

CHAPTER 2

METHODS OF EXTRACTION AND REFINING OF METALS

Extraction of metals is, generally speaking, a process of **reduction**. Some energy is required to reduce (i.e. release) the metal present in a compound or in a solution and collect it in elemental form. During this process, the bulk of the metal is separated from the impurities in systems which invariably comprise of more than one phase (heterogeneous systems). While metal mainly constitutes a metallic phase, the impurities enter the nonmetallic phase or phases. The driving forces behind such transfers are governed by thermodynamics which will be discussed in Chapter 4.

Metals produced in bulk are often impure and need to be refined in order to improve their properties. The refining process not only improves the quality and value of the metal but may also lead to recovery of valuable by-products. It should be remembered that 'purity' of a metal is an ambiguous term unless it is defined in terms of an intended use of the metal. An impurity at a given concentration may be negligible from the point of view of one property but it **may** be significant from the point of view of another. For example, traces of oxygen in copper may hardly change the mechanical properties but may drastically lower the electrical conductivity.

In this chapter, we will discuss some general principles pertaining to extraction of metals and then some methods employed for refining impure metals.

2.1 PYROMETALLURGY

Pyrometallurgical methods of metal production are usually **cheaper and suited** for large scale productions. Among the many advantages of **pyrometallurgy**, the following are specially noteworthy.

1. Reaction rates are greatly accelerated at high temperatures. Small units can, therefore, achieve high production rates.
2. Some reactions which are not thermodynamically possible at low temperatures become so at higher temperatures.
3. There is greater ease of physical separation of the product metal from gangue if the products can be melted or vapourised at high temperatures. Metal-slag separation, so common in the metallurgical industry, provides an example. Blast furnace reduction of zinc ores to obtain zinc vapours is another example.

All relatively inexpensive metals (e.g. iron, lead, zinc, copper, aluminium, magnesium, sodium, antimony etc.) are usually produced by processes where the

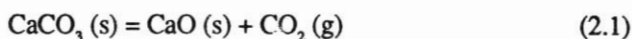
metal is obtained in liquid or gaseous state first.

2.2 SOME UNIT PROCESSES FOR PRELIMINARY TREATMENT OF ORES

A very large number of unit processes are used in pyrometallurgy. A systematic description of these is outside the scope of this book. Some commonly used processes are briefly described here to make the reader familiar with the basic concepts and terminologies.

2.2.1 Calcination

Calcination is the thermal treatment of an ore to effect its decomposition and to effect elimination of volatile products (normally carbon dioxide and/or water). Decomposition of CaCO_3 is an example.



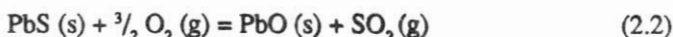
In this case, the pressure of CO_2 reaches one atmosphere at about 910°C which is often known as the decomposition or calcination temperature. Most other carbonates have lower decomposition temperatures ($\text{MgCO}_3 \sim 417^\circ\text{C}$, $\text{MnCO}_3 \sim 377^\circ\text{C}$, $\text{FeCO}_3 \sim 400^\circ\text{C}$). Hydrates (e.g. $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) also decompose at relatively low temperatures and kilns may be run at about 700°C for calcination of hydrated aluminium oxide.

2.2.2 Roasting

Roasting usually involves heating of ores below the fusion point in excess of air. It brings about chemical conversion and renders the raw materials more suitable for subsequent reduction. Earlier, the major application of roasting included removal of sulphur or other elements such as arsenic and tellurium as volatile oxides. At present, however, roasting implies a wide variety of more complicated operations. It can be defined as the process of heating of the ore below the fusion point to change it chemically to a form more amenable to subsequent treatments for ultimate extraction of the metal.

The following are some of the more important roasting operations.

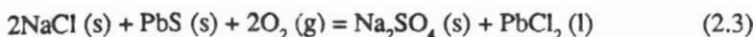
1. *Oxidizing roasting*: This is carried out to burn sulphur from sulphides with conversion of sulphides in whole or in part into oxides. For example,



Under certain conditions, oxidizing roasting may involve other reactions, leading to formation of sulphates or even the release of the metal itself in elemental form.

2. *Volatilizing roasting*: This is done to eliminate volatile oxides such as As_2O_3 , Sb_2O_3 and ZnO .

3. *Chloridizing roasting*: This is carried out to convert certain metal compounds to chlorides from which the metal may be subsequently obtained by reduction. The reaction is of the type



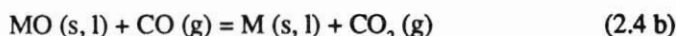
2.3 SOME UNIT PROCESSES FOR METAL EXTRACTION

2.3.1 Smelting

Smelting is a process for the production of a metal or a metal-rich phase such as **matte**. Generally, it refers to reduction of a metal oxide to metal, carbon being by far the most common reducing agent. During smelting the gangue is removed as **slag** with the help of fluxes. In **matte smelting**, no bulk metal is produced. The products are molten matte and slag. Matte is essentially a mixture of metal sulphides and some metal. No reducing agent is required in matte-smelting as explained later in this chapter.

Carbon occupies a unique position as a reducing agent on account of its easy availability and low cost. Moreover, while the element itself is virtually nonvolatile, it forms two volatile oxides, viz. CO and CO₂, which are automatically eliminated from the system. The lower oxide (CO) becomes more stable at higher temperatures whereas all metal oxides generally become less stable. Therefore, theoretically speaking, carbon can reduce any metal oxide provided the temperature is sufficiently high.

The reduction of a metal oxide by carbon is represented by the following equations.



It should be obvious that the temperature required for reduction would be higher if the stability of the metal oxide concerned is greater. However, if the temperature is too high then carbon may dissolve in the metal to form stable carbides. This happens in the case of blast furnace reduction of iron ore also. However, iron carbide (Fe₃C) is not detrimental towards the properties of iron. In most other cases, however, the carbide is an undesirable impurity. Moreover, when found necessary, carbon can be eliminated from iron with ease during subsequent refining.

