

RECENT ADVANCES IN THE EXTRACTION OF COPPER, NICKEL AND COBALT

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It is believed that amount of various metals a society consumes is a direct indicator of the advancement of that society. Among non-ferrous metals copper, nickel and cobalt, due to their highly specialized applications, have played important roles in improving standards of living of the people. Therefore, continued production of these metals and their use is essential for society's development.

The global demand for refined copper is around 18 million tons out of which 88% comes from primary production-new copper that is mined from the ground. The demand-supply gap (12%) is met with secondary copper i.e. from recycling of copper scrap.

With many widespread uses, copper demand is growing by an average of 4% per year. In India major producers of refined copper are Birla Copper, Sterlite Industries and Hindustan Copper, and a total of 6.5 lakh tons copper is produced annually. Indian

demand for refined copper is around 4.5 lakh tons which is 3% of the global copper market. Thus India is emerging as a net exporter of refined copper. However, 90% of the concentrate requirement is imported. Copper is the most extensively used metal next only to steel and aluminum. Copper's chemical, physical and aesthetic properties make it a material of choice in a wide range of domestic, industrial and high technology applications. For instance, copper is used for conducting electricity and heat, electronics and communications, construction of buildings, transportation, making sophisticated machinery and equipment, making statues and other form of arts, consumer and general products, etc (Fig. 1). In India two major states owned telecommunications service providers BSNL and MTNL consume 10% of country's copper production. Further, growth in the building construction and automobile sector would keep demand of copper high.

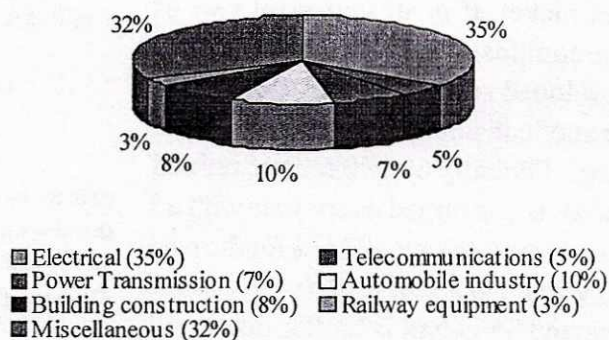


Fig. 1 : Copper Consumption

Among base metals, nickel is the most volatile owing to its strong demand and tight supply. Global demand for nickel is about 1.3 million tons and the consumption rate is increasing at a

rate of 3% a year. Nickel finds its usage in various industries such as engineering, electrical, electronics, infrastructure, automobile components, packaging, battery etc. Nickel's primary uses (Fig. 2) are 65% in the manufacturing stainless steels, 20% in other steel and non-ferrous alloys, 9% in electroplating and about 6% in coins and nickel chemicals. Due to lack of nickel reserves, nickel market in India is totally dependent on import. India imports around 30,000 tons of nickel. With a growth in the stainless steel sector, the nickel import is expected to increase in the coming years. Steel scrap has emerged as a good substitute for the primary metal.

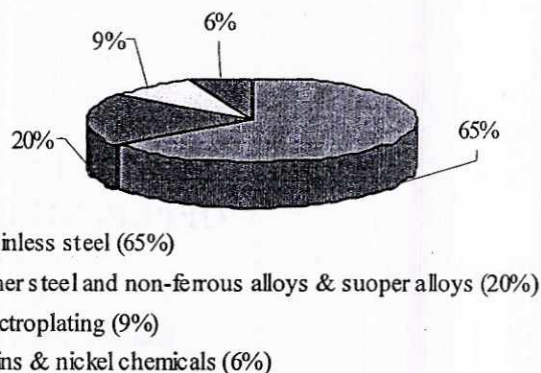


Fig. 2 : Nickel Consumption

Although cobalt is one of the least abundant elements compared to copper and nickel, it is an important part of the composition of nearly all alloys developed since 19th century and has been of considerable interest in recent years. Globally 60,000 tons of refined cobalt is consumed every year with an annual growth rate of 6.6% for the past 10 years. On a sector basis the current demand for cobalt is broken down and shown in Fig. 3. The cobalt market in India is comparatively small because manufacture industry in India has not undergone any major expansion, and consumes around 700 tons of cobalt every year for application in the metallurgical and chemical sectors.

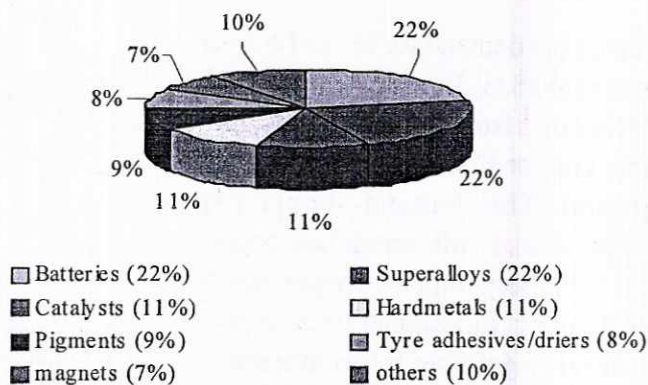


Fig. 3 : Cobalt Consumption

Thus it is clear that with time the demand for various metals is increasing. But due to continuous mining and processing mineral grades of primary resources are declining. However, newer and energy efficient processes are being developed to recover metals from low grade ores and secondaries to meet the requirement of the society. Therefore, it is essential to update ourselves with recent advances in extraction processes of copper, nickel and cobalt.

Extraction of Copper

Copper exists in nature mostly in the form of copper sulfide. Oxides or oxidised ores are found only in limited quantities. Some of the common minerals of copper are: Chalcopyrite CuFeS_2 ; Covellite CuS ; Chalcocite Cu_2S ; Cuprite Cu_2O ; etc. Among aforesaid minerals chalcopyrite is most abundant copper bearing minerals, which accounts for approximately 70% of the world's known copper reserves. A sulphide ore that contains 0.5-2.0% copper is considered satisfactory for copper extraction by concentration followed by pyrometallurgy. In the case of poorer grades, copper is extracted by hydrometallurgical processes.

