Quadrant II – Notes

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Module Name: Principles involved in the extraction of Elements (Smelting)

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Notes :

Principles involved in extraction of elements (Smelting)

Elements have been broadly divided into metals and non-metals on the basis of their physical and chemical properties. Metals have generally low ionisation energies, low electron affinities and low electronegativities which are responsible for their high electrical and thermal conductivities, high malleability and ductility, metallic lustre and hardness. Of the 108 elements known at present, about 70 are metals. In the present chapter, we shall study the occurrence and general methods used for the extraction of metals from their ores.

Occurrence of Metals

Metals occur in nature sometimes free but mostly in the combined state The earth's crust is the biggest source of metals. Some soluble salts of metals are also found in sea water.

Noble metals which have little or no affinity for oxygen and which resist the attack of water and other chemical reagents, occur in the free, ie, the native state. Thus, metals such as silver, gold and platinum occur in nature in native state along with alluvial impurities such as clay and sand. Sometimes lumps of pure metals are also found. These are called nuggets .

The standard electrode potentials (i.e., reduction potentials) of noble metals are always positive which means that the ions of such metals have a tendency to accept electrons and get reduced to the corresponding metals. That is why these metals occur in metallic, i.e., native state.

The standard electrode potentials of active metals, on the other hand, are negative which means that these metals have a tendency to get oxidised to their ions. In other words, the ions of such metals are reluctant to get reduced to the metallic state. That is why the active metals occur in nature in the form of their compounds, i.e., in the combined state. These compounds are known as minerals.The minerals from which metals can be conveniently and economically extracted are referred to as ores

Active metals occur in the form of the following categories of ores:

Sulphide ores: Metals such as iron, mercury, copper, etc., occur as their sulphides, e.g., iron pyrites (FeS), galena (PbS), cinnabar (HgS), copper pyrites ($CuFeS_2$), zinc blende (ZnS), etc.

Oxide ores: metal such as iron, aluminium, manganese, tin, zinc, etc., occur as their oxides, e.g. haematite (Fe_2O_3), bauxite (Al_20_3, $2H_20$), pyrolusite (MnO_2), cassiterite (SnO_2), zincite (Zn0), etc.

Carbonate ores: The important carbonate ores are of magnesium, iron, copper, zine and lead, eg.. magnesite ($MgCO_3$), dolomite ($CaCO_3$, $MgCO_3$), siderite ($FeCO_3$), malachite

[$Cu(OH)_2$. $CuCO_3$,].Cerussite ($PbCO_3$), calamine ($ZnCO_3$), etc.

Halide ores: Chlorides ores are the most common among the halide ores.The chlorides of sodium, potassium and magnesium are found in salt beds on the surface of the earth and in sea water. Carnallite ($KClMgCl_2$ $6H_2O$), rock salt (NaCl) and horn silver (AgCl) are common examples of chloride ores.

Bromides and iodides of potassium and magnesium are present in small amounts in sea water. The fluoride ores include flourspar (CaF_2) and cryolive (AlF_3, 3NaF).

Sulphate ores:

Many sulphide ores get converted into sulphates by atmospheric oxidation The common sulphate ores are barytes ($BaSO_4$), anglesite ($PbSO_4$),epsomite ($MgSO_4$,$7H_2O$), and anhydrite $CaSO_4$etc.

Metallurgy

The process of extracting metals from their ores is called metallurgy. The metallurgical process would necessarily depend upon the nature of the ore which is to be worked out for the extraction of the metal. It is not possible to chalk out a universal scheme for the extraction of all metals since the extraction of each metal involves individual procedure depending upon its nature and properties. However, heavy metals such as copper, iron, zine, lead, tin, etc., are extracted from their ores by the conventional 'Roasting and Smelting processes.The active metals such as alkali metals, magnesium, calcium, aluminium ete, are obtained by the electrolysis of their chlorides, oxides or hydroxides in fused state and the noble metals such as gold and silver are obtained by the amalgamation or the cyanide process. Various Steps Involved in Metallurgical Processes.

