

Chapter 7

Copper

7.1 Introduction

The end of the eighteenth century saw Swansea as the largest copper (Cu) producer in the world. The technique of modern copper metallurgy owes a great deal to the early work done in Wales. The reverberatory, which still plays a very important part, was largely developed there; and later, Welsh smelters brought their experience to bear in all parts of the world. The nineteenth century saw the decline of Welsh copper smelting. America gradually assumed ascendancy in the art of copper smelting and continued in the lead.

Copper is the most important non-ferrous metal. Not only does it form extremely useful alloys with metals such as Zn and Sn, but it also has unique properties (such as being a good conductor of electricity) in the unalloyed state.

7.2 Sources

Copper exists in nature mostly in the form of copper sulphide with or without other sulphides. The sulphide minerals are the predominant feature in copper metallurgy, yielding over 90% of the copper supply of the world. Deposits are in general low grade, the majority being worked today containing 2% copper or less. The common minerals of copper (figures within the parentheses give the chemical composition and percentage of theoretical copper contained): (a) chalcopyrite (CuFeS_2 , 34.5% Cu); (b) chalcocite (Cu_2S , 79.8% Cu); (c) bornite (Cu_5FeS_4 , 55.5% Cu); (d) covellite (CuS , 66.5% Cu); (e) enargite (CuAsS_4 , 48.4% Cu); (f) malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, 57.3% Cu); (g) azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, 55.1% Cu); (h) cuprite (Cu_2O , 88.8% Cu); and (i) chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$, 36.2% Cu). Chalcopyrite is the most commercial ore. Minerals theoretically contain large amount of copper, but actually ores contain only small amounts of copper due to presence of other

sulphides and gangue minerals. Actually, a sulphide ore that contains 0.5–2% Cu is considered as good for extraction after concentration.

7.3 Extraction of Copper

The extraction of copper by the convention route (concentration, roasting, smelting, converting and refining) is shown in Fig. 7.1. The main steps involved are as follows:

1. Enrich the ore by concentration.
2. Roast for partial elimination of sulphur contained in the copper concentrate.
3. Smelt in a reverberatory furnace to concentrate the copper into matte and to eliminate the gangue materials as slag.
4. Convert matte to blister copper, which is cast as anode.
5. Electrolytically refine impure copper.

7.3.1 Concentration

A sulphide ore normally contains 0.5–2% Cu. The ore is crushed and ground up to 40 μm for froth flotation. The p_H of froth flotation is controlled by the addition of CaO; xanthate reagent is used as a collector. A differential flotation is used to selectively recover copper sulphide from the mixture of copper sulphide, lead sulphide and zinc sulphide. The concentration of copper sulphide contains 15–35% Cu, 15–35% Fe, 25–35% S and 3–35% gangue.

7.3.2 Roasting

The object of roasting is to burn off part of the sulphur and the purpose of roasting is to partially oxidize the iron sulphide present in the copper sulphide concentrate in order to remove it in the form of a slag at the smelting stage. The affinity between copper and sulphur is greater than between sulphur and any other metals present. In smelting, the copper will take enough of the sulphur to form Cu_2S , the residual sulphur combining with the iron to form FeS. The amount of FeS, which will accompany the Cu_2S in the matte, is entirely dependent on how much sulphur is left to combine with the iron after all the copper has been satisfied; the amount being controllable by the preliminary roasting, which in turn controls the grade of matte.

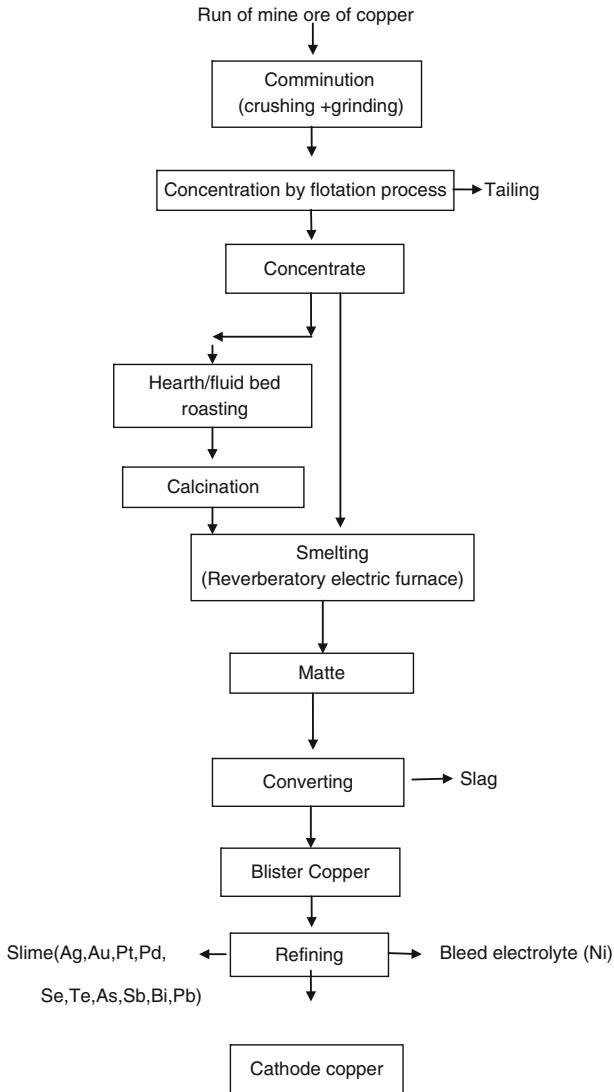


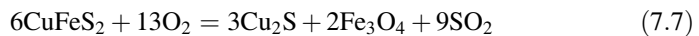
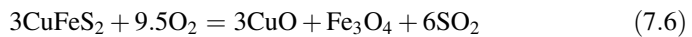
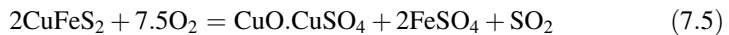
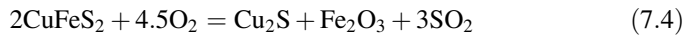
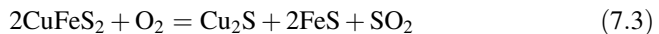
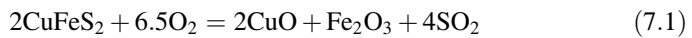
Fig. 7.1 Flow diagram for copper extraction

The extent of roasting determines the copper grade of the matte produced in the smelting stage. If a high grade matte is required, the roasting is carried to a high degree, and for a low grade matte the roast would not be pushed to the same extent. The more usual grade of matte ranges from 35–45% copper. The highest grade of matte (i.e. the one containing the greatest concentration of copper) is not necessarily the most economic to aim at as it requires a high degree of roasting and gives rise to high costs and dust. Also, copper losses in smelting tend to follow the grade of

matte; in other words the higher the grade of matte, the higher the copper losses in the slag.

For concentrates with a high iron sulphide content and a low copper sulphide content (< 25% Cu) roasting is necessary; but for high grade copper concentrates (> 30% Cu), roasting is not necessary. The bulk of sulphur elimination is due to the oxidation of ferrous sulphide and not to the sulphide of copper, any excess sulphur after the formation of the Cu_2S is expelled. Complete elimination of sulphur is neither sought nor desired, the oxidation of the iron supply provides sufficient heat in the roasting operation. Sulphates will form at low temperature with excess of air and sulphur dioxide, but at higher temperature will react with sulphides, resulting in the formation of oxides. High temperature and low sulphur dioxide concentration favour the formation of oxides (like Fe_2O_3 , Fe_3O_4 etc.).