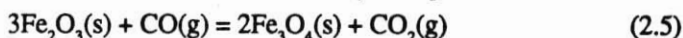
2.3.2 Production of Pig Iron in Blast Furnace

Extraction of iron, tin, lead, zinc and various ferro-alloys is achieved by carbothermic reduction of oxide ores. The production of pig iron in the blast furnace is by far the most noteworthy process of extraction due to its large tonnage.

The most abundant ore of iron is hematite, where iron is present as the mineral Fe₂O₃. It usually also contains gangue materials such as SiO₂, Al₂O₃ etc. The ore is charged with adequate amounts of limestone and coke into a blast furnace shown schematically in Fig. 2.1. Some other materials are also charged depending on local conditions. Limestone serves as flux. It decomposes into CaO which combines with the gangue in the charge to produce a liquid phase called slag which is discarded.

Several reactions take place inside the furnace. These may be classified as follows.

1. Reduction of iron oxides. The reactions may be represented as follows:



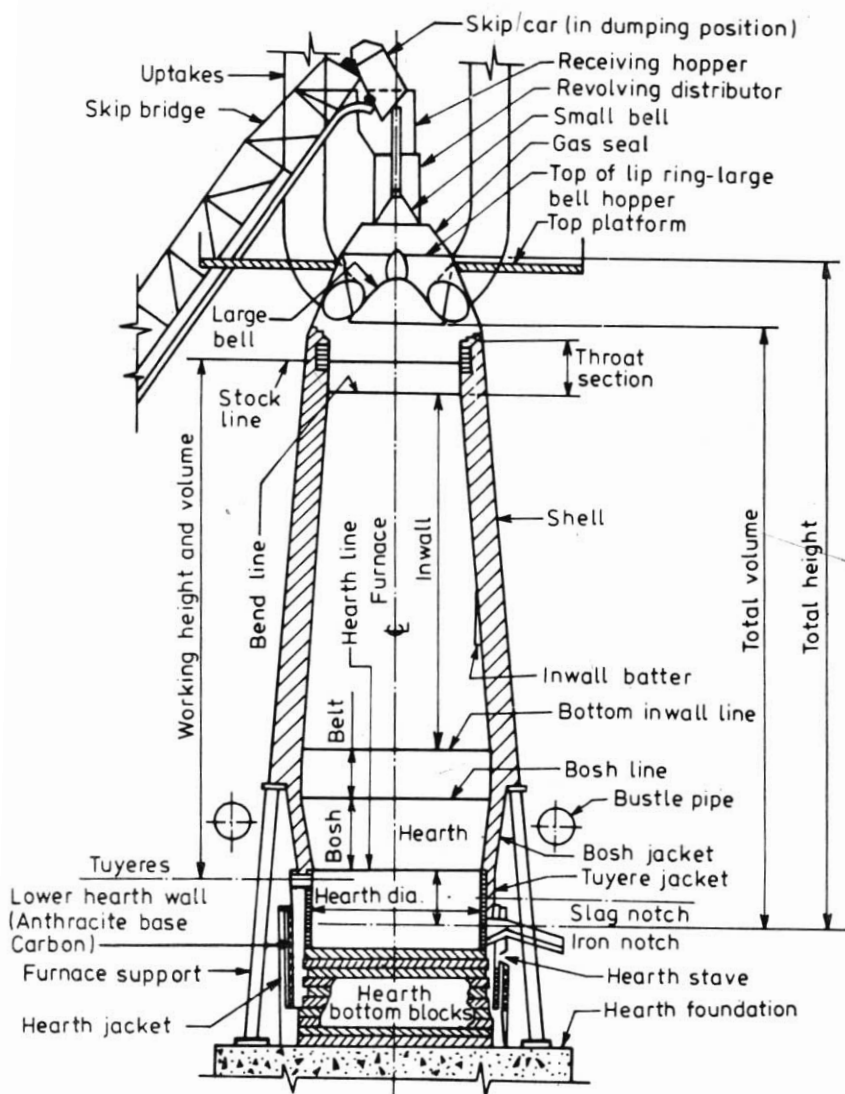
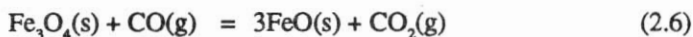


Fig. 2.1 Schematic diagram of a blast furnace



2. Gasification of carbon, represented by the reactions



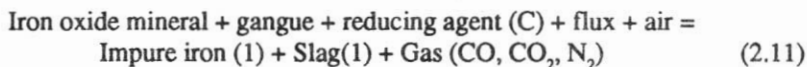
3. Reduction of other oxides such as SiO_2 , MnO etc.

4. Slag formation and other miscellaneous reactions.

The hot gases, comprising mainly of CO , CO_2 and N_2 (from the incoming air blast) escape through the top of the blast furnace. Because of the high temperatures prevailing, FeO is reduced to iron in the lower regions and the liquid metallic product collects at the bottom region of the furnace, known as the **hearth**. Some of the other oxides in the gangue are also reduced to varying degrees and the elements so produced (2-3% of the total weight of iron) enter the metal phase. Iron also dissolves 3.5-4.5 percent carbon. The unreduced oxides combine with fluxes to produce the slag.

The slag is a solution of oxides. As an introductory generalization we may assume that molten oxides do not dissolve metals and vice versa. There occurs, therefore, distinct separation of the metal phase and the slag phase. For good separation and other desirable effects, the slag which mainly consists of SiO_2 , Al_2O_3 and CaO should be of good fluidity. The latter depends both on the melting point of the slag as well as its constitution. The melting points of Al_2O_3 and SiO_2 are, respectively, 2045°C and 1718°C . Addition of a basic oxide such as CaO produces ternary solutions with melting points as low as 1200°C . Therefore, basic oxide CaO and also MgO are charged, respectively, as CaCO_3 and MgCO_3 to produce slags with good fluidity.

