

PROCESSING OF POLYMETALLIC SEA NODULES : AN OVERVIEW

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ABSTRACT

Polymetallic sea nodules are the potential sources of copper, nickel, cobalt and manganese. As the land based resources of these metals are depleting very fast, a considerable R&D effort have been made all over the world to extract the metals from the sea nodules during the past four decades. The paper summarises the processes developed by various R&D organisations and metallurgical consortia for the extraction of metal values from the sea nodules.

Since the copper, nickel and cobalt in the sea nodules are in oxide forms and they associate in the lattices of iron and manganese minerals, for extraction of these metals the lattices are broken either by hydrometallurgical reduction or by reductive pyro-treatment. Based on this criteria, processing methods have been broadly divided into two categories : (i) pyrometallurgical treatment followed by hydrometallurgical processing and (ii) purely hydrometallurgical processing. Processes developed under these two categories have been discussed highlighting their merits and demerits. Pilot plant studies carried out by various metallurgical consortia like Knecott Copper Corporation, Deep Sea Ventures, Metallurgie Hoboken - Overpelt, International Nickel Company are also given. The R&D efforts made in India in the processing of sea nodules during last one decade and the future programme are also discussed.

KEY WORDS : Polymetallic nodules, Review, Various Processes, R&D work in India.

INTRODUCTION

The manganese and iron concretions known as manganese nodules or polymetallic sea nodules contain many valuable metals like Cu, Ni and Co besides trace amounts of Zn, Mo, Pb, V, Ti, Au, Pt, Ti, Zr, Ag, Cd etc., were first discovered by H.M.S. Challenger Expedition during 1872-76. As the land-based resources of nonferrous metals are rapidly depleting, interest in finding ways for recovering valuable metals from the sea nodules is increasing. It has been indicated that the land based reserves of non-ferrous metals particularly manganese, nickel and cobalt are meagre compared to the potential reserves in sea nodules. A comparison between land based reserves and ocean reserves for Cu, Ni, Co and Mn is given in Table-1 (Das, 1989).

TABLE - 1 (Das, 1989)
Estimated Reserves of Cu, Ni, Co and Mn

Metals	Reserve (Million tonnes)	
	Land Base	In Manganese Nodules
Mn	5400	6000
Ni	54	290
Cu	498	240
Co	1.5	60

The estimated total reserves of manganese nodules in the world ocean range from 1 to 3 trillion tonnes. These include mainly Pacific, Atlantic and Indian Oceans. This indicates that the exploration and exploitation of manganese nodules is necessary to meet the future demands of Cu, Ni, Co and Mn in the world. This is more relevant for a country like India where there is almost no primary resources for nickel and cobalt. Also the land based resources for copper ore are depleting very fast.

Although the economic potentiality of recovery of Cu, Ni, Co and Mn from nodules has long been recognised, it was only in the last two decade or so that experiments on extracting methods were conducted. Numerous processes for the extraction of valuable metals from sea nodules have been described in the literature. The present paper describes the basis for development of various extraction methods as well as some important processes carried out by different metallurgical consortia on pilot scale. The R&D efforts made in India in the processing of sea nodules during last one decade are also discussed.

ASSOCIATION OF METALS IN NODULES AND BASIS FOR EXTRACTION

The extraction of metals will be governed by the physico-chemical properties of the sea-nodules. The manganese dioxide and iron oxide phases in nodules are enriched with the metals. The particle size of these phases are so small (about 100 Å) that application of any physical separation method is practically of no use (Johnson and Glasby, 1968). As such, no mineral beneficiation procedure to concentrate manganese nodules is detailed in the literature. Another important physical characteristic of the nodules is their high porosity which is about 60% (Jana, Singh

and Roy, 1997) and due to this the moisture content is as high as 35% on weight basis (Han, 1971). This causes adverse effect on the efficiency and cost of the processing schemes that require prior drying of the nodules. It is seen that when nodules are heated in the temperature range of 100-1000°C, about 40-70% of the total heat supplied is used to evaporate water (Han and Fuerstenau, 1975). Another characteristics associated with the porosity of the nodules is their fragility. This decreases the energy consumption in crushing and grinding.