Roasting is carried out in multiple hearth roasters, the temperature of each hearth is gradually increased from room temperature to 550°C . During roasting, several reactions take place simultaneously as follows:



The roasted calcine (which consists of sulphides of copper and iron, oxides of iron, and mixed sulphides of copper and iron) is transferred to the smelting furnace in the hot condition.

7.3.3 Smelting

The sulphur elimination is bound up with smelting and in fact determines the grade of matte. To produce a high grade matte in the reverberatory furnace (as shown in Fig. 7.2) necessitates a high volume of slag which in turn is likely to lead to higher copper losses and possibly losses of precious metals which normally accompany the product of smelting, matte. The matte is not a true chemical compound, but rather a varying mixture of the two sulphides Cu_2S and FeS .

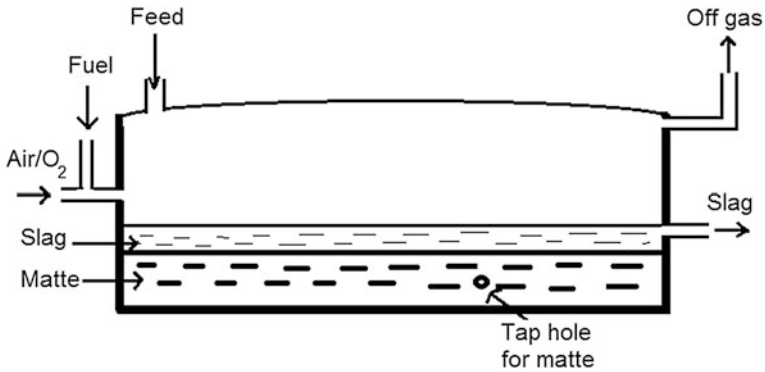


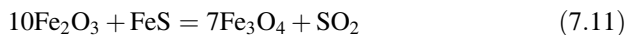
Fig. 7.2 Reverberatory furnace for copper smelting

Smelting separates the metal sulphides in roasted calcine or concentrate from the gangue. Such separation can be achieved by smelting the charge with suitable flux at a temperature of 1250°C. Two layers of liquid are formed, an upper slag layer (specific gravity in the range of 2.8–3.8) consists of gangue and flux; lower layer contains matte (specific gravity in the range of from 5.0–5.5) which consists of sulphides of copper and iron (35–45% Cu, 20–22% S and 25–35% Fe). Due to difference in specific gravities, a clear-cut separation of layers is observed.

During smelting, exchange reactions take place between the oxide/sulphate of copper and the iron sulphide, due to oxygen having a higher affinity for iron than copper:



The unoxidized iron sulphide reduces the higher iron oxides to lower oxides:



The resultant ferrous oxide (FeO) reaction with gangue (SiO_2) present in the concentrate/calcine forms iron silicate slag during smelting:



In the presence of lime (as flux), iron-calcium silicate slag is produced:



The melting point of the slag formed is about 1150°C, and to obtain a fluid slag with a low copper content, smelting is carried out at a temperature of 1250°C. The net result of the smelting operation is matte (containing Cu₂S and FeS), slag consisting largely of iron silicate, and sulphur dioxide gas.

Generally, the smelting operation is carried out in a reverberatory furnace fired with coal or oil. Thermal efficiency of reverberatory furnace is very low (30%) due to outgoing gases carrying a lot of heat. To improve heat utilization, outgoing gases are passed through air heaters, the efficiency then rising to 55–60%.

Submerged electric arc furnace is also used for smelting. Electric furnace is more advantageous, where the cost of power is low, than reverberatory furnace; because the generation of a large volume of combustion gases is avoided. Advantages of electrical smelting are low energy consumption, high thermal efficiency, steady operation, long life of refractory (basic) roof and lining, and a small volume of gases from which sulphur dioxide may be economically recovered.

7.3.4 Converting

The main purpose of converting is to remove iron, sulphur and other impurities from matte. The molten matte, produced by smelting operation, is charged into a side blown converter (as shown in Fig. 7.3). In the converter, which is lined with the chrome-magnesite refractory, the atmosphere is highly oxidizing compared with the neutral or mildly oxidizing atmosphere during smelting operation. Air or oxygen-enriched air (up to 32% by volume) is injected into the molten matte through side tuyeres. The isolation of the copper from the matte is achieved by a progressive oxidation in a converter. When air is blown through molten matte, iron sulphide is oxidized before the copper sulphide.

Slagging stage: In the slagging stage, iron sulphide present in the matte is oxidized and the oxide is slagged out by the addition of siliceous flux. Part of the iron oxide (FeO) is also oxidized to higher oxide:

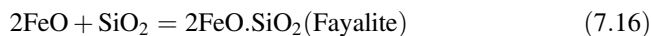
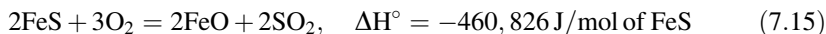
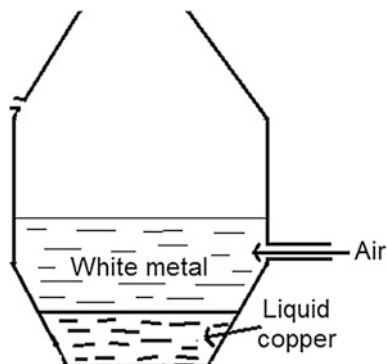


Fig. 7.3 Side blown converter for copper production



In the converter the heat, necessary to keep the reaction going on has to be provided by the oxidation of the iron sulphide [reaction (7.15)]. A high grade matte (containing low iron) therefore has difficulty in maintaining the heat essential for the conversion. Primary oxidation starts and slag begins to be produced, oxidation furnishing the heat necessary for the slagging action.

The slag consists of 40–50% Fe, 20–30% SiO_2 , 1–5% ($\text{CaO} + \text{MgO}$) and 2–9% Cu. The copper is recovered from the slag by transferring the slag to the smelting furnace. The iron oxide (FeO) is present in the slag mostly as fayalite saturated with magnetite (Fe_3O_4). The magnetite forms a coating on the chrome-magnesite refractory, which prevents slag attack on the refractory. Slagging is carried out in stages: (a) first freshly obtained matte is added to the converter and then air blowing is started; (b) slag formed is skimmed off by tilting the converter. The molten slag and matte phases are immiscible.

During converting, the oxidation of the iron sulphide produces sufficient heat [reaction (7.15)] to overcome the heat lost to the surroundings and to maintain the matte and slag in molten state. For a large converter where the blowing rate as well as the iron sulphide oxidation rate are high, heat generation is hence very high as well; this extra heat is utilized for melting of copper scrap which is generated in the plant.

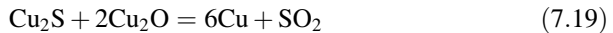
After an hour or so the reaction is completed, air turned off, the converter tilted and the slag poured off into a ladle. More matte and flux are added, air readmitted and the action recommences. The cycle of operations, charging and skimming of slag proceeds until sufficient copper sulphide (white metal) has been accumulated in the converter to complete the process by converting the white metal to blister copper [reaction (7.20)]. The time taken to run down matte and produce blister copper depends on a number of factors: (a) grade of matte and flux; (b) condition of lining, etc.