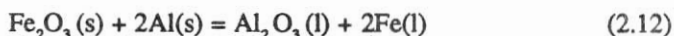
The overall reaction in the blast furnace may be indicated as



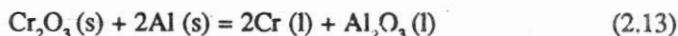
All other oxide-carbon reactions follow a similar scheme.

2.3.3 Metallothermic Reduction

Carbon reduction of metal compounds is sometimes known as **carbothermic reduction**. A compound may also be reduced by a **metallothermic** process using a metal such as aluminium or silicon as the reducing agent. These metals combine with oxygen to produce more stable oxides. The reduction of Fe_2O_3 by aluminium is the basis of a highly exothermic reaction used in a joining process called **Thermit Welding**. The reaction is



Many ferroalloys are produced by exothermic reactions of the type



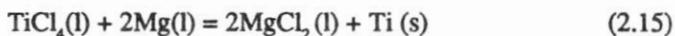
The reaction is made easier by producing chromium in the state of solution in iron which is added to the system either as scrap or through simultaneous reduction of iron oxides. In these reactions also, easy metal-slag separation is achieved by producing a fluid, low melting slag with the help of fluxing agents.

Many oxides can be reduced by calcium also because calcium forms a stable oxide, CaO. Reactions in such cases would be called **calciothermic reduction**.

Similarly, many metal halides can be reduced by other metals which form relatively more stable halides. Generally, magnesium, calcium, sodium etc. are used as the reducing agents. The reaction may be represented as



where M and M' are metals and X is a halogen, usually chlorine. This reaction has been the basis of many early processes for making of reactive metals and it continues to be used extensively. Reduction of halides by magnesium is known as the Kroll's process. The reaction for titanium production by this process is written as



Halides usually have relatively low melting points. If the metal produced itself is liquid, then a clean liquid-liquid separation of metal and slag is easily obtained.

2.3.4 Solid State Reduction of Oxides

We have seen that, generally reduction smelting refers to an operation involving a reducing agent and a slag to obtain liquid metal. This is not applicable where the melting point of metal is very high or where the ore is of very poor grade.

Consider the case of tungsten. The metal has a very high melting point. Again, tungsten ores generally contain only around 2% WO_3 , the rest constituting the gangue. It would be uneconomical to remove this gangue using fluxes. In this case it is advantageous to first produce pure WO_3 using extensive ore dressing and hydrometallurgical operations. WO_3 is, subsequently, reduced to tungsten powder by hydrogen at about 800—1000°C. The reaction is

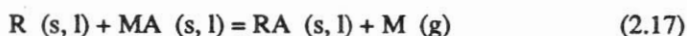


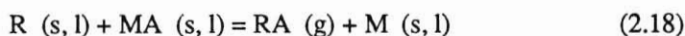
The metal powders so obtained are shaped into desired forms by pressing in moulds and then compacting into strong metal by prolonged heating at 3200°C which is close to the melting point of tungsten (3410°C).

2.4 PYROMETALLURGICAL PROCESSES UNDER LOW OR HIGH PRESSURES

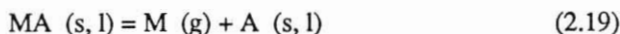
2.4.1 Low Pressure Processes

Most reactions that are favoured by low pressures may be classified as follows.
Thermal reduction—





Thermal dissociation—



Sublimation or distillation—



where R is the reducing agent,

M is the metal being extracted or refined,

A is the acid radical (e.g. S, O etc.)

and s, l, g represent solid, liquid and gaseous states, respectively.

In all the foregoing reactions, the thermodynamic equilibrium can be shifted by manipulating the pressure parameter. Operation under vacuum helps to eliminate one of the reaction products which is volatile thus driving the reaction towards completion.

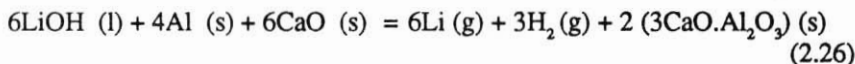
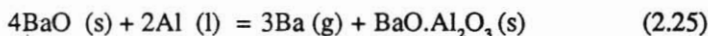
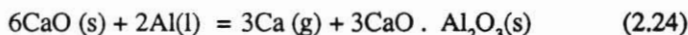
Although some sulphites, sulphates, carbonates and oxalates can be decomposed by vacuum into oxides, further decomposition of oxides seldom offers possibilities of metal extraction. Vacuum may be useful in dissociation and metallothermic reduction of some sulphides, halides, hydrides and nitrides. However, such processes have not been used industrially. Vacuum has, on the other hand, found industrial application in distillation. In titanium and zirconium metallurgy, the crude metal sponge is obtained by Kroll's process which uses, as mentioned previously, magnesium to reduce the chloride. The sponge is separated from residual magnesium and magnesium chloride by removing the latter by vacuum distillation.

The following are some reactions where vacuum is employed advantageously. Here (g) denotes the gas phase being removed by vacuum.

Ferrosilicon reduction of calcined dolomite (**Pidgeon's process**)—



Aluminothermic reduction of various oxides and hydroxides



Reactions (2.23)—(2.26) are generally made to take place above 1050°C under a pressure of around 1 torr (i.e. 1 mm Hg)

Gases dissolved in molten steel are sometimes injurious to the properties of the latter. Their removal can be facilitated by application of vacuum. For example,

the reaction between dissolved carbon [C] and dissolved oxygen [O], may be written as

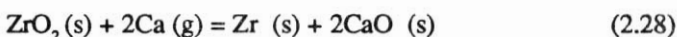


This reaction eliminates oxygen from molten steel being more favourable when pressure of CO is lower.