Conventional extraction of copper from chalcopyrite concentrate

In principle it is possible to roast sulfide ore of copper to oxide and then reduce it by carbon in the blast furnace. However, since the concentrate also contains iron sulfide, iron oxides will form. In fact oxidation of copper sulfide does not occur until iron sulfide is fully oxidised yielding Fe_2O_3 . This Fe_2O_3 is difficult to remove by slagging. Therefore, blast furnace smelting is not used for extraction of copper. Moreover, copper is extracted by matte smelting process without using any reductant. The process flow sheet for conventional pyrometallurgical extraction of copper from chalcopyrite concentrate is shown in Fig. 4.

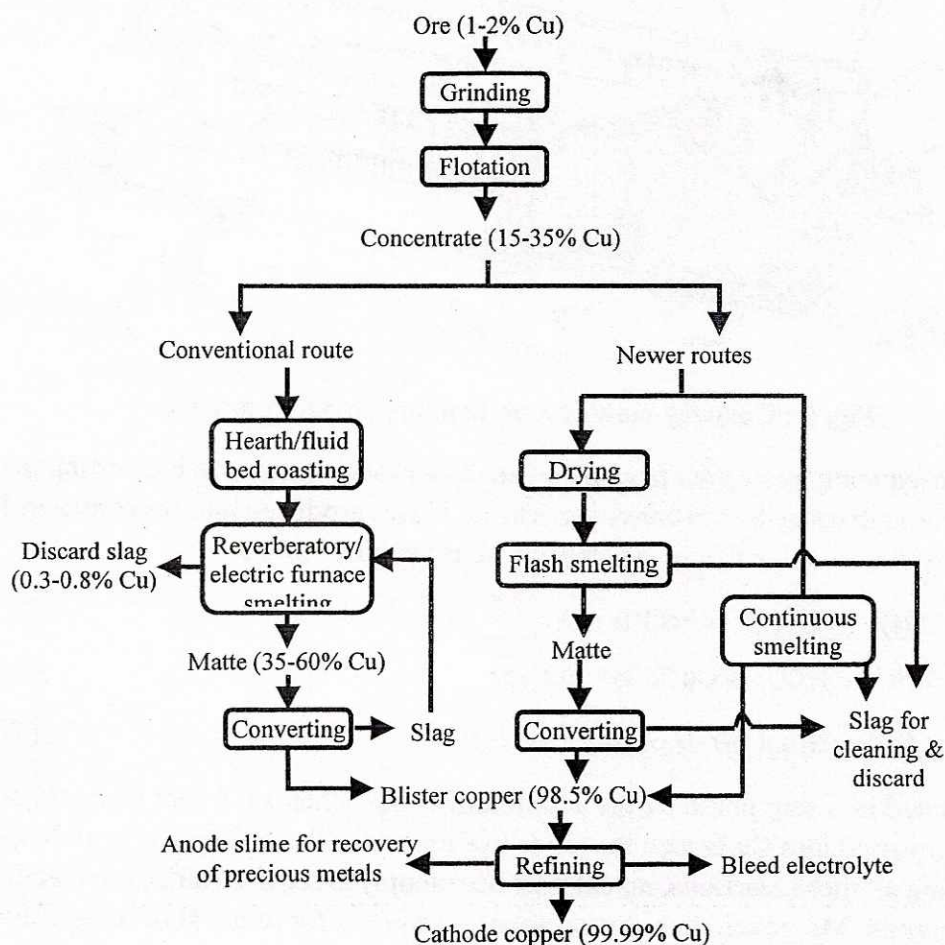
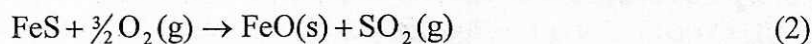
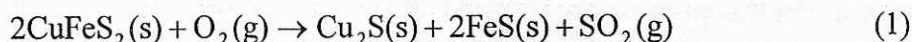


Fig. 4 : Pyrometallurgical extraction of copper from sulfide ores

The ores containing chalcopyrite minerals are upgraded by flotation and then roasted under controlled conditions. During roasting, iron sulfide 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 along with quartz (SiO_2). A reverberatory furnace for copper matte smelting is shown in Fig. 5. The charge is heated in the furnace to $1200\text{--}1300^\circ\text{C}$. Iron oxide (FeO) is removed as a slag containing mainly $\text{FeO} \cdot \text{SiO}_2$. The remaining sulfides melt collected 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.

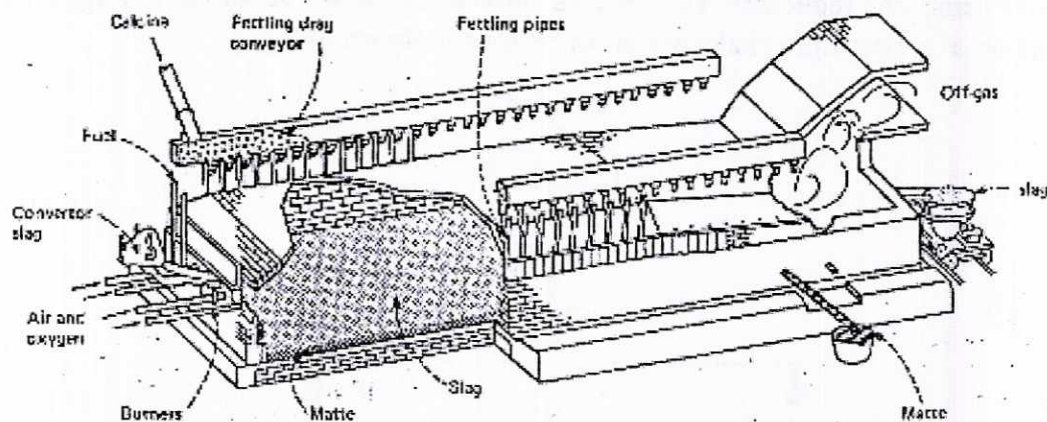
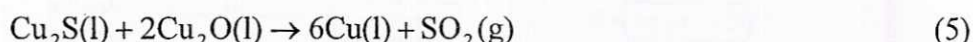
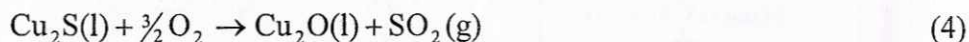
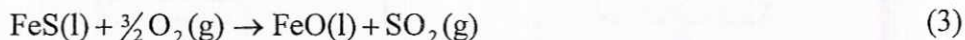