Blister formation stage: After slagging is completed, the converter essentially contains Cu_2S which is called “white metal” due to its appearance. Cu_2S is oxidized to form copper by the following two reactions:

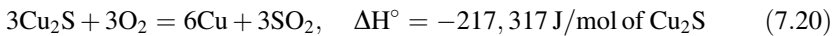
- (i) Copper oxide is formed:



- (ii) Copper oxide reacts with further remaining copper sulphide to produce blister copper:



The overall reaction (combination of Eqs. 7.18 and 7.19):



Reaction (7.20) shows the cuprous sulphide is reduced to blister copper without using any reducing agent; i.e. converting the white metal to blister copper. The final stages have to be given good attention owing to the chance of oxidation of copper. Boiling of the bath takes place due to evolution of sulphur dioxide gas from the molten bath. The heat necessary to maintain the charge is supplied by the oxidation of the iron and copper sulphides (reactions 7.15 and 7.20), the iron sulphide contributing by far the greater part. The amount of iron sulphide present is thus an important factor in the control of the operation. The highlights of the operation are as follows:

1. Production of white metal (Cu_2S) by oxidation of the FeS in the matte and its elimination as slag by combination with silica; and
2. Production of blister copper by further oxidation.

Air is blowing to the converter at a pressure of $9.842 \times 10^{-3} \text{ kg/mm}^2$. The amount of air required for the conversion of matte to blister copper is found to be in excess of that calculated and in fact amounts to some 150–160%. This is due to the following reasons:

1. Leakage through the lining.
2. Formation of oxides other than the calculated FeO.
3. Air escaping uncombined with the gases through the mouth of the converter.

Two important factors for slag formation are (a) temperature and (b) flux. The formation of slag requires a minimum temperature in the region of 1250°C . Lower temperature results in the formation of Fe_3O_4 which carries copper into the slag; on the other hand, too high a temperature shortens the life of refractory (magnesite) lining. The function of flux (i.e. silica) is to combine with FeO, which is formed by

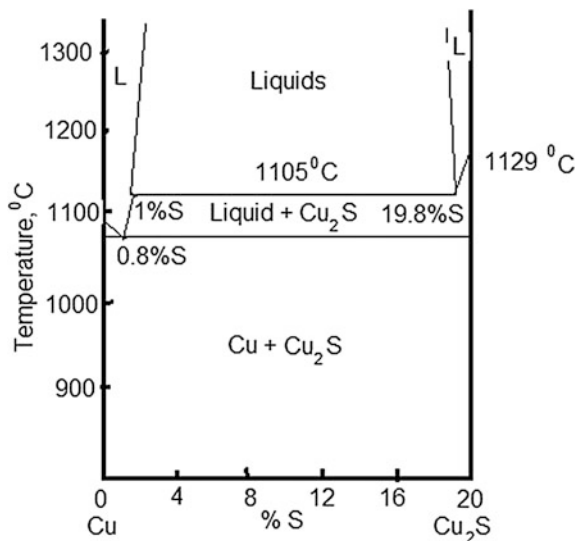
oxidation of iron in the matte, to form slag. The composition of the slag also depends on the amount and type of flux. The converter slag contains 5% Cu, which is returned to the reverberatory furnace where it mixes with the molten charge and is cleaned.

From the Cu–Cu₂S phase diagram (Fig. 7.4), we understand that when white metal (Cu₂S) is oxidized and the amount of sulphur in the bath decreases to below 19.8%, the bath splits into two layers, i.e. a top sulphide layer (less dense) and a bottom copper layer (more dense) containing 1.2% sulphur. As the oxidation continues the volume of the sulphide layer decreases and the volume of the copper layer increases. When the sulphur level reaches 1.2%, only the metallic copper phase remains in the converter. At this stage, care must be taken to avoid over-oxidation of metallic copper. The blistery (bubble-like swelling, i.e. small holes) appearance on the surface of the sample of copper gives the name blister copper to the product, which contains 0.02–0.05% S along with 0.2–0.5% O. During solidification, these dissolved S and O in metal react to form SO₂ gas ($\underline{S} + \underline{O} = \text{SO}_2$). Due to evolution of gas from the metal the surface become blistery.

7.3.5 Refining

The blister copper is unsuitable for direct commercial application owing to the amount of impurities (consisting of arsenic, oxygen, sulphur, bismuth, iron, gold, silver etc., and totalling usually from 0.5% to 1.5%). Many impurities, including gases, affect adversely the mechanical properties of copper, in particular, its

Fig. 7.4 Cu–Cu₂S phase diagram



plasticity. All impurities, except for the noble metals, have a detrimental effect upon electric conductivity of copper. Refining is therefore essential before the copper can be obtained in a suitable form for marketing. There are two purpose of refining: (a) to obtain the pure metal (for a higher degree of electrical conductivity), and (b) to recover the valuable precious metals.

7.3.5.1 Fire Refining

Refining involves the following stages: melting, oxidation of impurities and removal of slag, deoxidation (poling) and casting. Impurities are oxidized by air which is injected into molten copper through refractory-coated iron pipes. Oxidation takes place at the surface of air bubbles that float in the molten metal. Copper and all impurities, except the noble metals, are oxidized.

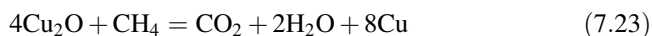


Cuprous oxide is soluble in molten copper and rapidly diffuses throughout the bath. Oxidation of impurities (particularly metals, M) may be described by the general equation:



As per the Ellingham diagram (Fig. III.1, p. 176), impurities (such as Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb) have a greater affinity for oxygen than copper; therefore they all are oxidized by cuprous oxide [as per reaction (7.22)]. Oxides of impurities are insoluble in molten copper; they float to the surface and form slag which is skimmed off. Sulphur, present in copper in the form of dissolved Cu_2S , is oxidized according to the reaction (7.19).

To remove sulphur from liquid blister copper as SO_2 gas by oxidation with air and to eliminate oxygen by introducing hydrocarbons, the surface of the blister copper is oxidized at frequent intervals. The furnace doors are kept open in order to allow a constant mild blast of air. As a result of this slow oxidation process (2–4 h), impurities such as S, Fe, Se and Zn are oxidized and the solid oxides rise to the top where they are skimmed off. Some copper is also oxidized during the process; the process is discontinued when the level of Cu_2O in the bulk of the metal reaches 6%. At this stage, almost all sulphur is eliminated from the metal. Slag should be thoroughly removed before copper is deoxidized; otherwise the impurities oxides will be reduced from the slag and again go to the molten copper. The bath is then skimmed clean of slag, covered with charcoal or coke, and poling is commenced. Once the oxidation is completed, Cu_2O is reduced by poling with green woods. On ignition, these woods generate hydrocarbons which reduce the Cu_2O . Vigorous stirring take place at the molten bath by bubbling of gases.

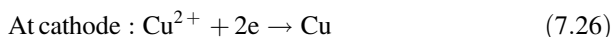
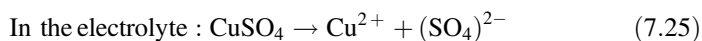
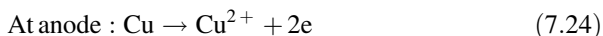


Pitch virtually refers to the oxygen content which is usually within the range of 0.02–0.1%. The *set* or appearance of the surface of a button sample taken from the furnace is a rough guide to the oxygen content. If too much oxygen is present, the set is concave; if too little, the set is convex. When oxygen is correctly positioned, the set is level. Other factors such as sulphur dioxide are, however, liable to affect set. Poling is continued until sample shows a level set indicating that oxygen content of 0.03–0.06% has been attained, this being the normal oxygen content of tough pitch copper. The purity of fire-refined copper is generally around 99.7%.