Reaction (2.23), i.e. the Pidgeon's process, is perhaps the best known example of vacuum metallurgy. $(CaO.MgO)$ is obtained by calcination of dolomite, $CaCO_3.MgCO_3$, and is reduced by silicon in the presence of iron. The boiling point of magnesium is $1107^\circ C$. However, it cannot evolve as a gas under atmospheric pressure because even at $1200^\circ C$ the equilibrium pressure of magnesium for the reaction is only a small fraction of the atmospheric pressure. If the pressure in the system is less than the equilibrium pressure, then magnesium continuously evolves in an attempt to establish an equilibrium. The metal is continuously condensed in a separate cool chamber so that equilibrium is never established and the reaction continues.

2.4.2 High Pressure Processes

High temperature reactions are favoured by high pressures provided they involve net decrease of volume in the system. That is, more number of moles in the gas phase should be consumed than generated. Although there are many reactions which fall in this category, high pressure techniques have not been employed widely for commercial extraction processes. In a small scale it is used for preparation of rare metals. Consider reduction of Zr from ZrO_2 by Ca.



Since the equilibrium partial pressure of calcium is quite high at required temperatures of reduction, a high pressure operation becomes necessary. This may be achieved by employing a thickwalled stainless steel high pressure vessel ('bomb') as the reduction chamber.

2.5 EXTRACTION OF METALS FROM SULPHIDE ORES

Several common nonferrous metals such as copper, lead, zinc and nickel are found in nature as sulphide minerals. The minerals are beneficiated through mineral dressing methods such as flotation to obtain concentrates rich in one of the metal sulphides. Such sulphide concentrates are subjected to a pretreatment process of roasting (oxidizing roasting) in the range of $550^\circ C$ to $800^\circ C$.

During roasting, sulphur is oxidized to SO_2 and sulphides of metal are partly or completely oxidized to oxides. The extent of sulphur removal desired depends on the metal. In the case of lead, the sulphide is completely oxidized to PbO (Eq. 2.2). For copper and nickel, only the iron sulphide impurity is oxidised partly and the other sulphides are retained as such. In roasting of ZnS , formation of zinc sulphate is sometimes preferred. The hot exhaust gases from the roaster, containing SO_2 and SO_3 , are utilized in the manufacture of sulphuric acid.

2.5.1 Metallurgy of Lead

The principal mineral of lead is Galena (PbS) which is found in nature in association with other sulphide minerals such as Sphalerite (ZnS), Pyrites (FeS₂), copper sulphides, some precious metals such as gold and silver and considerable amount of gangue. The lead ores may contain 3—10% lead.

The ores may be upgraded to 60—80% Pb (i.e. PbS with some impurities) by differential flotation. The sulphide concentrate is then fully roasted to oxide and reduced in the blast furnace by coke. A lead blast furnace is much smaller in size when compared to an iron blast furnace. It operates at a much lower temperature as well. The product, called lead bullion, is a solution of number of impurities in lead. The slag contains CaO, SiO₂ and FeO and melts below 1200°C. Some residual sulphides in the blast furnace charge collect as a separate phase called matte because carbon cannot reduce the sulphides. Therefore, matte is a solution of sulphides just as slag is a solution of oxides.

2.5.2 Metallurgy of Zinc

The main ore mineral of zinc is Sphalerite (ZnS) which occurs in association with other sulphide minerals, specially those of copper, lead and cadmium. The ores containing small amounts of precious metals and much gangue may average 2—10% zinc. Such ores are upgraded to a concentrate with high zinc content by flotation.

There are two principal methods of zinc extraction. In the pyrometallurgical method, the sulphide is converted to oxide by roasting and then the oxide is reduced by carbon at about 1200°C.

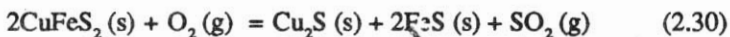


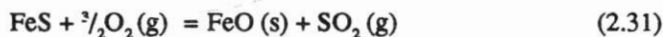
Zinc evolves as a gas under vacuum and is rapidly cooled in a condenser in order to avoid the reverse reaction. In the alternative approach, very pure (99.99%) zinc is extracted electrolytically by dissolving ZnO in sulphuric acid and electrolyzing the solution. This would be discussed in Chapter 10 on electrometallurgy.

2.5.3 Matte Smelting and Extraction of Copper

Extraction of copper and nickel are examples of matte smelting. Let us consider the former. In principle, it is possible to roast the sulphide ore of copper to oxide and then reduce it by carbon in the blast furnace. However, since the concentrate also contains iron sulphide, iron oxides will form. In fact oxidation of copper sulphide does not occur until iron sulphide is fully oxidized yielding Fe₂O₃. This Fe₂O₃ is difficult to remove by slagging. Moreover, the matte smelting process is carried out easily without the use of any reductant. Therefore, blast furnace smelting is not used for extraction of copper.

The principal ore mineral of copper is Chalcopyrite (CuFeS₂). The usual copper content in Chalcopyrite ores is less than 2%. The ores are upgraded by flotation and then roasted under controlled conditions. During roasting, iron sulphide is partly converted into FeO for subsequent removal by slagging.





The last reaction is not allowed to go to completion to ensure the absence of higher oxides. Higher oxides of iron are not amenable to easy slag formation.

The roasted solids are charged into a reverberatory furnace or flash smelting unit along with quartz (SiO_2) which is a flux. A reverberatory furnace for copper matte smelting is shown in Fig. 2.2.

