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Imperial Smelting Process

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By Product-recovery of ISP

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Zn from lead slag by slag furning

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Pg 399-400

451

Fig 7.32 (In endsem)

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(5) Electrolysis of the purified leach solution using a cell with a Pb-Ag anode and an aluminium cathode.

Figure 7.26 shows a simplified flowsheet for the hydrometallurgical zinc extraction process. As is evident from the flowsheet, the most important byproduct is perhaps cadmium. It should, however, be noted that the cadmium obtained by cementation normally contains some lead, copper, and residual zinc. To eliminate these constituents, the cadmium is first dissolved in sulphuric acid, when only zinc and cadmium go into solution. When this solution is subjected afresh to cementation by zinc dust, a purer variety of cadmium in the form of a sponge is precipitated. This sponge is redissolved in sulphuric acid, and the solution is electrolyzed in order to obtain pure cadmium.

7.16 IMPERIAL SMELTING PROCESS (ISP)

In this section, we discuss the ISP (already referred to at various places) in detail.

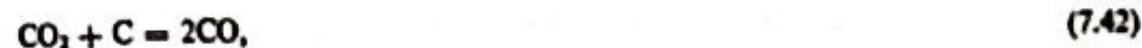
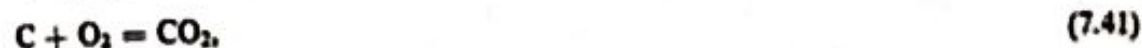
In the ISP, ZnO is reduced by carbon to produce zinc. The reduction is carried out in an Imperial Smelting blast furnace, in which, the zinc that is evolved in the form of a vapour is condensed by using molten lead.

Before taking up the actual process, we list some of the advantages that the ISP has over other processes:

- (1) It is possible to simultaneously smelt low-grade complex mixed charges of zinc and lead ores and concentrates in order to recover both zinc and lead.
- (2) Since the overall thermal efficiency is higher, the recovery of zinc becomes less expensive.
- (3) A wide variety of furnace sizes are available, the trend being towards units with larger capacities at lower operational costs.
- (4) The furnace operation is fully automated.
- (5) The mechanism is highly robust, i.e., it can withstand frequent shut-downs and restarts.

Figure 7.27 shows a simplified diagram of the Imperial Smelting blast furnace and Fig. 7.28 depicts the zinc recovery system.

The smelting reactions that take place in the blast furnace are



Besides the reduction of ZnO to Zn, PbO is reduced to Pb, Fe_2O_3 to Fe, and certain sulphates to sulphides. Reaction (7.43) proceeds in the forward direction, but can be reversed in some regions of the furnace. The amount of reduction per unit of carbon consumed is governed chiefly by the heat balance for the unit operation.

After the reduction has been completed, the molten slag and lead are taken out of the furnace hearth at a temperature that is approximately equal to the melting point of the slag,

whereas the gases generated emerge from the top of the furnace at a temperature slightly higher than the equilibrium temperature for reaction (7.43). The latter temperature is raised to 1000°C