Fig. 5 : Cutaway view of reverberatory smelting furnace

Copper is subsequently recovered from the matte by a process known as converting in which air is blown through a side blown converter. The air blast introduced into the converter brings about rapid oxidation of the matte and consequent removal of sulfur.



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 (Eq.5) 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 sulfur 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.

The copper produced in the converting stage is called blister copper due to its blistery appearance. For this purpose fire refined copper is cast in the form of anode. The cathode is made of a pure copper sheet. The electrolyte consists of copper sulphate solution containing $35\text{--}40 \text{ g/L Cu}$ and $200 \text{ g/L sulphuric acid}$. Electrolysis is carried out at a temperature of $50\text{--}60^\circ\text{C}$ using current density of 200 A/m^2 . During electrolysis, copper is transferred from the crude anode to pure cathode. Impurities in the blister copper such as Fe, Ni, Co, Se, and Te go to solution and the precious metals collected below the anode as anode slime. The copper produced

by electrorefining is 99.99% pure. Anode slime can be processed for recovery of precious metals. The value of these by-products compensates for the high expense incurred during the refining operation.

Flash Smelting

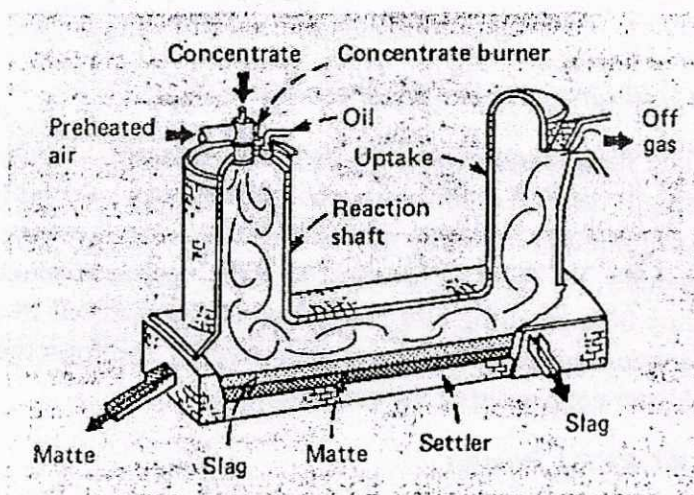
In the conventional process for extraction of copper from sulphide concentrate, reverberatory smelting is a melting process rather than an oxidation process. Its offgas is dilute in SO_2 , which is difficult to remove. Further, it is an energy intensive process because heat is not generated during smelting. Therefore flash smelting has been the most widely adopted copper smelting operation since 1970. This process combines two operations, namely roasting and smelting. Flash smelting entails the injection of air, oxygen, dried Cu-Fe-S concentrate, and silica flux into a 1250°C hearth furnace, inside which, the concentrate reacts with oxygen of the blast. This results in

1. Controlled oxidation of Fe and S - offgas strong enough in SO_2 for efficient recovery as H_2SO_4 .
2. Evolution of large amount of heat - making the process autogenous and energy efficient
3. Melting of the solids

There are two types of flash smelting - the Outokumpu process and the INCO process.

Outokumpu process

In the Outokumpu furnace (Fig. 6) dry particulate feed and pre heated oxygen enriched air are blown through the concentrate burners down into the furnace. This process can produce matte containing 45-65% copper under autogenous condition depending on the quantity of fuel used and the degree of oxygen enrichment employed. The slag always has a high copper content, i.e. 0.8-1.5 % copper and is subjected to either electric furnace treatment or slag flotation in order to recover copper. Outokumpu flash smelting is a closed process which can achieve up to 99% capture of sulfur rich gases from the smelting furnace for the production of sulfuric acid.



INCO process

The INCO process uses commercial oxygen (95-98 volume % O_2), rather than oxygen enriched air. Its blast and particulate feed are blown horizontally into the furnace (Fig. 7) through two burners in each end wall of the furnace rather than downward. In this process, virtually all of

the energy for smelting comes from oxidizing the Fe and S of the feed concentrate (no external fuel is used). The matte produced contains about 45% copper as in the case of conventional reverberatory smelting and the slag produced contains only about 0.5-0.6% copper, and can be discarded. The matte is further treated i.e. by converting to produce blister copper. The offgas contains 70-80 volume % SO_2 which is usually captured as sulfuric acid or liquid SO_2 .