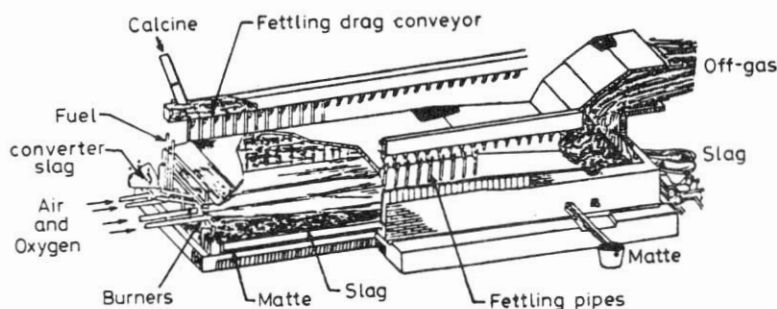
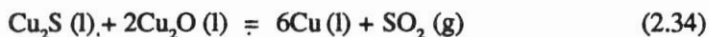
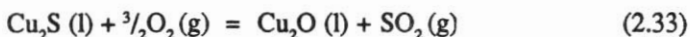
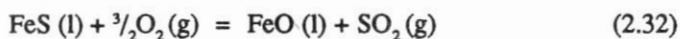


Fig. 2.2 Cutaway view of reverberatory smelting furnace

The charge is heated in the furnace to 1200—1300°C. Iron oxide (FeO) is removed as a slag containing mainly FeO , SiO_2 . The remaining sulphides melt and collect as matte. The matte is heavier than the slag and, therefore, collects at the bottom with good matte/slag separation. It should be noted that very little chemical reaction takes place during matte smelting.

The liquid matte is tapped out from the reverberatory furnace and charged into a converter shown in Fig. 2.3. The air blast introduced into the converter brings about rapid oxidation of the matte and consequent removal of sulphur.



FeO is separated in a slag phase by the addition of SiO_2 . When sufficient amounts of Cu_2S have been converted into Cu_2O then the oxide itself reacts with Cu_2S vide Eq. 2.34 to yield metallic copper. During all these reactions, no external heat supply is required since the reactions are highly exothermic. Moreover, no reducing agent is required for removal of oxygen from the oxide. The overall reaction simply corresponds to oxidation of the sulphur and iron. The separation of iron and copper and extraction of copper, are achieved in the converting step without external heat supply or reducing agent. This feature makes the matte route of extraction of copper economical and universally accepted.

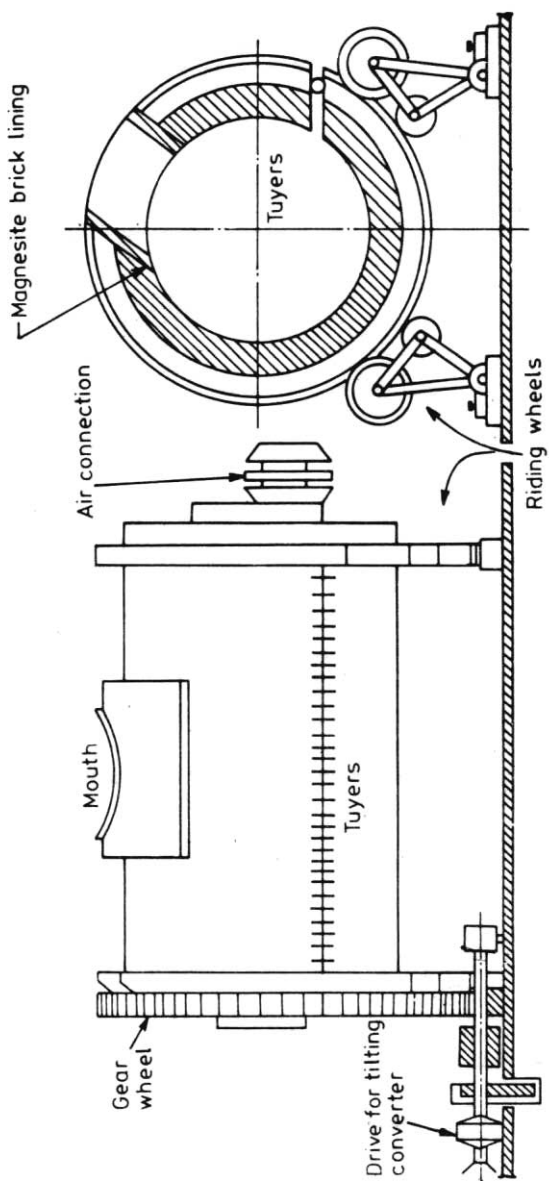
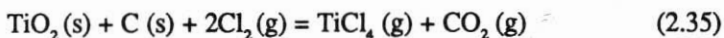


Fig. 2.3 Pierce-Smith copper converter

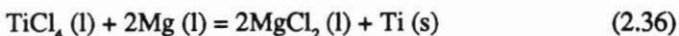
2.6 EXTRACTION OF SOME REACTIVE METALS

Many metals are highly reactive towards oxygen and, if reduced from the oxide, they are likely to still contain residual oxygen which adversely affects the mechanical properties. In such cases it is advisable to produce the metal from a halide. Thus titanium, zirconium, lithium, beryllium, tantalum, niobium, rare earth metals etc., although they are present in nature as oxide ores, are often produced via the halide route.

Consider the extraction of titanium which is found in nature either as Rutile (TiO_2) or Ilmenite ($\text{FeO}\cdot\text{TiO}_2$) associated with gangue materials. In the preliminary steps, almost pure TiO_2 is produced by mineral beneficiation processes. The oxide is then chlorinated according to the following reaction which takes place around 900°C .



Selective distillation of crude TiCl_4 yields pure TiCl_4 which is then reduced at 900°C by magnesium, the process being known as Kroll's process.



The metal produced is crude and it requires refining.

The use of such a chloride route makes it possible to avoid contamination by oxygen, carbon and nitrogen all of which adversely affect the mechanical properties of the metal.