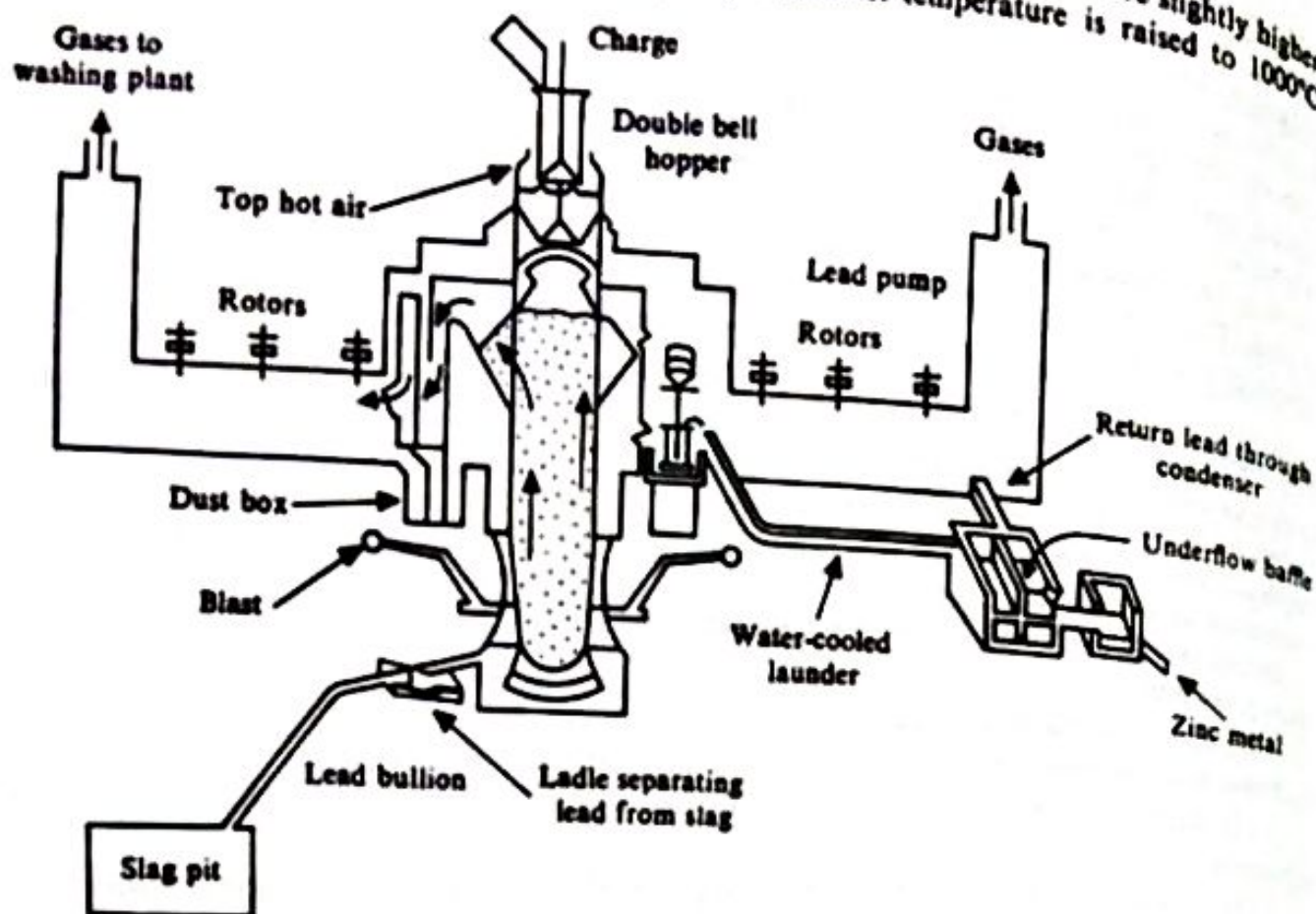


Fig. 7.27 Imperial Smelting Blast Furnace.

by admitting air above the top of the furnace charge in order to generate heat by the combustion of CO. At this temperature, zinc could be collected without back reaction. The heat balance for the blast furnace reduction of zinc oxide is much more favourable than that for the conventional retort reduction, i.e., the amount of zinc oxide smelted per unit of carbon consumed is much higher.

The basic process during the smelting of zinc oxide is the combustion of carbon in preheated metallurgical coke which produces gaseous carbon monoxide. This monoxide affects the reduction of ZnO and PbO in a sinter with a very low sulphur content.

Preheated coke (800°C) and sinter are charged into the top of the ISP furnace. The lead in the sinter, which is reduced to liquid metal, flows down to the bottom of the furnace. In so doing, it collects copper, silver, and gold together with other elements contained in the furnace charge. (This liquid lead is called lead bullion.) The other product that is removed from the bottom of the furnace is a relatively barren slag. This slag and the lead bullion are tapped together from the bottom of the furnace and are separated by the difference in their density values. This bullion is usually cast into one-ton ingots which are subsequently refined by conventional refining methods.

The ISP furnace is of a square cross-section and consists of a water-jacketed brick-lined shaft. Since the feed arrangement at the top of the furnace operates under a positive pressure,

it becomes necessary to introduce the preheated coke and sinter through a double bell charging system. The furnace gases generated during reduction, pass upward through the charge and are evenly divided between two condensers. These condensers serve two purposes, i.e., they very rapidly cool the furnace gases, resulting in the condensation of the zinc contained in these gases and they help in dissolving the condensed zinc in molten lead. Each condenser (see Fig. 7.28)