Mineralogically, the nodules are oxide ores and the major phases are (U.N.O.E.T.B., 1968; Cardwell, 1973):

- (i) Todrokit : Oxides of manganese, magnesium, calcium, sodium and potassium which may be chemically stated as $(Ca, Na, Mn^{2+}, K)(Mn^{4+}, Mn^{2+}, Mg)_6 O_{12} \cdot 3H_2O$.
- (ii) Buserite or 10\AA manganite : a sodium manganese oxide hydrate.
- (iii) Birnessite or 7\AA manganite : $(Na, Ca)_3 Mn_{70} O_{140} \cdot 28H_2O$.
- (iv) Vernadite or MnO_2 .

The elements Cu, Ni and Co occur as substitute for Mn^{4+} , Mn^{3+} , Mn^{2+} and Fe^{3+} in various manganese and iron oxide minerals (Burns and Burns, 1977). The minor elements may also occur as adsorbed species on manganese and iron oxide surfaces as co-precipitates along with the manganese and iron oxides (Murray, Healy and Fuerstenau, 1968). Since the valuable metals in nodules are present as integral part of the iron and manganese oxides, it is essential to release them by disintegrating the matrix of iron and manganese oxide lattice in order to achieve high recovery of metals. This can be achieved by subjecting the nodules to reducing condition. In pyrometallurgy such reduction is done by roasting with gaseous, liquid or solid reductants, while in hydrometallurgy this is done during leaching with reducing agents.

Processing of Nodules by Pyrometallurgical Methods:

A number of processes such as chlorination, sulphation, smelting etc. have been tried to extract valuable metals from sea nodules. In chlorination, hydrogen chloride in the temperature range 500-800°C has been used for roasting. The chlorides are then water leached (Lenoir, Van Peteghem and Feneau, 1981). Segregation roasting in presence of $NaCl$ & $MgCl_2$ has also been tried with carbonaceous materials (Hoover, Han and Fuerstenau, 1975; Diaz, 1958; Kane and Cardwell, 1973). The metals are segregated on carbon particles and can be separated by sieving, magnetic separation or leaching. Sulphation roasting has been tested by a number of investigators (Van Hecke and Bartett, 1973; Pahlman and Khalafalla, 1979). Metals in the nodules are converted to their sulphates by the action of sulphur dioxide and oxygen mixture. Baking of sea nodules with concentrated sulphuric acid also produces water soluble sulphates of copper, nickel, cobalt and manganese (U.N.O.E.T.B., 1968).

The reduction roasting of sea nodules with carbonaceous materials at 700-800°C followed by ammonia leaching has been tried by a number of investigators (Wilder, 1973; Srikanth et.al., 1997; Jana and Akerkar, 1989). Smelting of nodules is carried out in presence of carbon or coke at about 1000°C (Beek and Messner, 1970). The metallic alloy phase is treated hydrometallurgically for separation and recovery of metals.

Hydrometallurgical Processes

Hydrometallurgical processing of sea nodules includes mainly acid and alkali leaching with or without reducing agents. From the Eh-pH diagram (Fuerstenau and Han, 1983) it is evident that valuable metals in the sea nodules are soluble in acidic media particularly under reducing atmosphere. Simple sulphuric acid leaching at 100°C temperature yields good recovery of copper, nickel and cobalt after a long time (Han and Fuerstenau, 1975). Therefore to enhance the kinetics of the leaching, pressure leaching at higher temperature has been adopted (Nathsharma and