A large number of rare and reactive metals are produced by metallothermic reduction of the halides. Na, K, Li, Ca, Mg etc. which form stable halides, are the usual reducing agents. Halides usually have relatively low melting points. If the metal produced itself is liquid then a clean liquid-liquid separation of metal and slag is more easily obtained.

2.7 REFINING PROCESSES

There are three basic approaches for purification of metals. These are as follows:

1. Creation of proper thermodynamic and kinetic conditions for transfer of impurities away from the metallic phase during the extraction process itself.
2. Production of pure metal compounds for subsequent reduction to pure metals.
3. Production of impure bulk metal during extraction and subsequent purification by refining methods.

Creation of a proper slag and achieving a good slag-metal separation is an example of (1). The second procedure (2) is followed for a large number of reactive and rarer metals which are generally produced from specially prepared pure halides. These halides are produced from the natural ores using varieties of processes which are often rather sophisticated and complicated. Aluminium, molybdenum and tungsten are also produced from specially prepared purified starting materials. The

last approach (3) is the traditional mode of purification of several inexpensive metals which are produced in large quantities e.g. iron, lead, copper and tin. Sometimes more than one approach may be used in combination.

It should be noted that in all methods of purification, more than one phase is involved. The processes essentially depend on transfer of impurity element from one phase to another. Here we shall discuss only a few methods of purification which have been employed widely. These methods can be classified into three basic categories namely, physical methods involving unit operations, chemical and electrochemical methods involving unit processes.

2.7.1 Physical Methods

In the physical methods, the aim is to separate parent metal from the impurities by unit operations which involve no chemical reaction. Usually these operations involve phase changes. A few physical methods are briefly discussed.

1. *Selective distillation of impurities* : Figure 2.4 shows a schematic liquid-vapour equilibrium diagram.

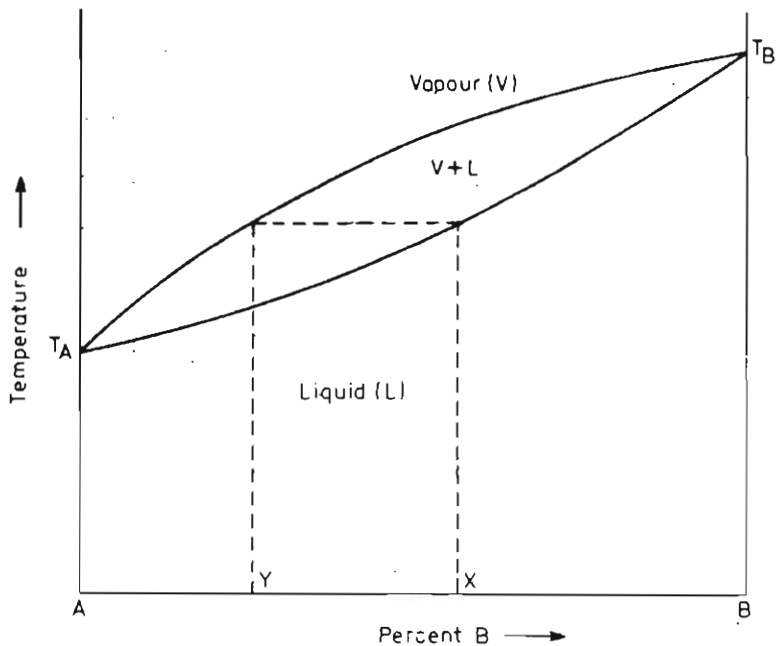


Fig. 2.4 Liquid-vapour equilibrium diagram

Species A has a boiling point (T_A) lower than that of species B (T_B). Therefore, on heating, A vaporizes more easily. When the liquid of composition X is heated, the first vapour has a composition Y which has a higher content of A. The

composition of the vapour and the liquid depends on the temperature at which they are at equilibrium. However, at any temperature, the vapour has higher fraction of species *A* compared to that in the liquid. Therefore *A* can be preferentially removed from *B* by distillation. Evacuation of the reaction chamber helps because it allows working at lower temperatures.

Figure 2.5 presents the vapour pressure versus temperature curves for some metals. It is obvious that a volatile metal like zinc may be separated from liquid lead by vacuum distillation. Similarly, many minor impurities such as As, Sb etc. are eliminated from liquid iron by vacuum distillation. Vacuum melting of many reactive metals such as tantalum, molybdenum also removes volatile impurities. Selective removal of volatile impurities under vacuum is capable of yielding products of high purity.

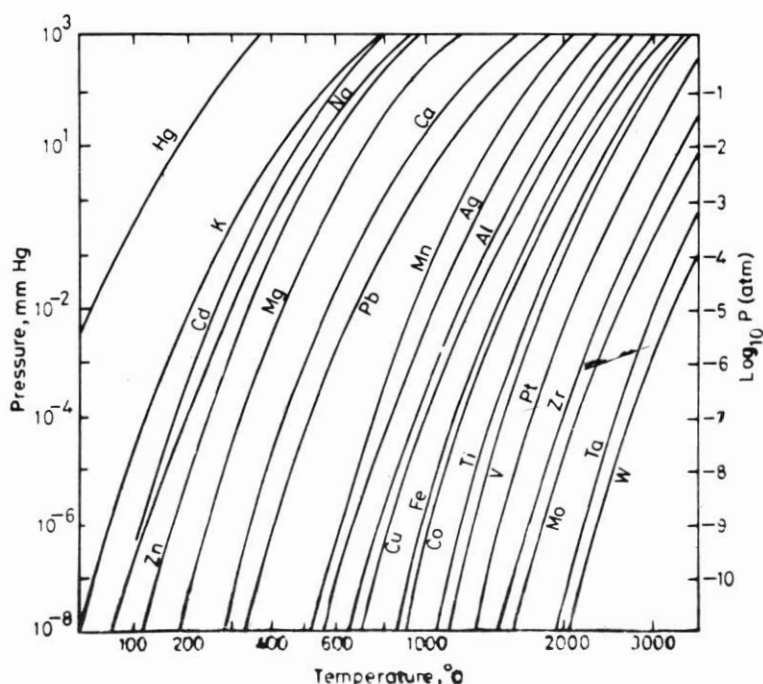


Fig. 2.5 Vapour pressures of some metals at various temperatures

[Source : J.E. Filiott and M > Gleiser, *Thermochemistry for steel making*, Vol. 1 Addison-Wesley (Reading, Mass., U.S.A.) (1960) Sec. 4]

It is customary to apply selective distillation when the impurities are more volatile. It is also possible to purify high vapour pressure metals from nonvolatile residues (impurities) but this will, obviously, need too much of heating and, therefore, power consumption.