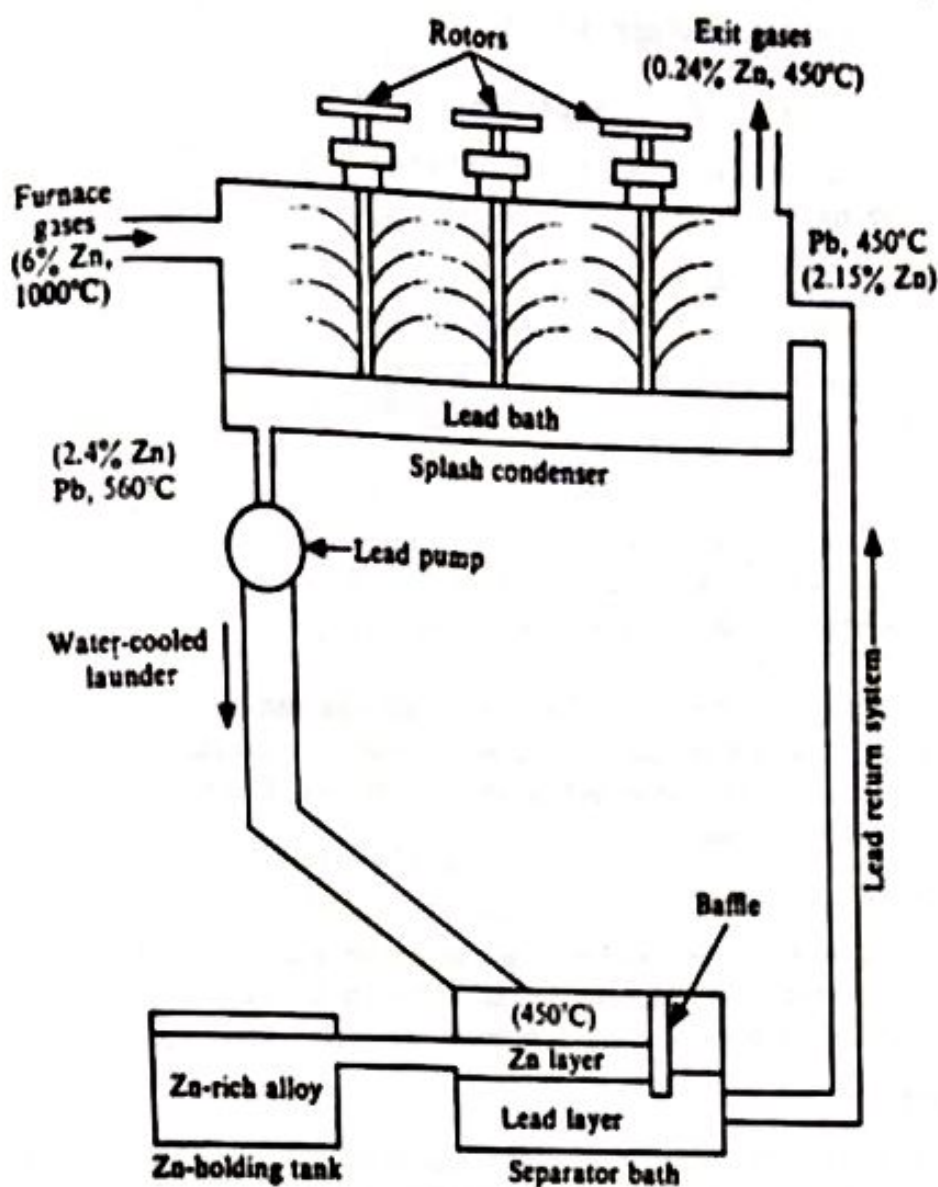


Fig. 7.28 Zinc Recovery System (after Pehlke, 1973).

consists of a bath of molten lead. Rotors capable of generating an intense spray of lead droplets over the entire volume of the condenser are immersed into the molten lead bath. When the furnace gases (containing zinc) pass through this spray, they are cooled very rapidly. (Such shock cooling minimizes the reoxidation of Zn by CO_2 .) As a result, the Zn vapour present in the furnace gases either goes directly into solution with the lead or forms liquid zinc, which, in turn, immediately dissolves in the lead.

The zinc-containing lead is constantly pumped out from the condensers at a temperature of about 550°C into water-cooled launders, where it is cooled to a temperature of about 440°C. During cooling, the lead becomes saturated with zinc, and any excess zinc emerges from the

lead and floats in the form of rivulets on the surface of lead because the density of zinc is less than that of lead. The supernatant zinc is separated and the lead is continuously returned to the condensers. The zinc is collected in a holding tank where it is treated with metallic sodium in order to remove arsenic. At this stage, the metal is of a high grade and is ready for casting.

At present, ISP furnaces operate in the U.K., Zambia, France, Germany, Rumania, Japan, and Canada. The construction of new units in other countries is under way.

PRODUCTION OF OTHER METALS BY ISP

The ISP is well suited to the treatment of a wide variety of complex ores because it combines in one operation the recovery of the zinc metal and the lead bullion containing precious metals, copper, and other elements.

Lead Recovery

In the ISP, a considerable quantity of lead can be produced along with zinc. In this process, additional carbon is not required for reducing the lead. Experimental evidence has indicated that the maximum lead content of the feed sinter should be restricted to 28 per cent; otherwise, the operation becomes difficult, presumably due to the premature softening of the charge.

The capacity of a single furnace, with an area of 27 sq. m, at Avonmouth, U.K., is 100,000 tons of zinc and 75,000 tons of lead per year. At present, the total global annual zinc production by the ISP is about 1 million tons and the total global annual lead production about 0.5 million tons.

In the ISP furnace, molten lead is reduced in a zone high up in the shaft. As this lead falls through the charge, it collects the nonvolatile metals present in the charge (such as silver, gold, copper, antimony, and bismuth) so as to form the lead bullion. This bullion is ultimately tapped from the bottom of the furnace.

Precious Metals Recovery

The precious metals, namely, silver and gold, present in the lead bullion that is tapped from the bottom of the furnace are recovered as in the case of bullion from the lead blast furnace. On an average, 95 per cent of the precious metal content of the sinter is recovered from the bullion.

Copper Recovery

All the copper present in the charge is essentially recovered by the lead bullion. The ISP furnace can treat a raw material in which the ratio of Zn to Cu is 5 to 1.

Arsenic, Antimony, and Bismuth Recovery

In the ISP furnace, arsenic volatilizes and collects in the condensers. It is more of a nuisance because it gives rise to a dross which returns to the furnace; this arsenic eventually leaves the furnace circuit in the form of speiss, and is either tapped from the forehearth or disseminated in the slag.