7.3.5.2 Electrolytic Refining

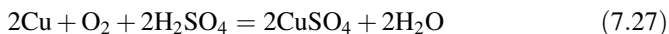
Fire refining method does not effectively remove such impurities as bismuth, tellurium, selenium and nickel; nor does it recover the precious metals. Electrolysis was introduced to make good these deficiencies. Fire-refined copper can be further refined by electrolysis. An electrolytic cell is 3–5 m long, 1.0–1.1 m wide and 1.0–1.3 m deep; design of cell is based on the utilization of minimum space with maximum cathode and anode areas. Fire-refined copper is cast in the form of an anode that weighs about 250–320 kg. Suspended parallel to the anodes are connected to the positive poles of direct current. The cathode is made of a pure copper or stainless steel sheet; the electrolyte consists of copper sulphate (35×10^{-3} kg of Cu per litre), sulphuric acid (0.2 kg per litre), and some addition agents such as glue and alcohol. Electrolysis is carried out using current density of about 200 A/m² at a temperature of 50–60°C. When a direct current is passed through a solution of copper sulphate, anode copper goes into solution according to reaction (7.24), the liberated copper is deposited on the cathode. The anode plate will show a decrease in weight, due to copper going into solution, and the cathode a corresponding increase, due to copper having been deposited thereon.

During electrolysis, copper is transferred from the crude anode to the pure cathode as follows:



Impurities in the blister copper such as Fe, Co, Ni, Se, and Te go into the solution and the precious metals are collected just below the anode, which is known as anode slime. Impurities (like gold, and silver) are more positive than copper. They are settling out as anode slime. Anode slime consist of 10–40% Cu, 2–20% Pb, 0.5–5% As, 0–4% Te, 0–25% Ni, 2–10% S, 0.5–2% Fe, 0–25% Se and 8.5–14 kg of Ag/tonne, 0.25–1.7 kg of Au/tonne. The exact composition depends on the composition of the anode and the various, previous, metallurgical operations.

Cathode deposit is contaminated mainly by entrapped electrolyte and floating slime. To minimize this, part of the electrolyte is periodically removed from the baths and purified. Regeneration (i.e. purification) of electrolyte is necessary to avoid build-up of impurities and to remove excess copper. Copper accumulates in the electrolyte through partial chemical reaction involving participation of air or oxygen.



If impurities content is low and excess copper is only to be extracted, the electrolyte is processed by electrolysis in standard tank, but furnished with insoluble lead anodes. Copper of the electrolyte plates out at the cathodes in the process, oxygen evolves at the lead anodes, while some free sulphuric acid forms in the solution. Once copper is partially extracted, the electrolyte may be returned to the circulation system.

Actually, not all of the current is used to deposit the copper, and some current is lost because of short circuits between electrodes, current leakage and discharge of impurities' ions.

Some difficulties are encountered during electrolysis:

- (a) The concentration of Cu^{2+} ions in the electrolyte decreases. As a result, water is electrolyzed and releases hydrogen which lowers the current efficiency.
- (b) The concentration of Cu^{2+} ions in the electrolyte increases, and CuSO_4 may tend to be crystallized in the electrolyte.
- (c) The copper sulphate content of the electrolyte increases beyond a certain limit, resulting in dissolution of Cu_2O (blister copper).

These difficulties can be overcome by the proper stirring, circulation of the electrolyte; and by using an inert anode made of lead. This procedure brings down the CuSO_4 content of the electrolyte. Pure copper (99.99%) is removed from the electrolyte after removal of impurities (such as As, Sb, Bi, and Ni). Arsenic, antimony, and bismuth are removed during the last stages of copper refining with the inert lead anode. Nickel is removed together with iron and cobalt as sulphate form.

7.4 Newer Processes

The flow diagram of the newer processes is shown in Fig. 7.5.

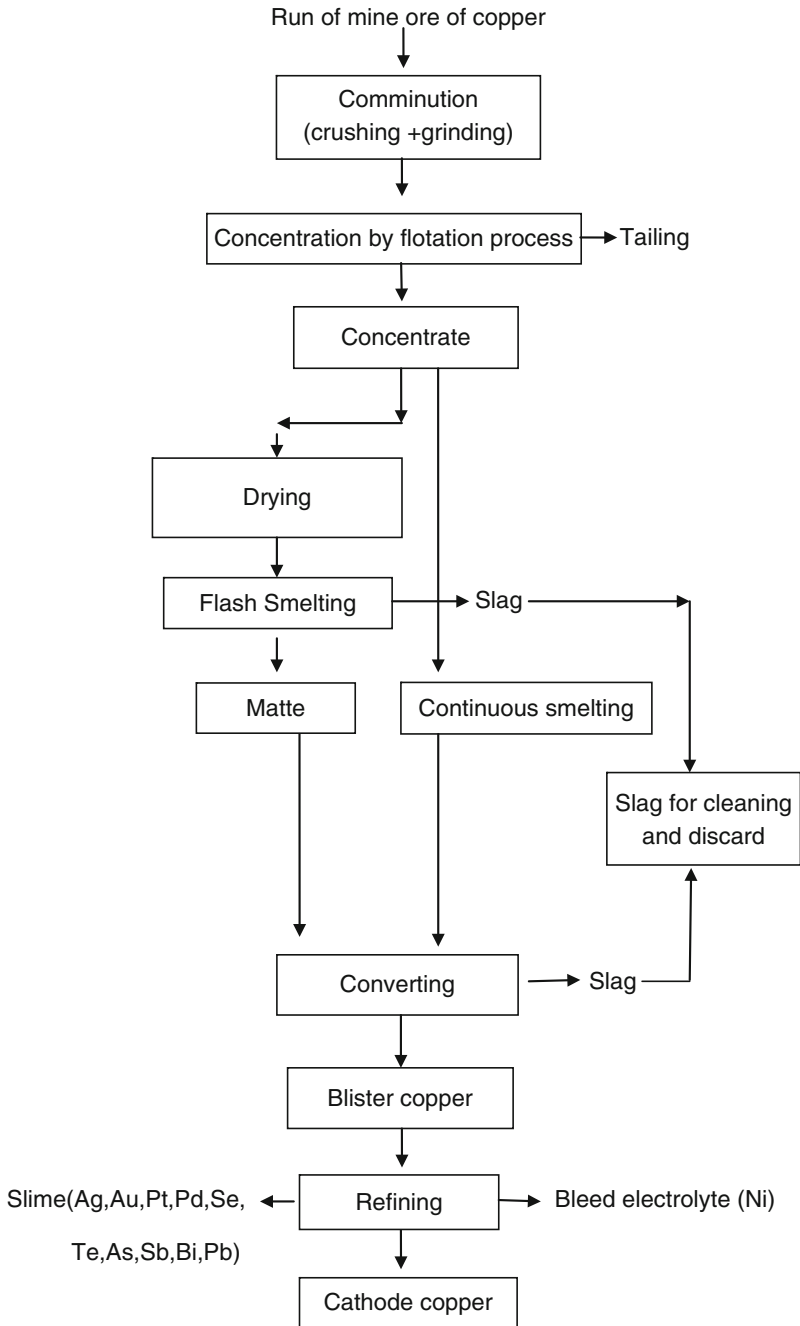


Fig. 7.5 Extraction of copper by other method

7.4.1 Flash Smelting Process

(a) The flash smelting process is the combination of two operations like roasting and smelting. Dried concentrate of copper and sand along with oxygen are injected into the flash smelter. The iron sulphides are combusted and generate the heat to smelt the concentrate to get matte, which is converted into the blister copper in converter. This process was developed by the International Nickel Company of Canada (INCO) and was operated commercially from 1953. Figure 7.6 shows the INCO flash smelting furnace. Most of the reactions are completed in the flame of the flash burner that leads to a high smelting rate ($2.54 \text{ tonne/day/m}^3$). INCO had developed a new design for the flash burner which could achieve faster smelting rate ($17.56 \text{ tonne/day/m}^3$). The new flash burner could complete smelting within two seconds and the composition of the smelter is almost equal to the value at equilibrium. No external fuel is used in this process; the matte contains about 45% Cu and slag contains only about 0.5–0.6% Cu. The off-gas of the INCO flash smelter contains about 80% SO_2 which can be used for the production of sulphuric acid.