The various steps essentially involved in the extraction of pure metals from their respective ores are as follows

1. Concentration of the Ore:

Metallic ores are often found mixed with rocky material, eg. quartz, felspar, mica and other silicates. These impurities are known as gangue. Before the ore is subjected to metallurgical process, it is necessary to remove these unwanted impurities mechanically. This operation is known as concentration of the ore.

The common methods of concentration are as follows:

Hand picking:Quite often, the ore is separated from the main stock in a sufficient degree of purity by simply picking it by hand and then eliminating the adhering rocky material by breaking with hammer.

Gravity separation: The ore can be concentrated by taking advantage of the differences in the specific gravities of metallic ore and the earthy impurities. The ore, after grinding, is washed with a running stream of water. The heavy ore settles down rapidly while the lighter earthy material (gangue) is washed away. The two common techniques of gravity separation are described below.

Hydraulic Classifier :Finely powdered ore is dropped into a conical reservoir, called hydraulic classifier, from the top. A powerful stream of water is introduced from the bottom of the reservoir. The gangue, being lighter, is carried away by water and the heavier ore particles accumulate at the apex of the cone. The conical shape of the reservoir helps in reducing the velocity of water and thus prevents the ore particles from being carried away along with the stream of water.

Wilfley Table:Wilfley table is a wooden table having a slanting floor on which long wooden strips called cleats or riffles are fixed. The powdered ore is suspended in a stream of water and delivered at the upper end of the table which is then given a bumping motion. The heavier ore particles are obstructed by the cleats while the lighter impurities pass over and are carried away by the stream of water. The ore particles which collect behind in the cleats move to one side as a result of the motion of the table and are collected

Magnetic separation. Ferromagnetic ores, as of iron, that are affected by a magnet, are separated from the non-magnetic impurities by means of magnetic separators. A magnetic separator consists of a leather belt moving over two rollers, one of which is magnetic . The powdered are is dropped on the belt at one end. Ar the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall farther off.

Electrostatic separation: This method is based on the fact that the particles which are good conductors of electricity become electrically charged as soon as they are brought into an electrostatic field and are consequently repelled by the electrode carrying the like charge. Lead sulphide and zinc sulphide ores which occur together in nature are separated by this technique. The mixed ore, after grinding, is fed upon a roller in a thin layer and subjected to the influence of an electrostatic field. Lead sulphide ore, being a good conductor, gets charged immediately and is thrown away from the roller due to electrical repulsion. The zine sulphide ore which is a poor conductor is not charged and hence drops vertically from the roller.

Froth Flotation: This process is based on the principle of preferential wetting of solids by liquids.Metallic sulphides for instance are wetted by certain oils,like pine oil, but not by water.

The finely divided ore is put in water to which a small quantity of oil (e.g., pine oil) has been added. The water is violently with air (Fig. 1) when froth is formed at the air-water interface. The ore which is preferentially wetted by the oil rises to the surface along with the foam while the stony matter (gangue) which is preferentially wetted by water remains in the water below the foam, as shown on the right of the figure. The foam separates out and, in due course, settles down as shown on the left of the figure. This process is known as froth flotation process.

GANGUE Fig. 1. Froth flotation process.

Leaching: This is a chemical method for the concentration of ores. In this method, the powdered ore is treated with some suitable reagent which may dissolve the ore but not the impurities. The impurities are filtered off and the ore is recovered from the solution by suitable chemical methods. For example, during the extraction of aluminium from bauxite ($Al_2O_3\ 2H_2O$) ore, the finely divided ore is treated with hot sodium hydroxide solution. Alumina present in the ore dissolves forming soluble sodium metaaluminate but impurities are left behind as such and are filtered off.

Calcination: Calcination is a process in which the ore is heated in a limited supply of air at a temperature insufficient to melt it. During calcination, organic matter, volatile impurities and moisture present in the ore are expelled and the remaining mass becomes porous. Calcination is also done to remove water from hydrated oxide ores or carbon dioxide from a carbonate ore. For example, when limestone is heated, carbon dioxide is given off and limestone is said to be calcined. When bauxite is calcined, water is removed and anhydrous alumina is left behind. Similarly, iron ores on calcination give anhydrous iron oxide. The various chemical changes are represented below:

$CaCO_3$ --------→ $CaCO_3 + CO_2$

$Al_2O_3.\ 2H_2O$---------→ $Al_2O_3 + 2H_2O$

$2Fe_2O_3.3H_2O$ -------→ $2Fe_2O_3 + 3H_2O$

Calcination is generally done in a reverberatory furnace (Fig. 2). It renders the ore porous and easily workable in subsequent stages.