Antimony is collected in the lead bullion, as is bismuth, the rate of recovery in both cases is over 90 per cent.

Tin Recovery

Tin is an objectionable constituent of zinc for some uses. So, if zinc refining is not practised, tin

the furnace feed should not be allowed to exceed 0.01 per cent. About 10 per cent of the tin input finds its way to zinc product and a separation can be made by the distillation of the zinc either by vacuum dezincing or reflux refining.

Cadmium Recovery

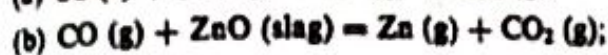
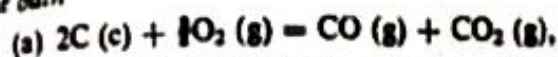
Cadmium is an important byproduct. During the sintering operation, cadmium compounds are volatilized and can be recovered by means of an ion exchange process from the leaching of sludges from gas cleaning. Further recovery of cadmium is effected if the zinc output is subsequently refined.

7.17 ZINC FROM LEAD SLAGS BY SLAG FUMING

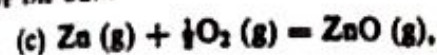
The slags produced in the lead blast furnace are high in zinc (15–18 per cent Zn) and are sent to the zinc fuming furnace for recovery. As zinc is almost always associated with lead, all the lead smelter slags containing zinc are treated for zinc recovery by slag fuming.

The initial development of zinc fuming was carried out by COMINCO in Canada. The molten lead blast furnace slag and the granulated blast furnace slag are charged into a slag fuming furnace. This furnace has no refractory, but has water jackets which ensure a solidified crust of slag to act as lining. Each furnace is 3 m wide, 3 m high, and 8 m long and has about 30 double inlet tuyeres located at a height of 178 cm from the bottom. The inner tuyere of diameter 19 mm is to inject coal and the outer tuyere of diameter 38 mm is for air injection. This furnace treats about 55 tons of slag per heat and about 700 tons of slag per day. In this process, pulverized coal and air at a fixed ratio are blown through the slag. The reactions taking place are:

in the bath



above the bath



Reaction (a) provides the reductant for ZnO reduction and also the heat needed to keep the bath molten. Reaction (b) is endothermic. Reactions (c) and (d) are exothermic and provide heat to the system. The excess heat is collected in boilers located in the gas collection system. The control of the coal to air ratio determines the extent of heat release and is used to maintain the bath at about 1200°C.

The zinc fumes from the slag are collected in bags/Cottrells as zinc oxide. The rate of zinc fuming is dependent on the amount of zinc in the slag as shown in Fig. 7.29. Zinc fuming is normally stopped when the zinc level is about 2 per cent, and the slag is discarded. The economic cut-off value of the zinc in the slag discarded depends on the prevailing zinc price and the operating cost.

The typical analysis of COMINCO slag fuming furnace feed products are shown in Table 7.9.

The recoveries of zinc and lead are 89 per cent and 98 per cent, respectively. The zinc fume is sent to a zinc plant for zinc recovery. In addition to lead and zinc, other trace elements such as

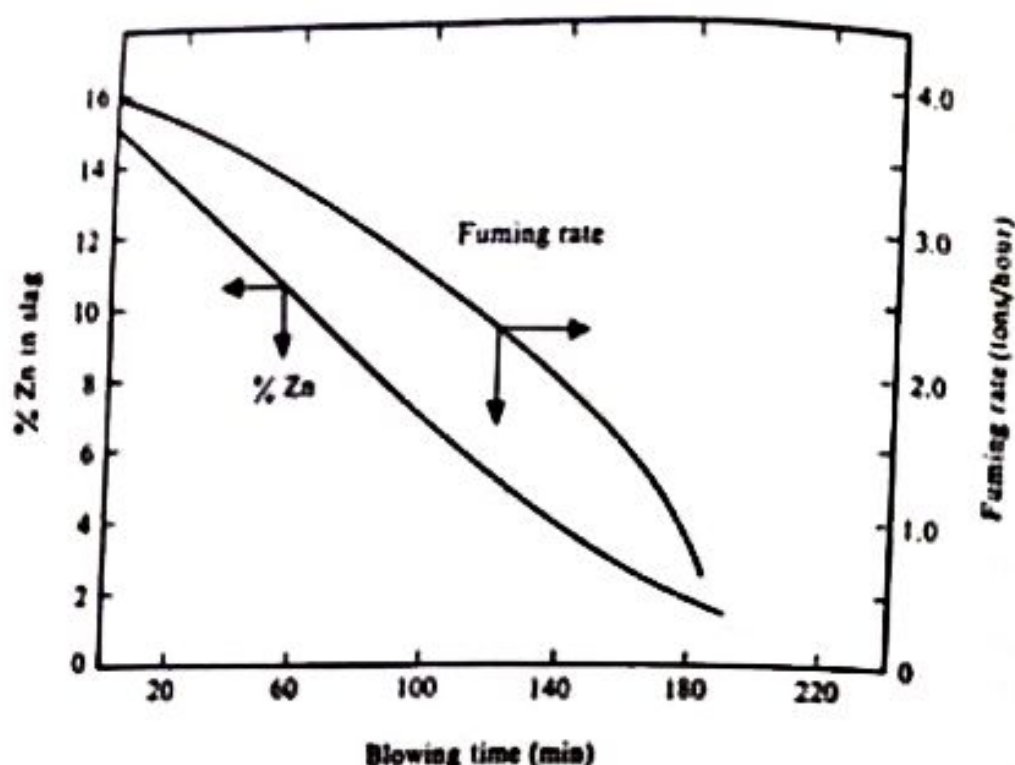


Fig. 7.29 Zinc Elimination During Slag Fuming.