(b) Another flash smelting process was developed around the same period by Outokumpu in Finland by using air, oxygen-enriched air or preheated air (Fig. 7.7). The matte produced in the Outokumpu flash smelting process contains 45–65% Cu depending on the quantity of the fuel (i.e. oil) and the degree of oxygen enrichment used. The smelting rates for preheated air and for enriched oxygen are $2.61 \text{ tonne/day/m}^3$ and $3.88 \text{ tonne/day/m}^3$ respectively. The slag contains high Cu content, i.e. 0.8...1.5% Cu.

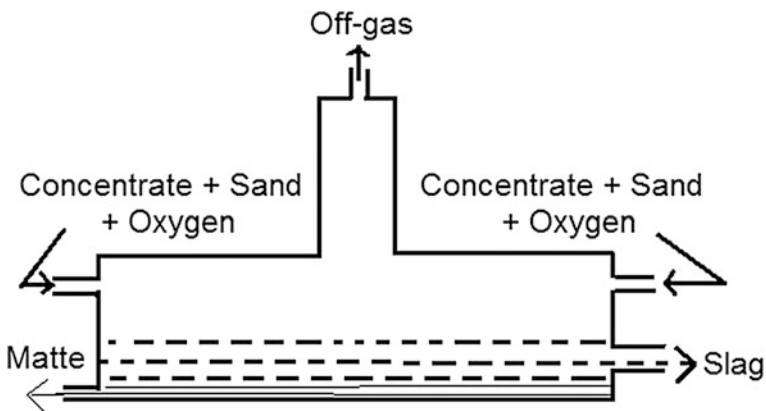
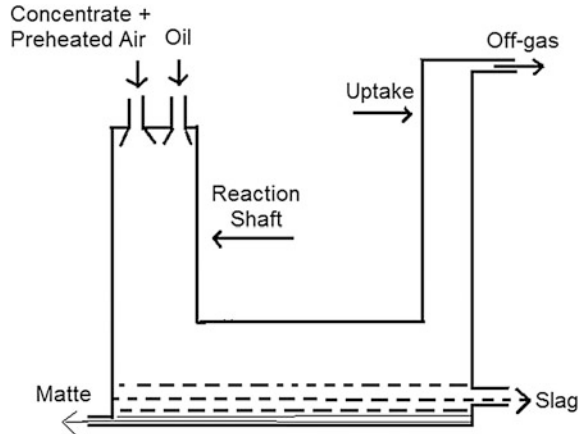


Fig. 7.6 INCO flash smelting furnace

Fig. 7.7 Outokumpu flash smelting furnace



7.4.2 Continuous Process

Continuous process is the combination of flash smelting and converting operations in a single vessel; the copper concentrate can be charged at one end and copper metal can be continuously tapping from the other end. Continuous smelting processes developments—namely, the WORCRA process (developed in Australia) and the Noranda process (developed in Canada)—were patented in 1967. Mitsubishi (in Japan) has developed a process in which smelting and converting are carried out in separate containers; however, there is a continuous flow of matte to the converter from smelter and a continuous flow of blister copper from converter.

7.4.2.1 WORCRA Process

The name WORCRA is derived by combining the first three letters (i.e. WOR) of the inventor's name (H.K. Worner) and CRA (Conzinc Riotinto of Australia Limited). The WORCRA process is based on the conservation of energy obtained during smelting and converting of sulphide concentrates by integrating several efficient continuous unit operations. In the WORCRA process, a single furnace combines the following continuous operations which occur in separate but inter-connected zones:

1. Smelting.
2. Converting.
3. Slag cleaning by conditioning and settling.

Figure 7.8 shows the three operations in a horizontal plane. The WORCRA process is characterized by the following main features:

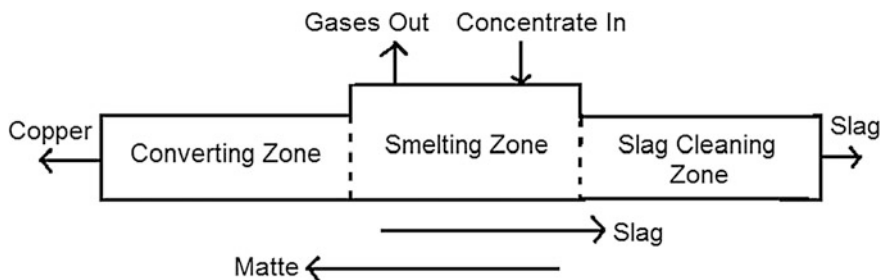


Fig. 7.8 WORCRA Reactor

- (1) The process directly produces the metal, rather than a matte, from the concentrate.
- (2) The heat generated by the oxidation reactions is utilized in the reactor.
- (3) In the smelting and converting zones, the baths are kept in a constant motion and turbulence.
- (4) The counter movement of the matte and slag takes place in the converting zone, the slag is moving under gravity.
- (5) After the slag has passed through the smelting zone and the slag cleaning zone, its copper content is drastically reduced to allow it to be discarded.
- (6) The gases, which contain SO_2 , generated in the smelting and converting stages leave the reactor and are suitable for the production of H_2SO_4 acid.

Several factors were expected to contribute to the efficiency of the WORCRA process. First, the process injects concentrate particles which possess a large surface area. This helps in accelerating the reaction with gases in the smelting and converting zones. In the converting zone, there is a complete dispersion of the slag and the matte; whereas in conventional smelting, the reactions between the slag and the matte take place only at the slag-metal interface. Second, the counter-movement of the matte and slag leads to the effective removal of impurities such as iron. Third, in the smelting zone, valuable copper present in the slag can be reverted to the matte phase by reactions with the ferrous sulphide present in the matte. Fourth, the process maintains appropriate oxidizing and reducing conditions in different zones.

7.4.2.2 Noranda Process

The Noranda process was developed by the Noranda Mines Limited, Noranda, Canada as a continuous smelting process to go into commercial operation in 1973. The reactor, which is fuel fired at ends, produces copper metal or a high grade matte directly from the sulphide concentrate. Initially sulphide concentrate is pelletized in pelletizer, then pellets are fed into the reactor at the feed end. First pellets are melted and then oxidized by air which is coming from tuyeres. Copper or matte is collected

from a tap hole of the reactor and slag is taken out from another tap hole. This slag contains high copper content; it is cooled slowly, milled and floated to get a low copper slag.

In the reactor, three layers exist together, namely, copper, matte and slag. When excess air is available, and then produces metallic copper and iron oxide, the excess air also oxidizes a part of matte to copper. This results in a decrease in the matte level and an increase in the copper level. When the amount of air is not sufficient, unoxidized iron and sulphur then tend to form matte in combination with copper. This increases the matte level and decreases in the copper level. By looking at these changes in the levels, the ratio of air to concentrate can be adjusted to yield the desired end product. The smelting rate is 4.48 tonne/day/m³.

7.4.2.3 Mitsubishi Process

The Mitsubishi process was developed in Japan, and is already operated commercially at the Mitsubishi plant, Japan with a capacity of 650 tonne/day. Three furnaces (i.e. smelting furnace, slag cleaning furnace and converting furnace) are in a line as shown in Fig. 7.9. In the smelting furnace, concentrate is smelted to produce a matte (containing 60–65% Cu) and slag. Both the matte and the slag from the smelting furnace are transferred by gravity to the slag cleaning furnace, where they are separated from each other. The matte is transferred to the converting furnace and the slag is discarded. In the converter, the matte is oxidized to blister copper by injected oxygen-enriched air through lances from top of the bath. Limestone is added as flux to form lime ferrite slag instead of iron silicate slag. This is to ensure that a blister copper with low sulphur content is produced and to decrease copper transfer to the slag. This slag is transferred to the smelting furnace for recovery of copper. The blister copper is continuously tapped. The smelting rate is 3.41 tonne/day/m³.