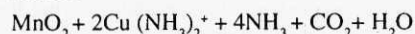
Sarma, 1987). Since hydrochloric acid has good reducing property, the recovery of metals in this acid is good even at ambient temperature and pressure (Kanungo and Jena, 1988). However, as the sea nodules contain major acid soluble materials such as calcium, magnesium, sodium, silicate etc. the acid consumption is relatively high in the acid leaching processes. Sulphur dioxide in acid medium and sulphurous acid have been widely used for leaching of sea nodules and recoveries of valuable metals are found to be good (Han and Fuerstenau, 1983; Kanungo and Das, 1988). Direct ammonia leaching of sea nodules in the presence of reducing agents such as Mn^{2+} or Cu^+ ions have been reported (Acharya and Das, 1987; Szabo, 1976). Sulphur dioxide or sulphurous acid is also used as reductant in ammoniacal leaching to improve the selectivity of leaching of valuable metals (Das, 1989; Pahlman and Khalafalla, 1979). The use of glucose, ferrous ion, acetylene black, thiosulphate etc have been reported in the ammoniacal leaching (Han, 1997). The other reducing agents used in the leaching of sea nodules in acidic medium are alcohols (Jana et. al., 1995), charcoal (Das, Anand, Das and Jena, 1989), hydrazine (Han and Fuerstenau, 1980), pyrite (Kanungo and Jena, 1988), sodium sulphide (Jana, 1993), hydroxyl amine hydrochloride (Han and Fuerstenau, 1980), matte (Chen, Chongyue and Di-Ji, 1992) etc. Use of all these reducing agents recover good amount of manganese also.

PROCESSES DEVELOPED BY VARIOUS METALLURGICAL CONSORTIA

Most of the information on research and development work on processing of sea nodules by various metallurgical consortia are available in the form of patent literature. The present review concentrates on the work carried out by four important consortia namely Kennecott Copper Corporation, Deep-sea Ventures (DSV), Metallurgie Hoboken-Overpelt (MHO) and International Nickel Company (INCO).

Kennecott Copper Corporation Process :

In this process leaching of sea nodules is carried out in ammoniacal solution in presence of cuprous ions. The objective is to recover Cu, Ni and Co in solution rejecting Fe and Mn in residue. The cuprous ions which forms ammine complex, acts as reducing agent and reduces manganese dioxide in the nodules, releasing Cu, Ni and Co into solution, while manganous ions precipitate as insoluble manganous carbonate. The cuprous ammine complex is oxidised to cupric state which is again converted to cuprous state by introducing carbon monoxide into leaching reactor.



The net overall reaction is :



A flow sheet of Kennecott process is shown in Fig. 1. Details of leaching process has been given in the patent literature (Szabo, 1976). The key unit operation of the Kennecott Process is the separation of copper, nickel and cobalt from ammoniacal leach liquor by solvent extraction route which is the subject of a number of patents and papers (Agarwal 1976; Skarbo, 1974; Skarbo and Galin, 1975)

Deep-Sea Ventures Process

Chloride and sulphate based routes have been developed by DSV. Direct leaching of manganese nodules in hydrochloric acid has been described in the literature (Kane and Cardwell, 1974; Kane and Carwell, 1974; Kane and Cardwell, 1974). The acid is sufficiently reducing in nature to reduce manganese to soluble divalent state thereby releasing valuable metals from its lattice.