cadmium, indium, tin, and silver are volatilized from the slag and are collected along with the dust.

It has been experimentally determined that the addition of lime to the furnace lead increases the zinc recovery. This is understandable because strong oxide formers such as CaO increase the activity of less stable oxides in ternary slags as per the slag model put forward by Richardson (1974).

Table 7.9 Slag Composition in Zinc-Fuming Furnace (per cent)

Feed/product	Zn	Pb	Cd	S	SiO_2	CaO	Fe
Lead blast furnace slag	17.5	2.5	0.09	1.8	20.8	10.3	27.5
Cleaned slag	2.5	0.05					
Zn fume dust	63.0	9.8	0.10	1.8	0.5	0.2	0.2
Boiler cleaning	59.6	10.5	0.09	0.7	1.8		2.5
Boiler clinker	42.8	14.0	0.06	1.0	6.0		8.0

7.18 PRODUCTION OF ZINC IN INDIA

The annual demands of zinc and cadmium in India are approximately 100,000 tons and 80 tons, respectively. More than half of the zinc demand is met by indigenous production. The entire

Solvent Extraction

A process has been recently developed for obtaining a clean separation of copper from the zinc present in leach solutions by solvent extraction and electrolysis. The leach liquor obtained by sulphate roasting and leaching is purified to remove iron, and zinc is selectively recovered by solvent extraction with a kerosene solution of ethylhexyl phosphoric acid and subsequently stripped from the loaded organic with sulphuric acid or spent electrolyte by conventional zinc electro-winning. If the copper content of the zinc raffinate is high, copper may be recovered directly by electrowinning.

2.2 NICKEL

USES

Nickel and chromium are two strategically important alloying elements that are being increasingly consumed in the fields of chemical processing, space research, and nuclear reactor engineering. Accordingly, the present yearly world production of nickel has exceeded 0.5 million tons. India's nickel requirements are met by imports.

Many uses of nickel are dependent on the combination of the properties of strength and ductility, which the metal possesses. Nickel is also a valuable alloying constituent in more than 1000 commercial alloys which find wide application principally for their mechanical properties and resistance to corrosion and heat.

Steels that contain a high percentage of nickel and chromium are known for outstanding resistance to high-temperature oxidation and strong chemicals such as acids. Ductile nickel-alloyed steels are used in various structural applications. Electric heaters and thermocouples use heat-resistant alloys made of nickel, iron, and chromium.

Nickel forms an important group of alloys with nonferrous metals. Nickel-copper alloys, known as *monel metals*, are used in the chemical oil industry and the electrical industry in applications that require a combination of extraordinary corrosion resistance and strength. Nickel, copper, and zinc alloys, known as *German silver*, are easily formable and are accordingly used in the manufacture of ribbons, bands, and wires for various applications, for example, in medical instruments. Pure nickel is used as a catalyst in many reactions, for example, in the hydrogenation of vegetable oils.

2.2.1 EXTRACTION OF NICKEL BY PYROMETALLURGY

Nickel ores occur both in the oxidic and sulphidic forms. As seen from Table 7.10, production from the sulphidic ores had predominated, but in the future, the oxidic ores will play an ever-increasing role.

EXTRACTION FROM SULPHIDE ORES

The principal sulphide mineral of nickel is pentlandite $[(NiFe)_9S_8]$. Nickel also occurs to a minor degree as violarite (Ni_2FeS_4) and as a solid solution in pyrrhotite (Fe_7S_8) which often occurs with pentlandite. As seen from Table 7.10, Canada is the principal nickel producer and INCO accounts for nearly 80 per cent of this production. The process flowsheet used by INCO for nickel extraction is shown in Fig. 7.32.