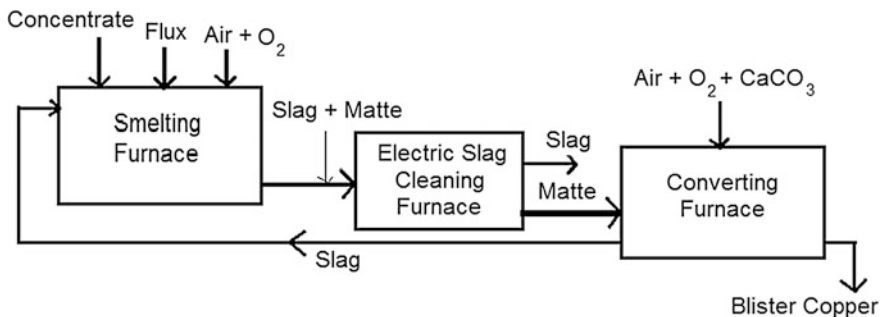


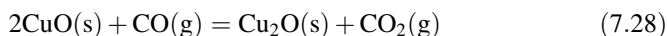
Fig. 7.9 Mitsubishi Continuous process

7.5 TORCO Segregation Process

The TORCO (treatment of refractory copper ores) process was developed to extract copper concentrate from oxidized copper ores, such as aluminosilicates, because normal leaching or flotation operations are unsuitable. Figure 7.10 shows the flow diagram of the TORCO process. In this process, grounded ore, which contains 2–6% Cu, is mixed with 0.5–2% coke or coal and 0.5–1% NaCl, then heated in a segregation reactor at a temperature of 700–800°C for about 0.5–1 h. Most of the copper gets precipitated on the carbon surface and the product consists of copper-coated carbon particles which form the segregate. The segregate and the gangue are separated from each other by flotation. The product from the reactor is continuously transferred into the flotation cell to produce a concentrate of 30–50% metallic copper. This product is sent to a smelter. The recovery of copper from this process is 85–90%.

Reactions involved in the segregation process are as follows:

- (1) First of all, copper oxide is reduced to cuprous oxide by CO gas.



- (2) Sodium chloride is hydrolyzed in the presence of water vapour to form HCl.

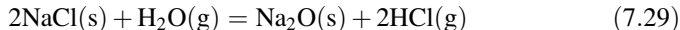
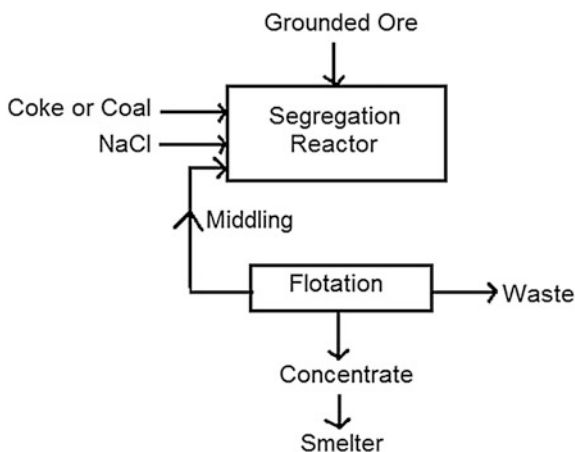
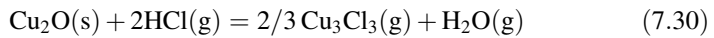


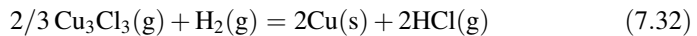
Fig. 7.10 TORCO Segregation process



- (3) The copper oxide is reacted with HCl to product gaseous copper chloride.



- (4) The cuprous chloride and water vapours are diffused on the carbon surface, where cuprous chloride is reduced to metallic copper by hydrogen gas (H_2O vapour is reduced to H_2 gas by carbon).



- (5) The regenerated HCl is again used for chloridization.

7.6 Recovery of Precious Metals

Recovery of precious metals from anode slime is shown in Fig. 7.11. Anode slime consist of 10–40% Cu, 2–20% Pb, 0.5–5% As, 0–4% Te, 0–25% Ni, 2–10% S, 0.5–2% Fe, 0–25% Se and 8.5–14 kg/tonne of Ag, 0.25–1.7 kg/tonne of Au. To remove Cu, the slime is first leached with dilute sulphuric acid and residue is treated again by sulphuric acid at 200°C to get all Cu in solution. The copper solution contains tellurium which is recovery by cementation with active copper. After removal of copper, the slime is roasted at 700°C in air, selenium oxide is formed from which selenium is recovered. The selenium free slime is then smelted with flux and passing air to make lead slag and metals consist of tellurium, silver, gold platinum and palladium. These metals is treated with soda ash, silica and borax ($\text{Na}_2\text{B}_4\text{O}_7$) to get silver rich alloy (> 90% Ag). The alloy is cast in the form of an anode and electrolyzed in the silver nitrate bath to recover silver and anode slime containing Au, Pt and Pd metals.