2. Liquefaction : In liquefaction, the impurity separates out from the parent metal due to immiscibility, the efficiency of separation being dependent upon the nature of the metal-impurity phase diagram. An example is provided by the purification of lead through zinc removal.

On cooling impure, lead and solid zinc separate out leaving a liquid poorer in zinc and, therefore, richer in lead. This method, which basically depends on differences in melting points and in densities of immiscible phases is, however, uneconomical and, therefore, rarely employed commercially.

3. *Selective dissolution* : In the preceding example the impurity was removed by selective crystallization. One can sometimes remove an impurity element by selective dissolution in a solvent metal. For example, during refining of lead bullion obtained from the lead blast furnace, molten zinc is added to recover minor amounts of silver contained in lead. Zinc dissolves silver preferentially and forms a separate phase which is collected and processed for silver recovery. This process is called **Parke's process**.

4. *Zone refining* : Zone refining is generally employed to produce ultra-pure metals in laboratory scale. The principle of zone refining may be understood with reference to Fig. 2.6 where A represents the primary metal with a small concentration of the impurity metal.

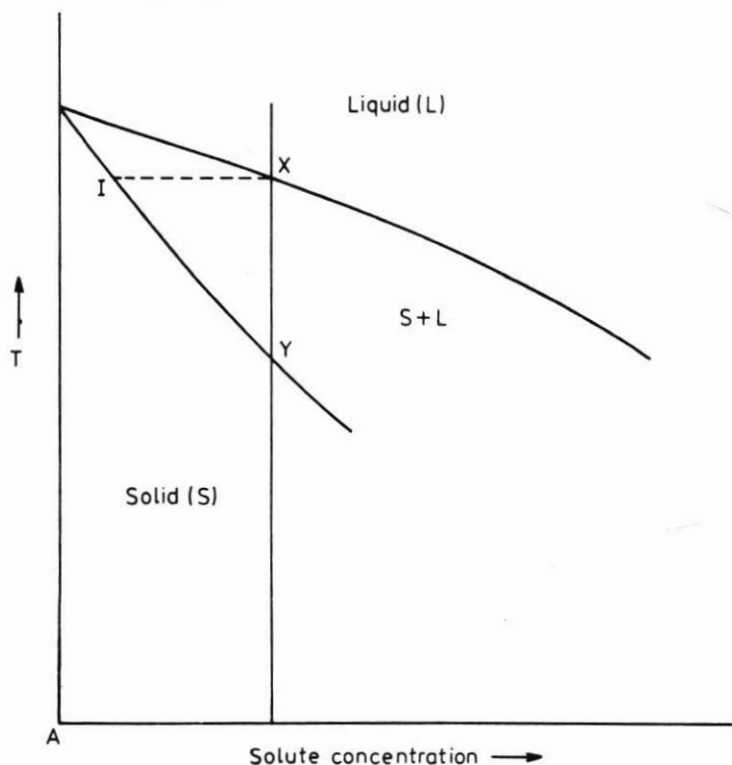


Fig. 2.6 Portion of binary phase diagram showing the metal rich end

The vertical line XY indicates the initial composition. If a liquid of this composition is cooled slowly, then solidification begins at a temperature corresponding to X. The initial solid has a composition corresponding to point L. So the solid is purer. As the temperature is lowered further, more and more solid

separates, the final solid formed having the composition corresponding to Y. It should be noted that as the temperature decreases from X to Y, the solids that crystallize are less and less pure. However, at all times, the impurity concentration is lower in the solid than in the liquid at equilibrium, being preferentially concentrated in the liquid. This principle is exploited in zone-refining using a technique shown schematically in Fig. 2.7. In the actual technique, a small molten zone moves through a long charge of impure material. The differences in the impurity concentration between liquid and crystallizing solid lead to segregation of impurities into the moving liquid zone and corresponding purification of the solidifying material.

Zone refining by passing a single molten zone along a length of solid material is illustrated in Fig. 2.7. As the molten zone moves forward, the solid crystallizing at the trailing end is left purer and the molten zone is enriched in the impurity solute. As the zone traverses along the length, it is continually enriched. As a result, the impurity profile of the bar after a single pass will be as shown by the bold line in the lower figure in Fig. 2.7. The profile changes as shown if the whole process is repeated: Several passes of molten zone would thus yield a bar which is very pure at one end but impure at the other end.