Table 7.10 World Production of Nickel Ores (in 1000 tons)

Location/source	1960		1975		1990 (estimated)	
	Sulphide	Oxide	Sulphide	Oxide	Sulphide	Oxide
Europe	2.1		5.0	8.6	5.0	65.0
Asia						
India		0.6		25.1		5.0
Other Asian countries						185.0
Africa	3.2		40.7		75.0	
Canada	194.6		244.8		340.0	
U.S.A.		11.4		13.2		
South America and Central America				29.6		15.0
Australia			60.0			135.0
New Caledonia		53.5		110.0	50.0	70.0
Sea nodules						225.0
Total	199.9	65.5	350.5	186.5	470.0	450.0

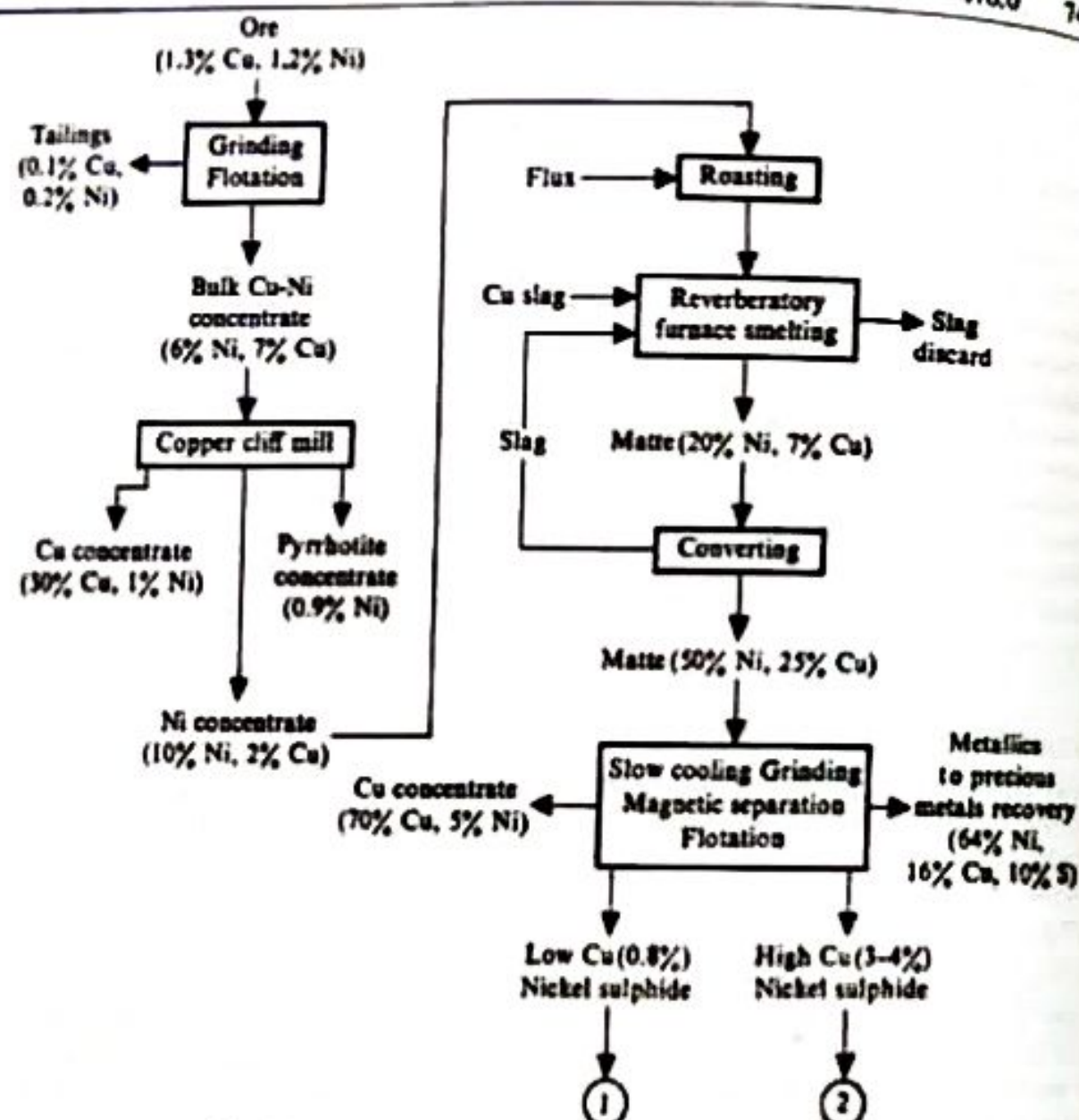


Fig. 7.32 Nickel Extraction (INCO process) (cont.).