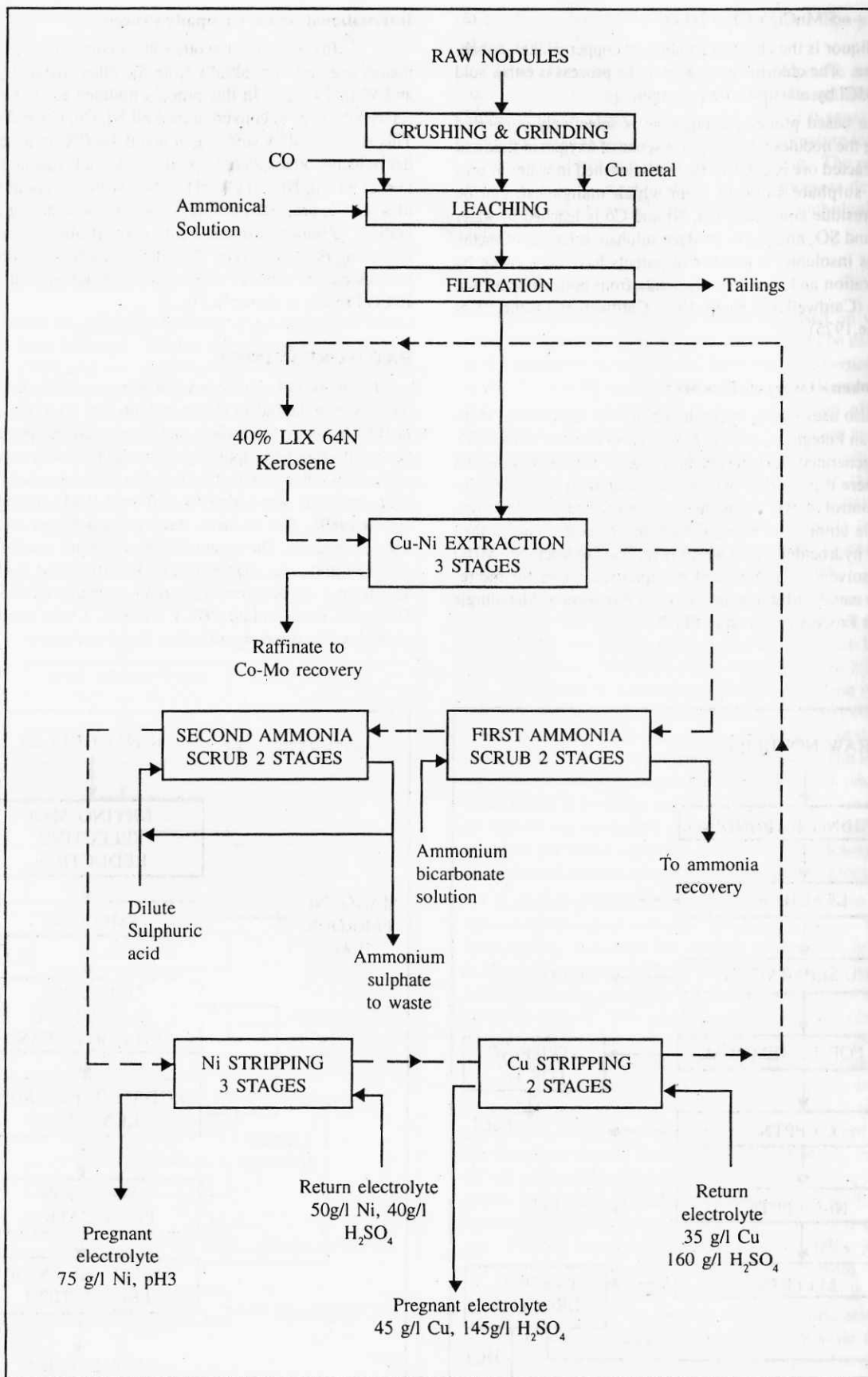
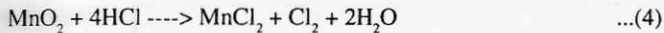


Fig. 1 : Kennecott Process



The pregnant liquor is the chloride solution of copper, nickel, cobalt, iron and manganese. The chlorine generated in the process is either sold or reconverted to HCl by reaction with hydrogen.

In the sulphate based process, manganese is selectively converted MnSO_4 by reacting the nodules with SO_2 in absence of oxygen in fluidised bed reactor. The reacted ore is counter-currently leached in water to produce manganese sulphate solution from which manganese can be electrowon. The residue containing Cu, Ni and Co is leached in water in presence of air and SO_2 mixture to produce sulphate solutions of metal, while iron remains insoluble. A number of patents have been taken by DSV for the separation and recovery of metals from both chloride and sulphate solutions (Cardwell and Kane, 1975; Cardwell and Kane, 1975; Cardwell and Kane, 1975).

Metallurgie Hoboken - Overpelt Process :

This process also uses strong hydrochloric acid as leachant for manganese nodules (Van Peteghem, 1977). However, in contrast to the DSV Process, chlorine generated from the leaching reactor is passed to the end of the process, where it is used to oxidise the manganous chloride solution after proper control of pH. Manganese is precipitated as mixed manganese oxide while chlorine is reduced back as chloride. This is then utilised to produce hydrochloric acid which is recycled to leaching. MHO process involves solvent extraction and precipitation routes for the recovery of valuable metals (Monhemius, 1980). A flowsheet of Metallurgie Hoboken-Overpelt Process is shown in Fig. 2.