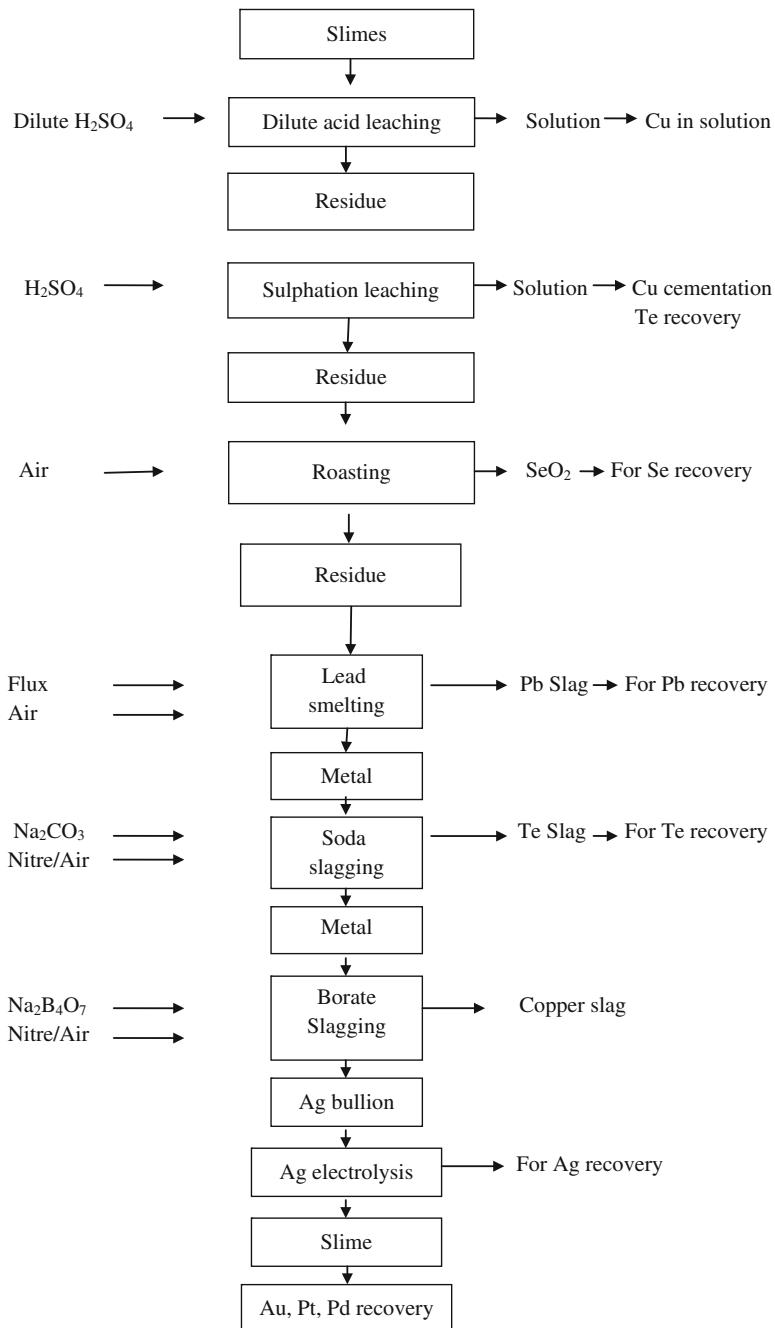


Fig. 7.11 Flow sheet for recovery of precious metals

7.7 Hydrometallurgical Process of Copper

About 80–85% of the world's total production of copper is done by the pyrometallurgical process, rest is by the hydrometallurgical process. The hydrometallurgical process is mainly used in the extraction of copper from oxidized ores or low grade sulphide ores.

7.7.1 Ferric Chloride Leaching

It is well known that chalcopyrite mineral is difficult to leach. However, it is found that ferric chloride can be used as leaching reagent for chalcopyrite. The reaction between chalcopyrite and ferric chloride is as follows:

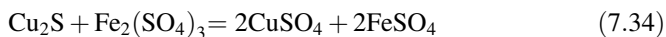


This reaction is not only dissolved copper but also produces elemental sulphur. This is a distinct advantage over the pyrometallurgical process which emits SO_2 gas.

Figure 7.12 shows the flow sheet for hydrometallurgical process of copper extraction. Copper is recovered by cementation and fire refining. The ferric chloride is regenerated by the chlorination of the ferrous chloride solution which is a by-product of the process.

The most extensively applied solvent for oxidized copper ore is dilute sulphuric acid, for not only does it readily dissolve the metal but also renders it in a form suitable for subsequent precipitation and recovery. A disadvantage, however, is that, in addition to the oxidized copper minerals, the gangue, when composed of such compounds as carbonate, silicate and oxide is also attacked. These dissolved impurities are objectionable not only from the viewpoint of the amount of acid they consume, but also because they tend to accumulate in the solution when recycled.

Ferric sulphate has been used in copper leaching for in addition to oxidized copper ore it also acts as a solvent for sulphides.



7.7.2 Leaching of Low Grade Ores

Hydrometallurgical process of copper extraction is the best suited for low grade copper ore (Fig. 7.13). The low grade ore is accumulated in the form of a heap and dilute acid is percolated through it. After percolation, the leach solution is either

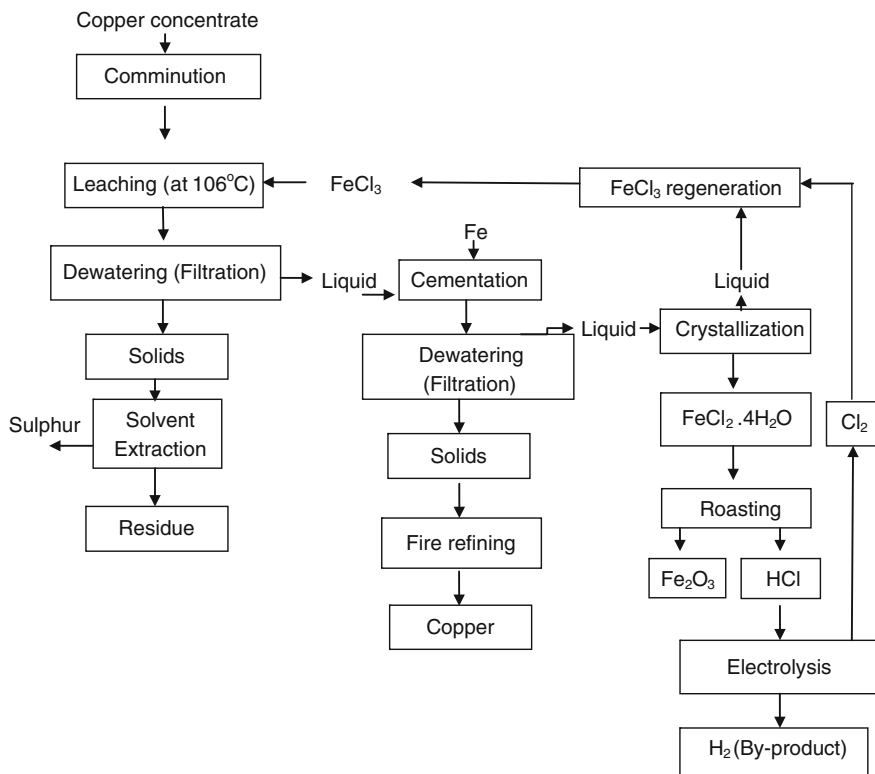


Fig. 7.12 Flow sheet for hydrometallurgical process of copper

treated with scrap iron to recover cement copper or subjected to solvent extraction to extract copper and also to provide a solution suitable for electro-winning. To accelerate the leaching rate bacteria can be used.

In case of an oxidized copper ore, leaching is carried out by using a spent copper electro-winning electrolyte that contains about 100 g/l H_2SO_4 . The resultant leach liquor that contains about 50 g/l copper is used for electro-winning metallic copper.

7.7.3 Leaching of Roasted Sulphide Concentrates

A sulphide concentrate of copper is roasted prior to leaching. In a fluid bed roaster, a roasting temperature higher than 650°C is required to achieve good roasting kinetics. During the subsequent electro-winning of the CuSO_4 solution (obtained from the dilute acid leaching of the roasted concentrate), H_2SO_4 is generated. The reaction is

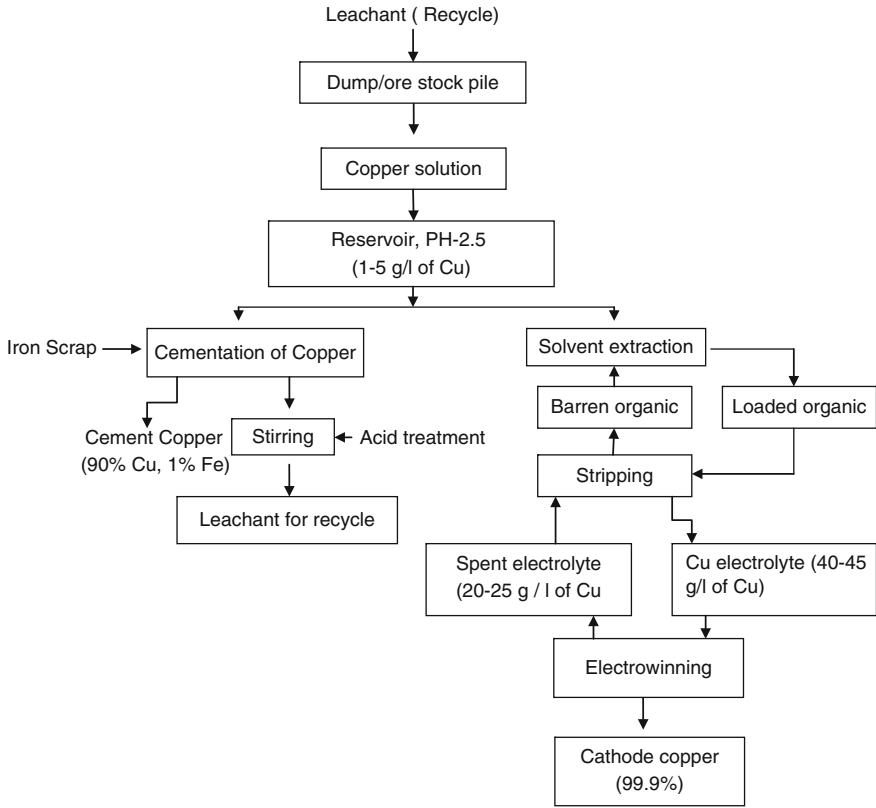
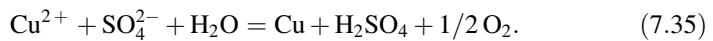


Fig. 7.13 Flow sheet of leaching for low grade copper ore



The sulphuric acid in the spent electrolyte is normally used for the leaching of copper oxide ores.