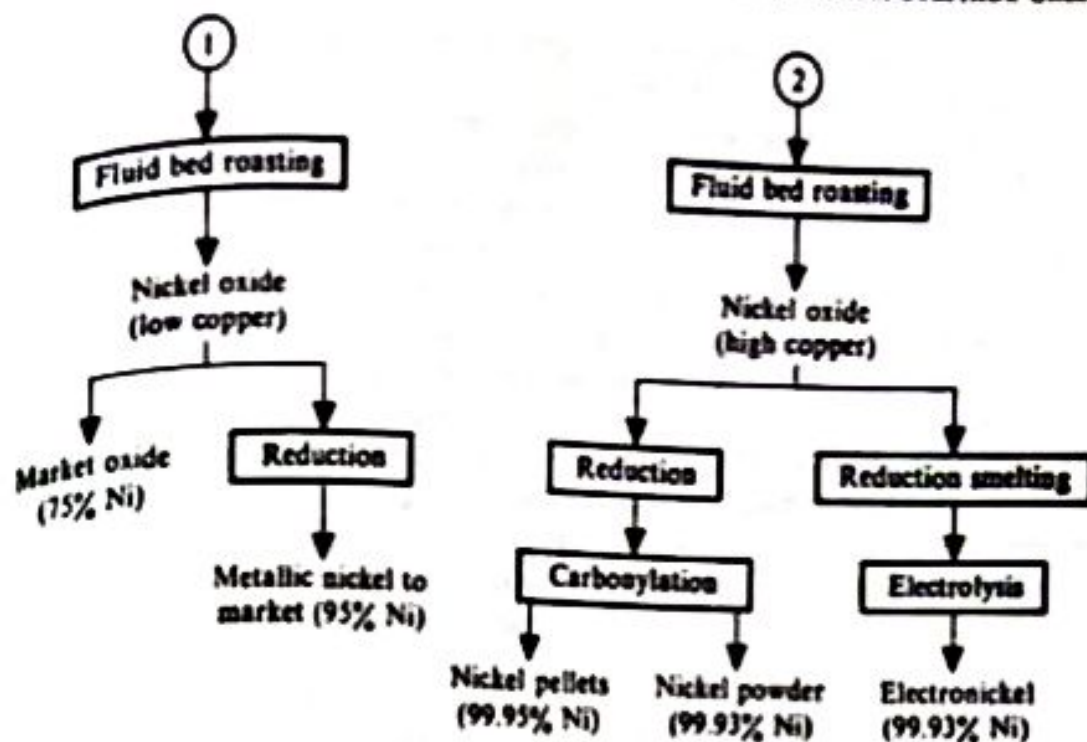


Fig. 7.32 Nickel Extraction (INCO process).

Nickel Sulphide Ore Processing at Sudbury (Canada)

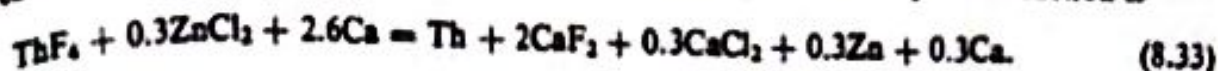
The ore at Sudbury is a mixed copper-nickel ore with nearly equal amounts of copper (as CuFeS_2) and nickel (as pentlandite and pyrrhotite). About 60,000 tons per day of 1–1.5 per cent Cu and 1–1.4 per cent Ni ore are mined from 14 mines and sent to four different mills. These mills employ grinding and froth flotation to produce a bulk concentrate which is sent to the Copper Cliff mill for separation into copper concentrate, nickel concentrate, and pyrrhotite concentrate. The copper concentrate is subjected to oxygen flash smelting described for copper extraction. The pyrrhotite concentrate, which is essentially iron sulphide with about 0.8 per cent Ni, is roasted in order to yield iron oxide, from which nickel is recovered by leaching. Subsequently, iron ore pellets are produced from the leached iron oxide. The nickel concentrate containing about 10 per cent Ni, 2 per cent Cu, 40 per cent Fe, and 30 per cent S is sent to a smelter for nickel extraction.

Smelting of nickel concentrate

As in the case of copper, nickel, too, has to be separated from the iron present in the sulphide concentrate. In the conventional process, this is done in both the smelting and converting stages. To aid iron rejection in the smelting stage, the concentrate is first partially roasted to selectively oxidize the iron sulphide. This is done either in a multiple hearth roaster or in a fluid bed roaster. The latter is preferred because of its high throughput and the rich SO_2 gas stream it generates. During partial roasting in the temperature range 550–600°C, about 40 per cent of the sulphur is oxidized and enough heat is generated to make the roasting in the fluid bed autogenous.

The roasted calcine, which also contains the desired amount of siliceous flux, is smelted in a reverberatory furnace to produce a matte containing the Cu and Ni values and a slag containing the gangue and oxidized iron. The matte typically contains 20 per cent Ni, 7 per cent Cu, 40 per

in this case. ZnCl_2 also aids in the formation of a low melting Th-Zn alloy. The reaction is



The alloy normally contains 5-7 per cent zinc and melts at about 1200°C ; the metal yield is more than 90 per cent. To obtain pure thorium from the alloy, zinc may be distilled off in a graphite crucible by applying a vacuum less than $10\text{ }\mu\text{m}$ and heating to a temperature of about 1000°C . Thorium remains behind as a sponge which is subsequently consolidated.

FUSED SALT ELECTROLYSIS

The electrolytes that have been tried for the fused salt electrolysis of thorium compounds so far may be classified as (1) chlorides, (2) fluorides, and (3) oxides. We now list some of the baths employed along with the advantages and disadvantages associated with them:

Electrolyte	Remark
ThCl_4 in NaCl or KCl ; graphite anode and molybdenum cathode; temperature $750\text{--}850^\circ\text{C}$	The hygroscopic nature of the chloride creates problems; these may be overcome by preparing the chloride <i>in situ</i> by chlorinating a mixture of ThO_2 and starch at 850°C A more or less continuous operation is possible
KThF_6 in NaCl and KCl ; graphite anode and molybdenum cathode; temperature $750\text{--}770^\circ\text{C}$	Fluorides are not hygroscopic, but unlike chlorides, they accumulate in the electrolyte, raising the melting point of the bath and the electrical resistance A continuous operation is difficult
ThO_2 in KF-ThF_4 mixture or in NaCl-KCl-ThCl_4 mixture	Laboratory investigations have reported successful electrolytic dissociation of ThO_2

Thorium may be further refined by electrolytic processes that are analogous to copper refining processes or by the Van Arkel iodide process.