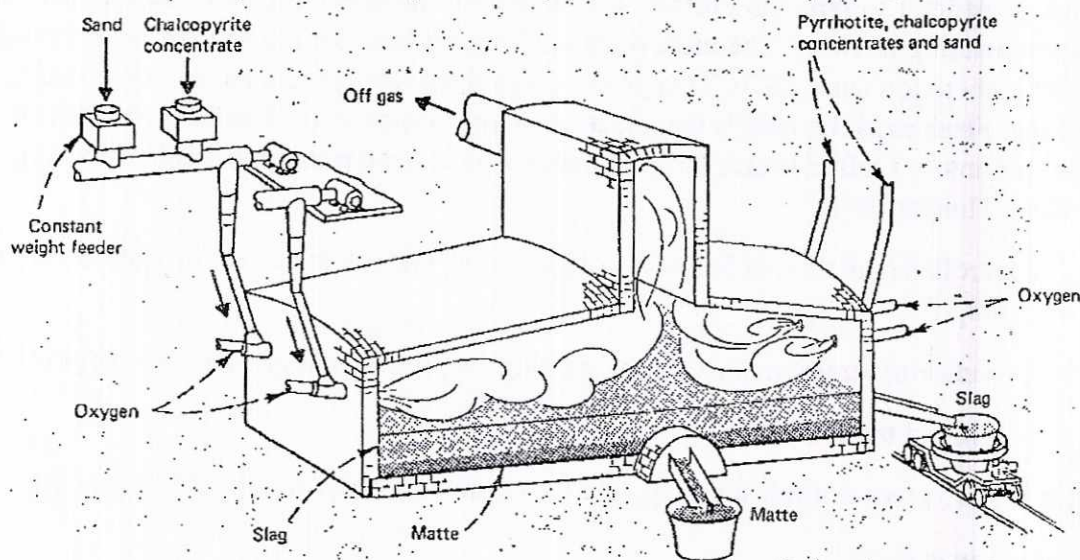


Fig. 7 : Cutaway view of INCO oxygen flash smelting furnace

Continuous Copper Production

The flash smelting can be logically extended to encompass smelting, and converting in a single vessel, i.e. the copper concentrate can be charged at one end and copper metal can be continuously withdrawn from the other end. Two such continuous smelting processes are namely, WORCRA process and Noranda process. In Japan, Mitsubishi has developed a process in which smelting and converting are carried out in separate vessels. However, there is a continuous flow of matte to the converter unit from the smelting unit and continuous flow of blister copper out of the converter unit.

WORCRA Process

The WORCRA process seeks to maximize the conservation of energy obtained during smelting and converting of sulfide concentrates by integrating, to a high degree, several efficient continuous unit operations. The WORCRA process also seeks to reduce the capital and operating cost by eliminating the handling of solids and liquids in batches.

This process combines smelting, converting and slag cleaning operations in a single furnace, so that occur in a separate but interconnected zones. Process flowsheet for WORCRA process is given in Fig. 8, and Fig. 9 depicts an idealized vertical section of a straight horizontal form of the WORCRA reactor. The WORCRA process is characterised by the following features:

1. The process directly produces metal, rather than matte from a concentrate
2. The heat of exothermic oxidation reaction is utilized in the reactor itself
3. In the smelting and converting zones, the bath is kept under constant state of motion and turbulence
4. In the converting zone, generally, the countermovement of the slag and the matte takes place, the slag moving under gravity
5. The copper content of the slag generated is so low that it can be discarded without further recovery of copper from the slag
6. The SO_2 gas generated in the smelting and converting zones combine and leave the reactor in a continuous stream which is suitable for the manufacture of sulfuric acid

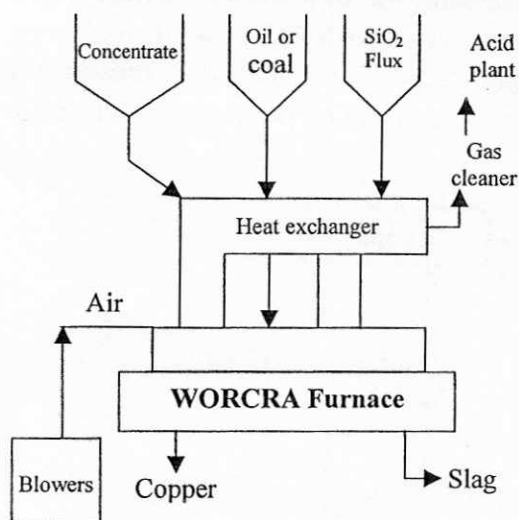


Fig. 8 : WORCRA process for copper product

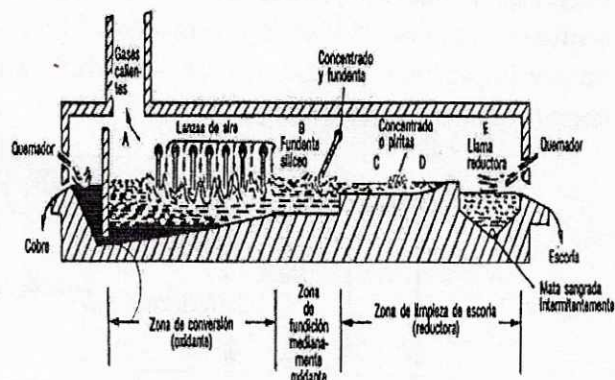


Fig. 9 : Schematic diagram of WORCRA reactor

Several factors contribute to the efficiency of operation of the WORCRA process.

1. The process injects particulate solids and gases into the bath, which maximizes the reaction surface area in the smelting and converting zone. In the converting zone, particularly there is a complete dispersion of the slag and matte, whereas in conventional reverberatory smelting, the reaction between the slag and matte takes place only at the slag-matte interface.
2. The counter movement of slag and the matte leads to the effective removal of impurities such as iron
3. In the smelting zone valuable copper present in the slag can be reverted to the matte phase by reacting slag with ferrous sulfate present in the matte

Noranda Process

In this process, the reactor (Fig. 10), which is fuel fired at both the ends, produces copper metal or a high-grade copper matte directly from the sulfide concentrate. Figure 11 gives the flowsheet for the Noranda process. The pelletised feed which is charged into the reactor at the

feed end is melted and then oxidized by air which is blown through the tuyers. Copper or matte is collected from a tap hole and the slag is skimmed off from another tap hole at the slag end. The slag has a high copper content. It is collected slowly, milled, and floated to yield a low copper slag and a concentrate which is recycled to the reactor. Thus in the reactor, three layers namely, copper, matte and slag exist together. The level of formation of desired product can be controlled by adjusting the air in the reactor. In practice a high-grade matte is produced (70-75% Cu) which is further blown to blister copper in Pierce-Smith converters. The ability to produce blister copper directly is limited by the presence of certain impurities (notably As, Bi, Sb) which imposes a constraint on producing anode grade copper of acceptable quality.