7.8 Properties

Atomic weight of copper is 63.54. Specific gravity of copper is 8.96. Melting point and boiling point are 1083°C and 2580°C respectively. At metallurgical processing temperatures the pressure of vapours of copper, its oxides and sulphidies are so small that they may be considered practically non-volatile. Copper and its alloys have a unique combination of properties, such as, high electrical and thermal conductivities, adequate mechanical properties, and high resistance to various types of corrosion. The properties of copper differ depending on the nature of the impurity

present in it. Oxygen adversely affects the electrical properties of copper. When present in very small quantity, oxygen (0.02–0.04%) is not harmful; in fact, it actually increases the electrical conductivity by removing other impurities from the solid solution. Impurities such as sulphur, selenium, bismuth, antimony, and tellurium have harmful effects on both the mechanical and electrical properties of copper and have to be removed during refining. Annealed copper when work-hardened loses about 3% of its conductivity; after re-annealing, however, restores it. The electrical conductivity of copper is affected to a great extent by the addition of other elements; phosphorus, silicon and arsenic are highly decreasing, whereas silver, cadmium, zinc and oxygen (in small amounts) have little influence on the electrical conductivity of copper.

Copper is next to silver in respect of its thermal conductivity. The effect of temperature on the thermal conductivity of copper is very little. By rising to 200°C, the loss of thermal conductivity is less than 1%. The effect of impurities leads to a reduction of thermal conductivity in approximately the same degree as its electrical conductivity. The thermal conductivities and electrical resistivities of silver, copper, gold, and aluminium (as shown in Table 7.1) are outstanding when compared with those of other metals. Since silver and gold are highly expensive, they cannot be used on a commercial scale for electrical applications. In this area, copper has been found ideal.

By location in the Periodic table (Fig. 1.1), close to copper are metals of the same subgroup like gold and silver. They do not oxidize in air and occur naturally in native state. Molten copper, gold and silver are readily soluble in one another.

Oxygen-free copper is in demand for welding and brazing, in addition to operations involving heavy degrees of cold work such as deep drawing. Deoxidized copper contains up to 0.04% phosphorus, the presence of which has an adverse effect on the electrical conductivity, diminishing it by some 20%. Arsenic (up to 0.5%) is added to copper with the intent of obtaining increased strength and toughness, also raising the softening temperature by about 100°C.

Under severe conditions of atmospheric corrosion, copper is extremely resistant to attack, as a result of the formation of a film of oxide. When exposed to the action

Table 7.1 Selected physical properties of some metals

Metal	Specific gravity	Melting point (°C)	Thermal conductivity at 20°C (cal cm ⁻¹ s ⁻¹ °C ⁻¹)	Electrical resistivity at 20° C (10 ⁻⁶ Ω cm)	Relative electrical conductivity (copper = 100)
Silver (Ag)	10.49	960	1.00	1.59	106
Copper (Cu)	8.94	1083	0.94	1.67	100
Gold (Au)	19.32	1063	0.71	2.19	72
Aluminium (Al)	2.7	660	0.53	2.66	62

of air or water for long periods, this oxide skin is converted to sulphides or to complex basic sulphates and carbonates. Copper is excellent resistance to most acids and alkalis, other than the strong mineral acids and ammonia.

Since copper is ductile in nature, it may readily be worked cold by any process involving rolling, wire-drawing, spinning and pressing etc. Cold working increases both strength and hardness but decreases elongation. If the metal is required in the soft condition after cold working this may be achieved by annealing at 400–600°C. Due to its exceptional plasticity, copper can be rolled, extruded or forged over a wide range of temperatures. Tensile strength of cast copper is about 15.75 to 17.325 kg/mm². Rolling, forging or other types of hot and cold working followed by annealing raises its tensile strength to upwards of 22.05 kg/mm² with about 45% elongation. Izod impact values of most commercial copper in the fully annealed condition vary between 54.24 and 67.8 J.

7.9 Applications

Copper is the most important non-ferrous metal. It can be used in alloy as well as unalloyed state; the world output of this metal is greater than any other non-ferrous metal. The addition of a metal or metals to copper forms alloys which have superior hardness, mechanical and other special properties, and they are in wide use for many applications. Copper can make alloys with Zn, Sn, Be, and Ni. Pure copper is used extensively in electrical applications due to its very good electrical conductivity. Nowadays, aluminium is gradually replacing copper in the power transmission lines and in other electrical applications.

In non-electrical applications, copper is used in the form of an alloy. Some of the commonly used alloys are Cu–Zn brasses, Cu–Sn bronzes and Cu–Ni–Zn alloys. Cu–Zn brasses that contain up to 36% Zn are known as α -brasses, and have exceptional cold working properties. Cu–Zn brasses, which contain between 37 and 45% Zn, are known as α - β -brasses; those which contain more than 45% Zn are known as β -brasses. α - β -brasses are suited for hot working, which improves as the zinc content increases, reaching a maximum at about 40%.

Cu–Sn bronzes, which have a higher mechanical strength than metallic Cu, and fatigue-resistant and corrosion-resistant properties. Cu–Ni alloys containing 50–70% Cu have excellent ductility and offer a high resistance to corrosion.

Cu–Al bronzes form a range of alloys based on copper and aluminium with additions of iron, nickel and manganese. The protective film of aluminium oxide formed on the alloys by heating. Cu–Al bronzes are among the best of the copper base alloys for service at moderately elevated temperatures. They show good resistance to all normal forms of corrosion. Aluminium content for normal cold work is about 8%; 10% Al–Cu bronze can be fabricated in hot conditions and can be used for casting.

Addition of silicon to copper (silicon bronze) not only increases the strength and gives good resistance to corrosion, especially by acids, but also improves the

weldability since silicon is a strong deoxidizer and helps to maintain the molten weld metal in a deoxidized condition. Addition of silicon to brass enhances the mechanical properties and increases the fluidity of the molten metal for die castings. The most promising alloy contains 15% Zn, 4% Si, and the rest Cu. This bronze gives good clean castings and can be easily extruded, hot or cold worked.

The copper manganese aluminium alloys are ductile and malleable and certain of these alloys possess a low temperature coefficient of electrical resistance. Thus, they (85% Cu, 13% Mn and 2% Al) are particularly suitable for the fixed resistances of electrical instruments. Although manganese is non-magnetic, alloy containing 65% Cu, 25% Mn and 10% Al can be magnetized to form permanent magnets. This material is relatively soft and ductile and can be formed by bending and machining into any shapes which would be difficult for magnetic steels.

An alloy containing 2% beryllium, after suitable heat treatment, is the hardest and strongest of all copper base alloys, and is used for producing tools. The resistance to fatigue and corrosion shown by the alloy is responsible for its main outlet, namely spring material, bushings and bearings.