PRODUCTION OF THORIUM IN INDIA

At present, thorium is produced on a pilot plant scale at BARC. The method adopted involves the calciothermic reduction of ThO_2 pellets on a 10-kg scale. The powders obtained are pyrophoric and special methods have been adopted to overcome pyrophoricity. The sintered and machined pellets produced by powder metallurgy show 98 per cent of theoretical density and are ductile so that a 25-mm-diameter pellet can be rolled into a thin strip to an extent of 90 per cent reduction in thickness by cold rolling without intermediate annealing. Large-sized billets are to be produced by vacuum arc melting of consumable electrodes.

8.9 EXTRACTION OF ZIRCONIUM

Before describing the extraction of zirconium, let us discuss some of its properties. The most important property of zirconium is the low value of absorption cross-section for thermal neutrons. This value is only 0.15 barn per atom as compared with 8.21 for aluminium and 2.4 for iron. The metal is therefore highly valued for application in a nuclear reactor as a cladding element.

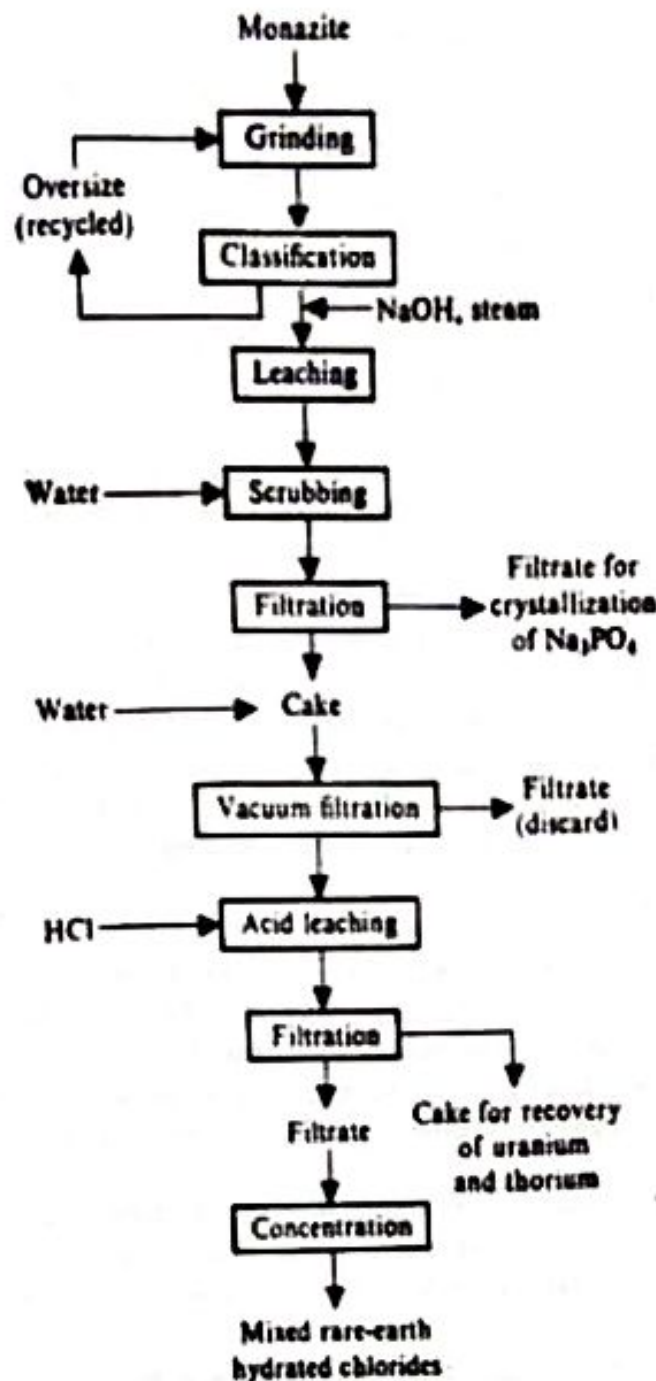


Fig. 8.21 Production of Rare-Earth Chlorides.

8.17 TITANIUM

Titanium is playing an increasingly important role in this age of special alloys. The strength-to-weight ratio of titanium is very high, almost twice that of steel, and its corrosion resistance is better than even 18-8 stainless steel. Titanium alloys retain their strength even at higher temperatures and show less creep. Many titanium alloys can be age-hardened to enhance their strength properties. The current percentage breakdown of the usage of titanium on a world-wide basis is broadly as follows:

- (1) Jet engine components, 45.
- (2) Air frames, 25.
- (3) Missiles and spacecraft, 20.