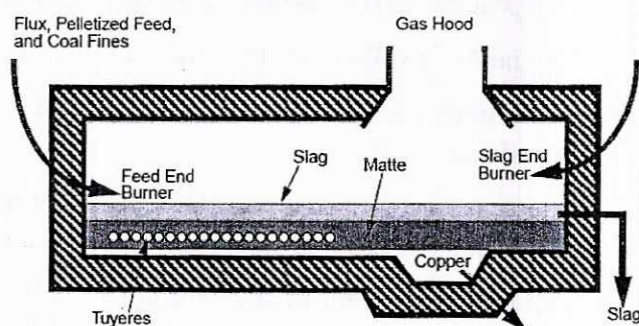


Fig. 10 : Schematic diagram of Noranda Reactor

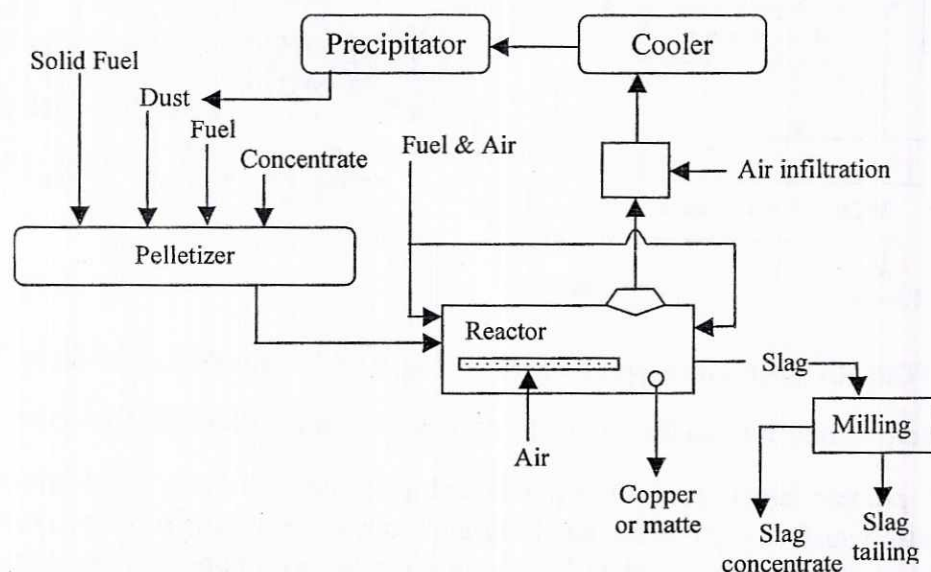


Fig. 11 : Noranda process

Mitsubishi Process

The process is a continuous, multi-step process which produces blister copper from concentrates in three interconnecting furnaces. In this process three furnaces namely, the smelting furnace, slag cleaning furnace and the converting furnace are connected in a cascade fashion as shown in Fig. 12. Concentrate and oxygen-enriched air (30-35% O_2) enter the smelting furnace through vertical lances and are smelted to produce a matte of 65% to 69% Cu and low-copper slag. Fuel must be burned to satisfy the heat balance in the smelter chamber. The high-grade matte flows to the electric slag cleaning furnace. From the slag cleaning furnace the matte flows to the converting furnace where it is oxidized to blister copper using enriched-oxygen (26-28% O_2). Fuel must be burned in the converting furnace to maintain the heat balance.

One of the most important principals of the Mitsubishi is the simplicity of its design, construction, operation, and maintenance.

- ❖ All of the furnaces are stationary and driving mechanisms, which are normally required for conventional converters, such as furnace tilting, tuyere punching, and hood driving are not required.
- ❖ Molten products are transferred by gravity to the next furnace through a launder eliminating the need for large cranes and ladles.
- ❖ Molten products overflow continuously through the outlet hole of the furnaces which eliminates the need for tapping and slag skimming operations.

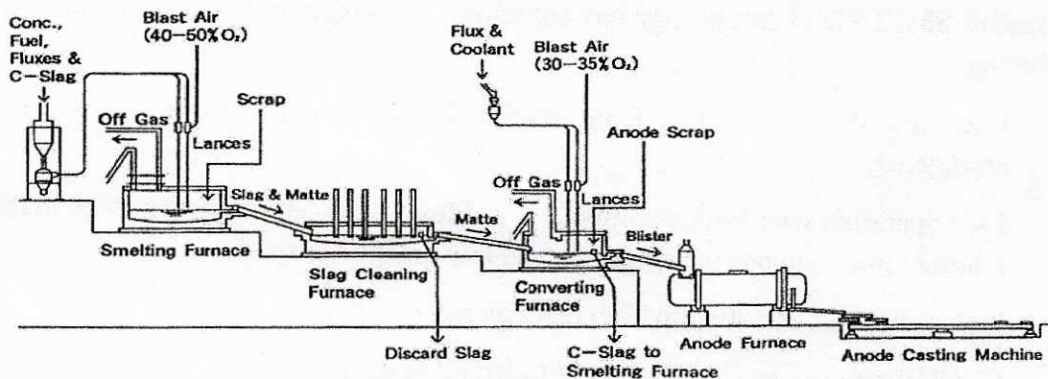


Fig. 12 : Mitsubshi continuous smelting process

One of the advantages of the continuous process is that it enables a straightforward and stable operation. Compared to other smelting processes, the smelting furnace is able to continuously produce a consistent amount and grade of matte, which is continuously converted in the C-furnace. (i.e. Converter). In conventional batch-wise converters, the condition of the melt is not constant with time and a lot of experience is required to operate the process.