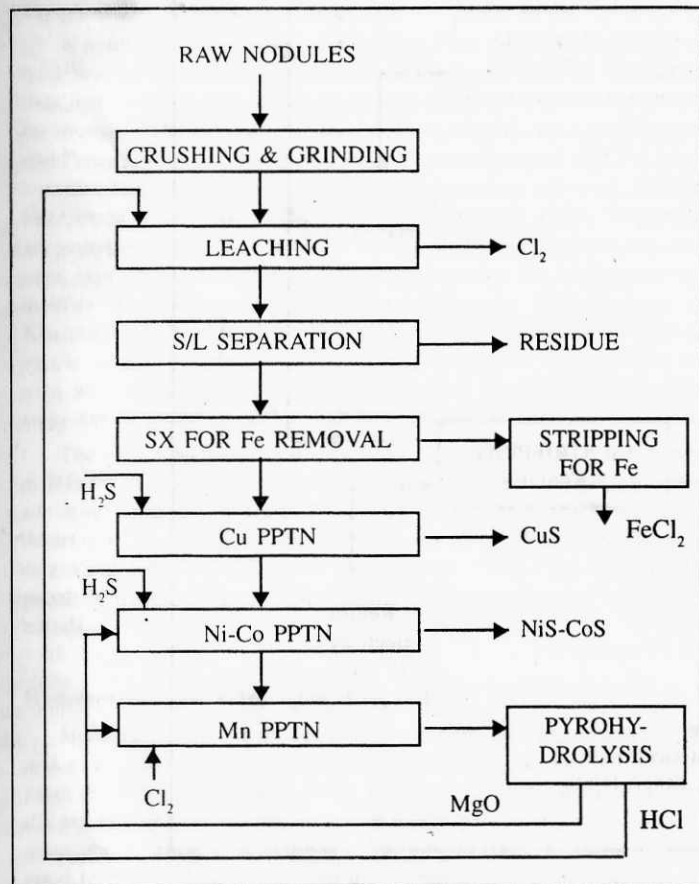


Fig. 2 : Flowsheet of MHO Process

International Nickel Company Process :

In contrast to the other processes, INCO process separates out manganese and iron initially from the other metals by smelting (Sridhar and Warner, 1976). In this process nodules are reduced at 1000°C in a rotary kiln so as to convert almost all Ni, Cu, Co and part of Fe to metal. This is followed by smelting at about 1400°C in an electric furnace under reducing atmosphere to produce Mn rich slag and an alloy containing almost all Cu, Ni and Co. The alloy which is about 6-8% of total nodules feed, is processed through oxidising, sulfidizing and converting operations to remove Mn and Fe, to convert alloy to matte and to remove remaining Fe respectively. The alloy is leached in sulphuric acid and solvent extraction route is suggested for metal separation. A flowsheet of INCO Process is shown in Fig. 3.

R&D WORK IN INDIA

The work in India started sometime in 1975 when NIO, Goa started the survey in the Indian Ocean and the first lot of nodules were collected in 1981 by them. Since then, in different cruise operation, NIO, Goa has been collecting and supplying sea nodules to different R&D laboratories to develop suitable extraction metallurgical processes. Initially about fifteen processes were tried by different R&D organisations (Jana and Nayak, 1989). Out of these, three process routes were chosen for scaling up operation. The organisations which are involved in the scaling up programmes are: (i) National Metallurgical Laboratory (NML), Jamshedpur (ii) Regional Research Laboratory (RRL), Bhubaneswar (iii) Hindustan Zinc Limited (HZL), Udaipur. A brief description of the work carried out by these organisations are given below.

