exchange properties of the montmorillonite.

High Alumina ‘Clay’ Minerals: High Alumina Clay minerals result from intense weathering and leaching where the silica gets dissolved away. A very humid subtropical climate is required for this stage of weathering. Diaspore and boehmite. Both $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Al_2O_3 , 55%; H_2O , 15%) are the chief constituents of diaspore clay which may run over 75% Al_2O_3 on the raw basis. Gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Al_2O_3 , 65%; H_2O , 34%) as well as the monohydrates occur in bauxite and bauxitic clays.

Chlorite and Vermiculate Minerals: Chlorite is widespread in argillaceous sedimentary rocks and in certain soils. The structure of chlorite is described as three layer phyllosilicates separated by a brucite, $\text{Mg}(\text{OH})_2$, interlayer or alternatively, as a four layer group of alternating silica tetrahedral and Mg octahedral sheets. When gibbsite, $\text{Al}(\text{OH})_3$ proxies in part for brucite Al-Chlorite is formed. Chlorite like structures has been reported to be synthesized by precipitating Mg and Al between montmorillonite sheets.

In vermiculate, the interlayer sheet constitutes octahedrally coordinated six water molecules about Mg^{2+} , in contrast to brucite, $\text{Mg}(\text{OH})_2$ in chlorite. The cation exchange capacity of vermiculate is relatively high and may exceed that of montmorillonite. The regularly interstratified (1:1) chlorite and vermiculate form mineral corrensite.

Micas: The micas are a series of silicate minerals characterized physically by a perfect basal cleavage. They yield with ease, thin tough laminae that have a high degree of flexibility. Mica is widely distributed as small flakes in many igneous, metamorphic and sedimentary rocks. The major products of mica are United States, India, Mozambique, Canada, Australia, Argentina, France, Zambia, South-West Africa, Japan, Brazil etc.

Muscovite [$\text{K}_2\text{Al}_4(\text{Al}_2\text{Si}_6\text{O}_{20})(\text{OH})_4$] and Phlogopite [$\text{K}_2(\text{Mg}, \text{Fe}^{2+})_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH}, \text{F}_4)$] are the two naturally occurring micas and fluorophlogopite [$\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{20}\text{F}_4$] is the synthetic mica. The other micas are biotite (natural) [$\text{K}_2(\text{Fe}^{2+}, \text{Mg})_6(\text{Al}_2\text{Si}_6\text{O}_{20})(\text{OH})_4$] and barium disilicic [$\text{Ba}_2\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4$]. Muscovite is often called “white” or “ruby” mica to distinguish it from phlogopite, which is often called “amber mica”. Colour is a basis for industrial classification of muscovite into white (including yellow), ruby (amber, red, and brown) and green. When split into thin films, both muscovite and phlogopite are nearly colourless and transparent, although when viewed against a very white background, the green variety can usually be picked. Mica is classified according to the extent of separation, thickness, size, visual quality, electrical quality and thermal stability.

All mica crystallize in the form of flat, six-sided monoclinic crystals. The nearly perfect basal cleavage permits the crystals to be split into films, both muscovite and phlogopite are nearly colourless and transparent, although when viewed against a very white background, the green variety can usually be picked out. Mica is classified according to the extent of preparation, thickness, size, visual quality, electrical quality and thermal stability.

All micas crystallize in the form of flat, six sided monoclinic crystals. The nearly perfect basal cleavage permits the crystal to be split into films. The ultimate film thickness obtainable depends

entirely on mechanical considerations. The strength and elasticity of the films are characteristic of the commercial varieties of mica. A rough test is to wrap a thin film around a pencil; the best qualities suffer no permanent deformation or rupture.

Mica is virtually unaffected by fire, water, acids, alkalis or electricity. All natural micas do lose a little water upon heating to a high enough temperature but muscovite can be used for electrical purposes up to 1000°F and phlogopite up to 1850°F. The synthetic fluorine micas have no water in their structure and can be used to 2000°F or higher as a high electrical quality machinable dielectric and as a moldable high temperature electrical insulator. The major uses of a variety of mica are (block mica and film built up, scrap, ground mica, glass bonded mica) are: electrical insulation in household appliances, incandescent lamps, fuse plugs.

Film mica: dielectric in capacitors, particularly for the electronic industry

Built-up mica: insulating material in electric motors, generators and transformers (in the form of molding plate, segment plate, heater plate, flexible sheet and tape)

Scrap mica (raw): source material for all other forms of processed mica

Ground mica: coating for cores and molds in metal casting, annealing agent in metal treatment, Adsorbent for explosives and disinfectants, artificial snow and thermal insulation

Glass-bonded mica: Memory devices, microwave components, rectifiers, timing devices including Domestic appliances, transducer components, transformers, TV projectors, voltage control units, cable seals, fire detector terminals.

Mica sheet or paper: mica paper tapes for dc armature coils, automotive electrical systems, in pregmated laminate for high temperature uses, insulation interaction motors, sheet insulation for capacitors including jet engine ignition systems, tape, sheet and board insulation for small appliances.

The fluorine micas comparatively new materials are formed in high purity at ordinary or ambient air pressure by melting or by solid-state reaction of the proper raw materials. These can be synthesized in essentially unlimited quantity from abundant raw materials with low cost. Numerous varieties with unusual properties can be made by isomorphic substitutions.

Suggested Reading-

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