IsaSmelt/Ausmelt Process

The IsaSmelt and Ausmelt processes are closely related. The process was developed based on pioneering work conducted at Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia. This is a high-intensity smelting process for the production of matte from copper concentrate and secondary materials. A schematic image of an Ausmelt smelting unit with the lance submerged is shown in Fig. 13. It uses an extremely efficient top-submerged lance and a simple, stationary refractory-lined furnace. The lance tip is submerged into a bath of molten slag. Air, oxygen, and fuel are fed down the lance into the molten bath, creating a

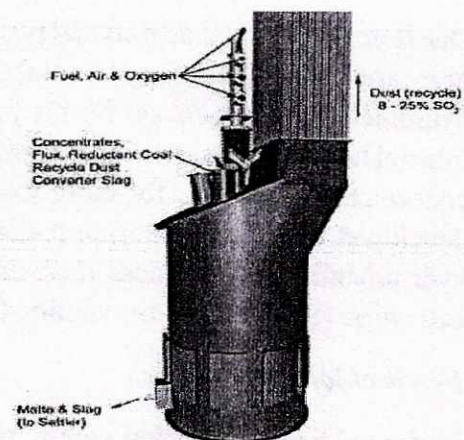


Fig. 13 : Ausmelt Smelting Furnace

highly turbulent environment that promotes very rapid reaction of raw materials. It can be used for a range of applications. Depending upon the application, the raw materials may consist of concentrates, metal bearing residues metal scrap, fluxes and solid fuel if required. These materials are fed on a continuous or semi-continuous basis through a port in the furnace roof.

In this process, mattes containing up to 75% copper can be produced, depending on the grade of copper materials. The matte and slag produced during smelting are tapped periodically into an electric or fuel fired settling furnace for matte/slag separation. The slag containing 0.6% Cu is discarded. The offgas (~ 35 vol. % SO₂) is drawn from the top of the furnace through a vertical flue. It is passed through a waste heat boiler, gas cleaning and on to a sulfuric acid plant.

Ausmelt's SMELTING technology has numerous advantages over other smelting systems, including:

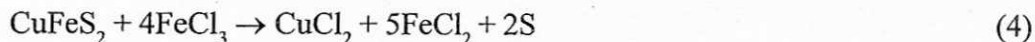
- Low capital cost resulting from simple furnace construction & peripheral system arrangement
- Low operating cost from a combination of low energy consumption, high availability, minimal maintenance requirements and low manpower needs
- Intense mixing, resulting in high reaction rates
- Flexibility to use various fuel types (coal, oil or gas)
- Ability to produce high grade product from low & high grade materials
- Low copper in smelt slag, typically < 0.6% copper, slag can be discarded
- Low fugitive & dust emission
- High sulphur capture in excess of 98%
- Small furnace footprint

Hydrometallurgical extraction of copper

Due to environmental aspects and possibility of increased exploitation of mixed and low grade ores and relatively small isolated deposits there has been worldwide interest in hydrometallurgical process for the production of copper. Since chalcopyrite is a very stable mineral because of its structural configuration, it is very hard to leach copper from chalcopyrite concentrate. However, for more than 30 years a number of leaching processes have been developed viz. ferric chloride leaching, pressure sulfuric acid leaching, bioleaching. The hydrometallurgical process recovers copper via leaching of copper followed by solvent extraction (SX) and electrowinning (EW).

Ferric chloride leaching

Under oxidizing condition copper can be leached from chalcopyrite concentrate, and ferric chloride leaching of chalcopyrite has received significant attention. In this process chalcopyrite is leached with ferric chloride solution in two stages.



The leach solution is then purified by solvent extraction and copper metal is produced by electrowinning. The chlorine generated at anode during electrowinning is recovered and used to reoxidise ferrous chloride generated during leaching.

Extraction of Nickel and Cobalt

The principal sulphide mineral of nickel is pentlandite $[(\text{NiFe})_9\text{S}_8]$. Canada is the principal nickel producer. On the other hand, cobalt does not have any primary ore except a few arsenical ores. Therefore, cobalt is extracted as a by-product of copper, nickel, zinc or precious metals. Lateritic nickel ores contain 0.08-0.15% Co along with 1.5-4% Ni.

Extraction of nickel from sulfide ore

The process flow sheet adopted by International Nickel Company of Canada for extraction of nickel from sulfide ore of nickel is shown in Fig. 14. In this process nickel concentrate is produced from the ore by grinding, froth flotation, and separating copper concentrate at copper cliff mill. The nickel concentrate containing 10% Ni, 2% Cu, 40% Fe, and 30% S is roasted in multiple hearth furnace or fluid bed roaster to selectively oxidise the iron sulphide. The roasted calcine is then smelted in presence of siliceous flux to produce a matte containing 20% Ni and 7% Cu. The furnace matte is converted in a converter at 1150°C to produce nickel enriched matte with 50% Ni, 25% Cu, and 20% S. The converter slag containing about 2% Ni is returned back to smelting furnace for nickel and copper recovery. The converter matte is then slowly cooled to 400°C. During cooling Cu_2S , Cu-Ni metallic alloy and Ni_3S_2 precipitate in phases. The slow cooled matte is subjected to grinding, magnetic separation, and flotation to separate copper sulphide concentrate, nickel sulphide concentrate and copper-nickel alloy. The nickel sulphide concentrate is recovered as low copper nickel sulphide with 74% Ni, 1% Cu, 1% Fe and 22% S and as high copper nickel sulphide with 72% Ni, 3-4% Cu, 1% Fe and 21% S. Both the nickel sulphide fractions are roasted in a fluidized bed roaster in the temperature range 1150-1250°C to produce granular nickel oxide. The low copper nickel oxide is directly marketed or reduced to produce nickel metal. The high copper nickel oxide is reduced and then refined either by carbonyl process or electrorefining producing > 99.9% nickel.