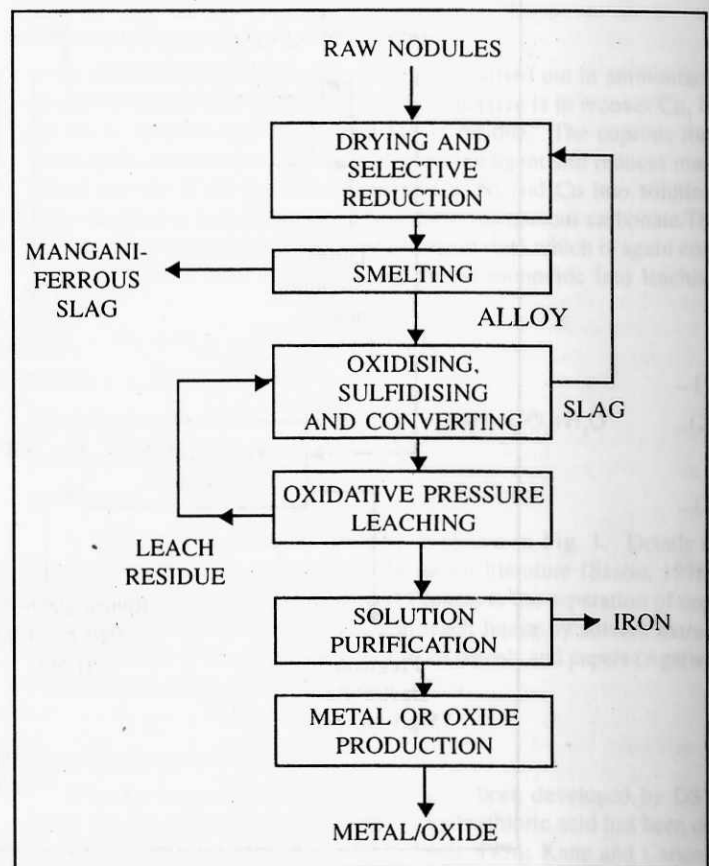


Fig. 3 : INCO Process

NML has developed the reduction roast ammonia leach route based on the Caron process for lateritic nickel ore. The process has the advantage of selective dissolution of copper, nickel and cobalt as their ammine complexes while precipitating iron and manganese in the residue. The process is a combination of pyro and hydrometallurgical methods and consists of the unit operations : (i) Material preparation and reduction roasting (ii) Ammoniacal leaching (iii) Solvent extraction-electrowinning (iv) Ammonia distillation and cobalt recovery (Puvvada et. al., 1997). The process flow sheet developed at NML is shown in Fig. 4. The process has been tested on 100 kg/day scale and a number of campaigns have been carried out to establish the technical feasibility of the process. The metals recoveries are found to be 90% Cu, 90% Ni and 60% Co.

At RRL, Bhubaneswar reduction leaching of sea nodules in ammoniacal medium has been followed. Sulphur dioxide has been used as reducing agent (Das, 1989), and two stage leaching is followed under pressure. In this process both iron and manganese report in the leach liquor. The leach liquor, after iron and manganese removal is subjected to solvent extraction-electrowinning treatment for recovery of copper. Nickel, cobalt and zinc from the raffinate are precipitated as sulphide. The precipitates are dissolved in acid under pressure. The final solution is treated for SX-EW operation for recovery of Ni, Co and Zn. The process has

been chosen for scaling up to 500 kg/day. The process flowsheet is shown in Fig. 5.

Hindustan Zinc Limited carries out sulphuric acid leaching of nodules at elevated temperature and pressure (Basu,1989). Under these conditions, iron becomes insoluble and most of it separates out in the residue. The process consists of preleaching, pressure leaching, impurity removal and solvent extraction-electrowinning. The process flow sheet is shown in Fig. 6. A comparison of the processes developed by various metallurgical consortia and in India on technical basis is given in Table-2.

CONCLUDING REMARKS :

The choice of the process should be based on whether manganese along with the copper, nickel and cobalt should be extracted or not. Most of the published investigations have been concerned with the recovery of Ni, Cu, and Co and less frequently on Mn. However, it has been seen that recovery of manganese have a significant effect on the overall economy of the extraction operation. In that case acid leaching process where manganese remains in solution, have the more advantage over the ammoniacal leaching process where separate residue treatment is necessary for the recovery of manganese. It was found that in the leaching with reducing reagents, manganese is readily dissolved and cobalt also exhibits a good recovery. Therefore, these processes deserve a close examination for treatment of manganese nodules.