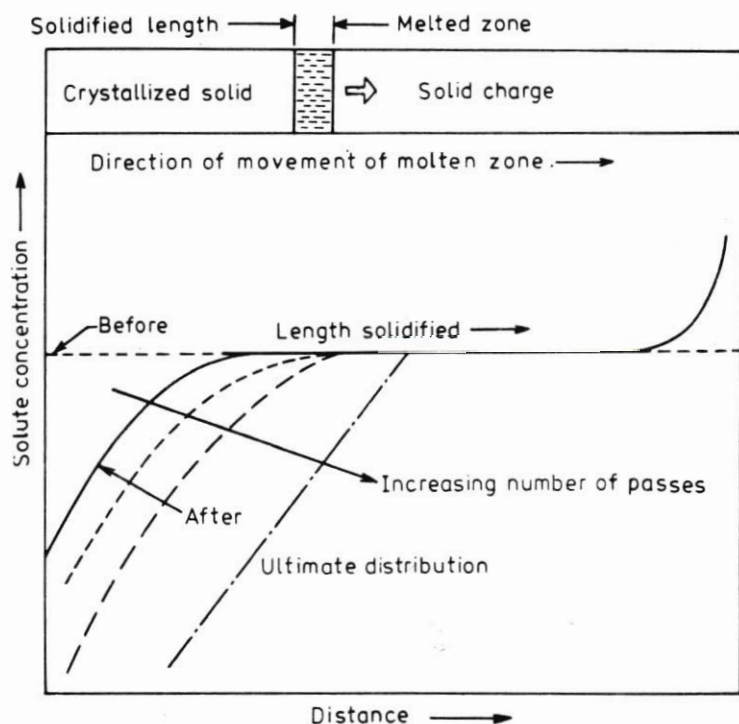


Fig. 2.7 Zone refining and solute concentration profile

Zone refining is primarily employed in the semiconductor industry for refining germanium and silicon. In principle, however, it is applicable to all metals provided the solid charge is small and the nature of the impurity element is such that it lowers the melting point of the parent metal. Zone refining has been used to purify not only metals but various inorganic and organic materials also.

2.7.2 Chemical Methods

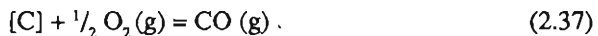
In the chemical methods the impurity elements are converted into compounds by adding refining agents which react preferentially with these elements. The chief reagents are oxygen, sulphur and chlorine. The compounds are then separated from the metal in the slag, salt, gas phase or as insoluble compounds.

The following industrial refining practices are worth mentioning.

1. Oxidation is practised to remove :
 - (i) C, Si, P and Mn from iron (steelmaking)
 - (ii) Pb, As, Sb, Sn, S, Mg, Al and Fe from copper (fire refining of copper)
 - (iii) Sb, As, Sn, and Zn from lead (cupellation of lead)
2. Sulphidation is practised to remove :
 - (i) Cu, Ni and Co from lead
 - (ii) Cu from tin
3. Chlorination is practised to remove :
 - (i) Zn from lead
 - (ii) Zn, Cu and Pb from bismuth

The cheapest reagent, of course, is atmospheric oxygen. Sometimes the oxygen is supplied as a reducible oxide. In pneumatic steelmaking processes, iron is oxidized by blowing air or oxygen into the melt directly.

Steelmaking : Steel is purified pig iron with controlled amounts of impurities. The purpose of steelmaking is not to produce pure iron, but iron purer than pig iron produced by the blast furnace. The selective oxidation of impurities in pig iron during steelmaking reactions may be written as follows.



Here [C], [Si], [Mn] and [P] denote the respective impurities dissolved in iron. While CO escapes as gas, the other oxides formed enter the slag phase, denoted by (). Although there are several methods of steelmaking differing in the manner in which oxygen is introduced, the basic refining reactions are the same.

Refining of metals via intermediate gas phases : Refining of metal via an intermediate gas phase may be looked upon as a process of reactive distillation for metals which have high melting points and, of course, still higher boiling points. For example, it is practically impossible to distil refractory metals like titanium or zirconium. However, they may be made to react with gaseous reagents to produce

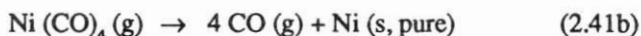
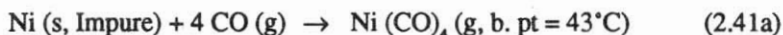
volatile compounds at relatively low temperatures. These compounds are subsequently decomposed by heating or cooling to yield pure metal and the original reagent can be recycled. The two step process may thus be written as :

Step 1 : Impure metal + Vapour 1 \rightarrow Vapour 2

Step 2 : Vapour 2 \rightarrow Pure metal + Vapour 1

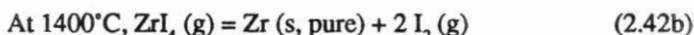
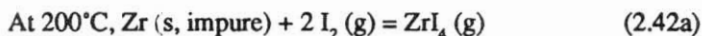
The overall reaction is an 'indirect' distillation of metal usually at relatively low temperatures. The process of deposition of metals from vapours is generally known as **chemical vapour deposition**. The process has many variations depending on the nature of vapours. Some well known reactions are as follows.

(a) Purification of nickel by carbonyl process

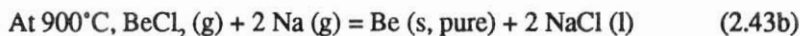
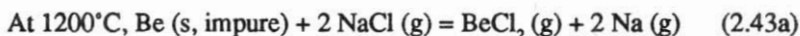


While the carbonyl formation is carried out at around 45°C , it is decomposed at about 240°C .

(b) Iodide process (also known as Van Arkel or de Boer process) for purification of zirconium



(c) Purification of beryllium



2.73 Electrochemical Methods

In the electrochemical method of refining, the metal to be refined is made the anode and the pure metal is deposited on a cathode. The starting cathode sheet may be a pure strip of the metal itself or some other metal. The electrolyte contains an ionizable salt of the metal. A large number of metals are electrorefined in aqueous electrolytic solutions. These include Cu, Ag, Au, Ni, Co, Pb, Sb, Bi, In, Hg, Sn etc. Reactive metals such as Al, Ti, Zr or Mo must be electrorefined using a suitable molten salt as electrolyte. Electrolytic refining is very versatile, flexible and is capable of yielding metals of high purity. It is possible to separate both more reactive as well as less reactive impurities from the metal. It is commercially the most important method for obtaining highly pure metals.

General reading

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