Extraction of nickel and cobalt from lateritic ore

Laterites are weathered, metal rich rocks (i.e. oxides) either in the form of limonite or serpentine. Limonites are mainly iron oxide containing nickel and cobalt and minor amount of magnesium silicate. Serpentine comprise nickel ferrous hydrated magnesium silicates. From such lateritic ores nickel and cobalt are extracted either by high-pressure acid leaching (Fig. 15) or reduction roasting followed by ammonia leaching (Caron process) (Fig. 16). In general, serpentines are not treated by high-pressure acid leaching as their high magnesium content results in excessively high acid consumption. After purification of the leach liquor, nickel and cobalt are separated by solvent extraction to produce nickel/cobalt metal by electrowinning or their salts.

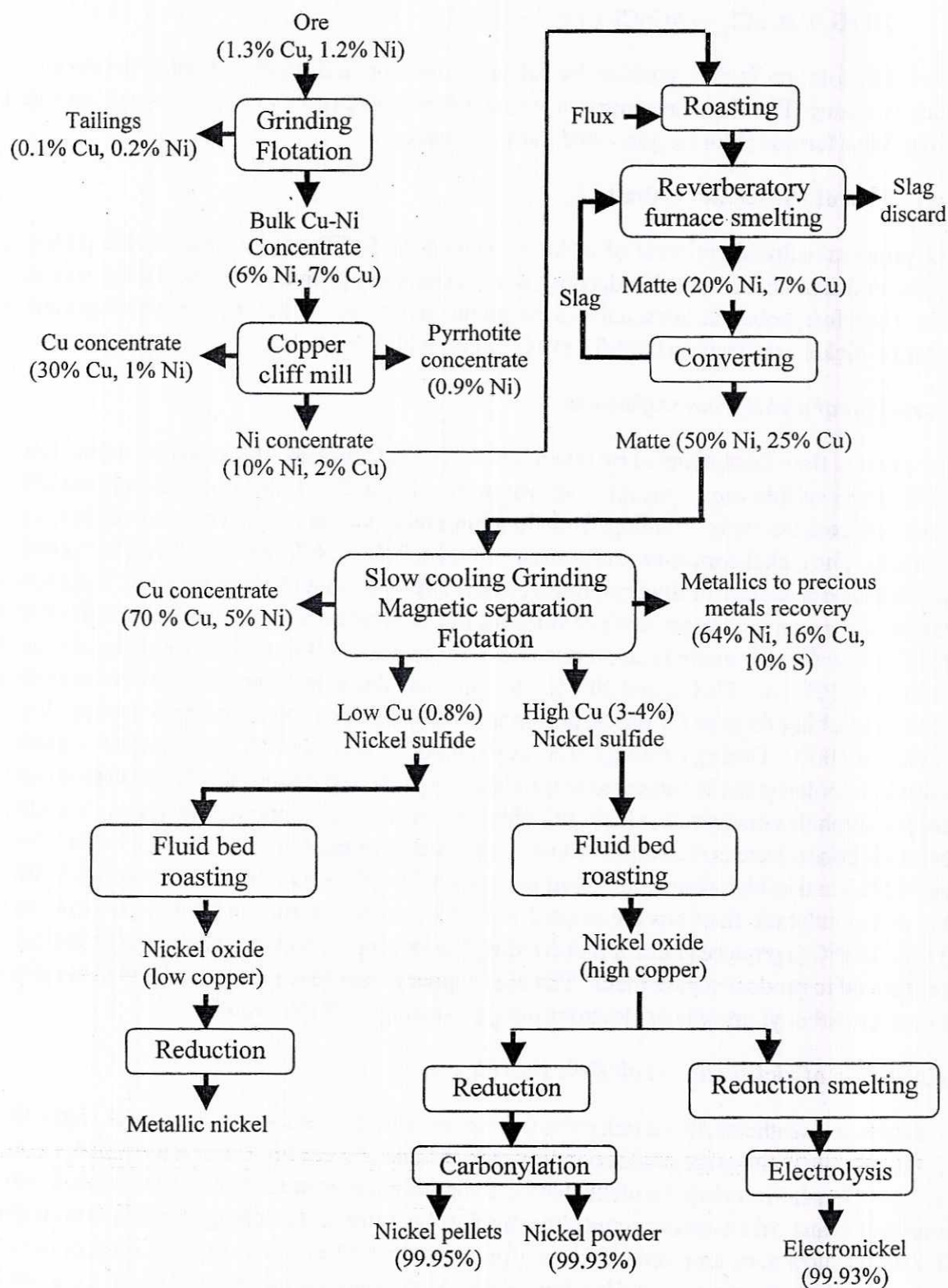


Fig. 14 : Nickel extraction (INCO process)

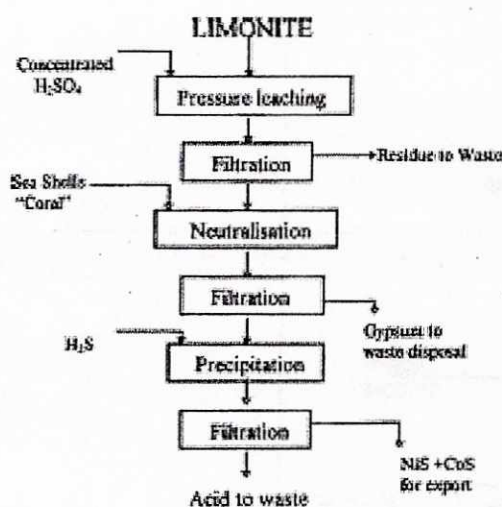


Fig. 15 : Recovery of nickel and cobalt from limonitic laterite by acid leaching

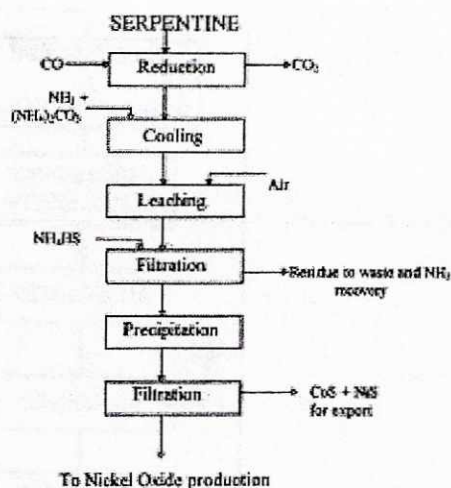


Fig. 16 : Recovery of nickel and cobalt from serpenyinic laterite by ammonia leaching