Roasting:

Roasting is a wider term used to denote the process in which the ores (usually sulphide ores) either alone or with the addition of other materials, are subjected to the action of heat in the presence of air temperatures well below their melting points, in order to bring about their oxidation.

$2PbS+3O_2$ ---→ $2PbO+2SO_2$

$Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

Sometimes, during roasting, oxidation of sulphides takes place only upto sulphates.

For example,

$2ZnS + 3O_2$ ---→ $2 ZnO + 2SO_2$

Smoking: 1. Furnace made of steel plates, lined inside with fire clay) blowing in air near the base, as shown in the figure. It is and a tapping hole for taking out the metal.

2. A reverberatory furnace. 3. A blast furnace.

Smelting: Reduction of Metal Oxides by Carbon:

A large number of metal oxides obtained during roasting can be reduced to metals by heating with carbon at elevated temperatures (>10000) This process is called smelting.

The roasted ore is mixed with a suitable quantity of carbon (coal or coke) and heated to a high yer-altice ahove the melting point of the metal. Carbon and carbon monoxide (produced by the incomplete combustion of carbon) reduce the oxide to the free metal. For example,

$Fe_2O_3 +3O_2$ --→ $2Fe + 3CO$

$Fe_2O_3 +3CO$ --→ $2Fe +3C0_2$

$PbO+C$ ----→ $Pb +CO$

$PbO +CO$ ---→ $Pb+CO_2$

During reduction, an additional substance, called the flux, is added to the ore. It combines with impurities to form easily fusible product known as slag.

Impurities + flux (present in ore) -------→ fusible product (slag)

Slag is not soluble in molten metal. Being lighter, it can be easily skimmed off from the surface of molten metal.

The choice of flux depends upon the impurities present in the ore .For example, if the ore acidic impurities such as SiO_2. P_2O_5., then basic flutes like lime (CaO), magnesite ($MgCO_2$), haematite (Fe_2O_3), ctc., are used.

SiO_2	+ CaO----------- >	-$CaSiO_3$
Acidic impurity	Basic flux	Slag

On the other hand, if the ore contains basic impurities such as CaO, FeO, $MgCO_3$ then acidic fluxes like sand and borax are used.

FeO + SiO_2 ------------- >$FeSiO_3$

Basic impurity   Acidic flux   Slag

Smelting is generally carried out in a reverberatory furnace or a blast furnace in a controlled supply of air.

In the case of metals which are volatile in nature (for example, zinc), smelting cannot be done in an open furnace. In such cases, reduction of the oxide ore is carried out in fire-clay retorts The vertical retort, which is now in common use. Heating is done by producer gas

It is to be noted that reduction with carbon is practical only if the required temperature is achieved conveniently which may not be so always.

Reduction by controlled heating in air: In the case of less active heavy metals whose oxides are unstable towards heat, only roasting in air is enough for the separation of the metal. For example, roasting of the sulphide ore of mercury (cinnabar) gives the metal rather than its oxide

$HgS + O_2$---------→ $Hg + SO_2$

PRODUCER GAS

A vertical retort furnace for the smelting of Zinc ore.

Mercury vapours are condensed to the liquid state in the condensing chambers. This process is known as air reduction process The Idrian furnace commonly used for the process .

Idrian furnace for the extraction of mercury.

Sulphide ores of several metals such as Pb, Cu, Sb, may be first roasted in a limited supply of air to partially convert them to oxides. These are further roasted in the absence of air when the sulphides and the oxides formed react to give the metals. For instance,

Roasting in limited supply of air Cu_2O --→ $Cu + 5O_2$

Roasting in absence of air Cu_2S ------→ $Cu + SO_2$

This process is known as self reduction.