As stated earlier, India does not have any primary resource for nickel and cobalt. Therefore all Indian refiners depend on imported feed materials. The type of material imported to India for the recovery of nickel and cobalt values include sludge, waste catalyst, metallic scrap, metallic grinding dust, slags from non-ferrous metallurgical producers, etc. Figures 17-19 show typical processing routes adopted by Indian companies for treating metallic scrap, sludge and slag.

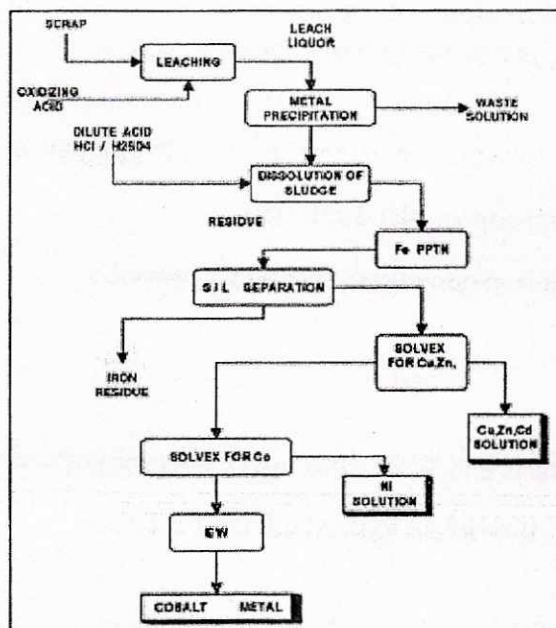


Fig. 17 : The process to recover nickel and cobalt from scrap

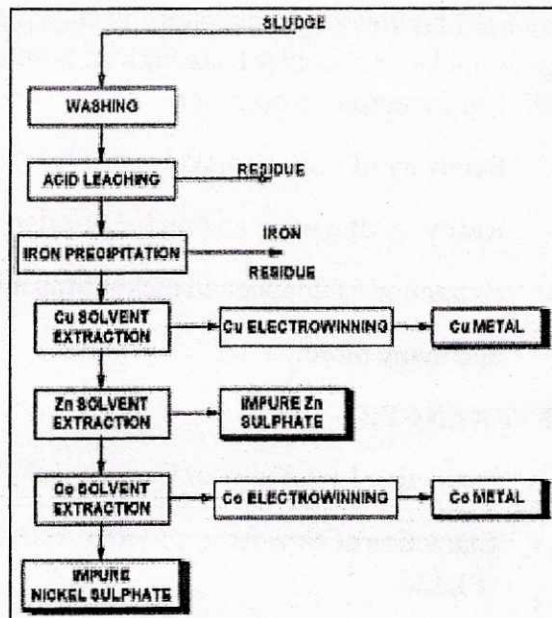


Fig. 18 : The process to recover nickel and cobalt from sludge

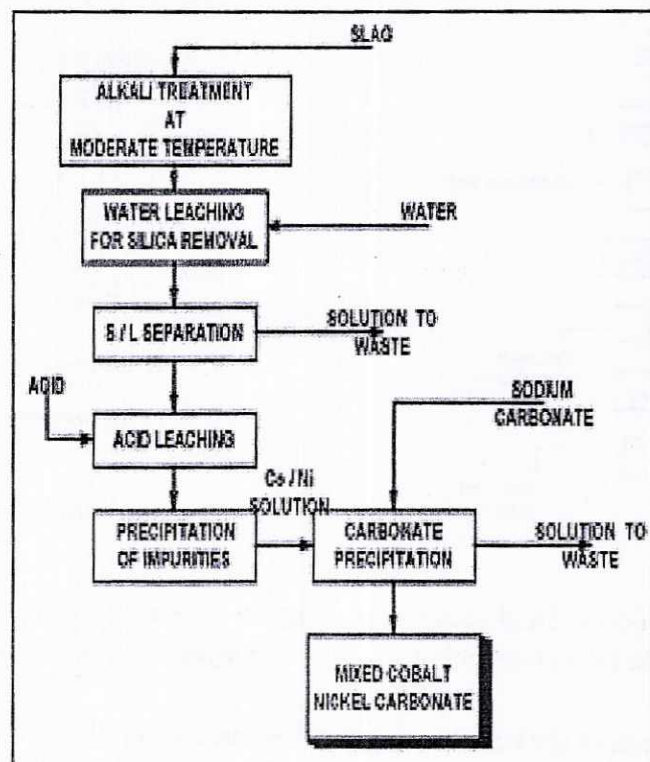


Fig. 19 : The process to recover nickel and cobalt from slag

NML'S PROCESSES

National Metallurgical Laboratory is engaged in development of processes for recovery of copper, nickel and cobalt from various by-products and secondaries. For example recently, NML has developed process for

1. Recovery of copper, nickel and cobalt from a by-product generated at UCIL, Jaduguda.
2. Recovery of copper and nickel powders from copper bleed solutions
3. Extraction of copper and nickel from a high iron containing secondary resource
4. and many more...

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