Among the various pyrometallurgical process, smelting route followed by INCO appears to be attractive. Here all the manganese and much of the iron go into the slag phase, which can be used to produce ferromanganese. The alloy phase which is about 8% of the feed material, is subjected to leaching and further separation of metals. Thus the solution volume will be much smaller than those generated by the direct leaching process. However, much of the energy in this process is lost in evaporation of moisture content in the nodules. The low temperature pre-reduction followed by ammonia leaching of sea nodules developed by NML seems to be viable as it is very selective as far as extraction of Cu, Ni and Co are concerned and proven technological plant for treatment of nickel ore exists using this process route. However, a separate residue treatment plant is necessary to recover manganese in this process.

A number of hydrometallurgical processes have been developed by various metallurgical consortia as well as in India. The cuprion process developed by Kennecott has realistic approach. The new route devised is direct ammoniacal leaching of raw nodules which is accomplished by utilising reducing properties of carbon monoxide, with dissolved copper acting as catalyst. This procedure eliminates the reduction roasting step which is energy intensive. The drawbacks of the process are generation of carbon monoxide is costly and the gas is health hazardous. The chloride based route developed by Deep Sea Ventures uses strong HCl as leachant and about half of the acid is oxidised to chlorine which is not utilised at the end of the process. This problem has been solved in the process developed by Metallurgie Hoboken-Overpelt. Using potential-pH relationship, the chlorine generated in the leaching step is recycled within the process. Both the processes suffer from the drawbacks of corrosion and pollution problems due to involvements of HCl and chlorine gas. The SO₂ - ammonia leaching route though seems to be an attractive process, however, the removal of iron and manganese from the leach liquor is tedious and recovering manganese from the residues may offset the economics of the process. The sulphuric acid pressure leaching of sea nodules is being carried out on bench scale at HZL. Since it is not yet tried on large scale it may not be possible to comment on it at present.

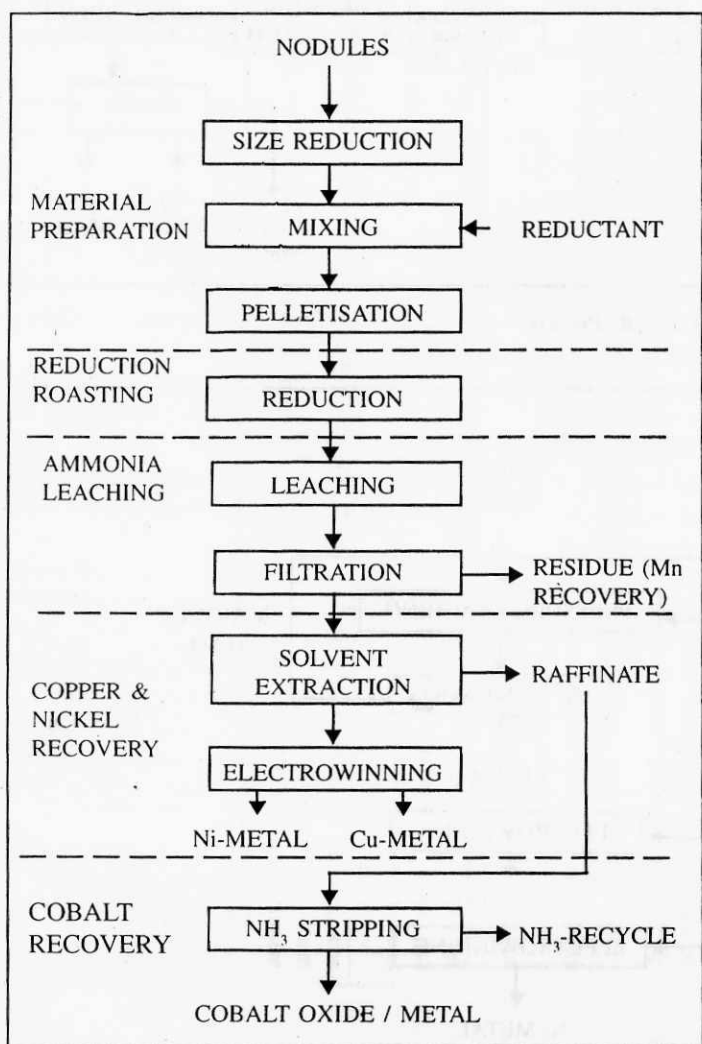


Fig. 4 : Flowsheet of NML Process

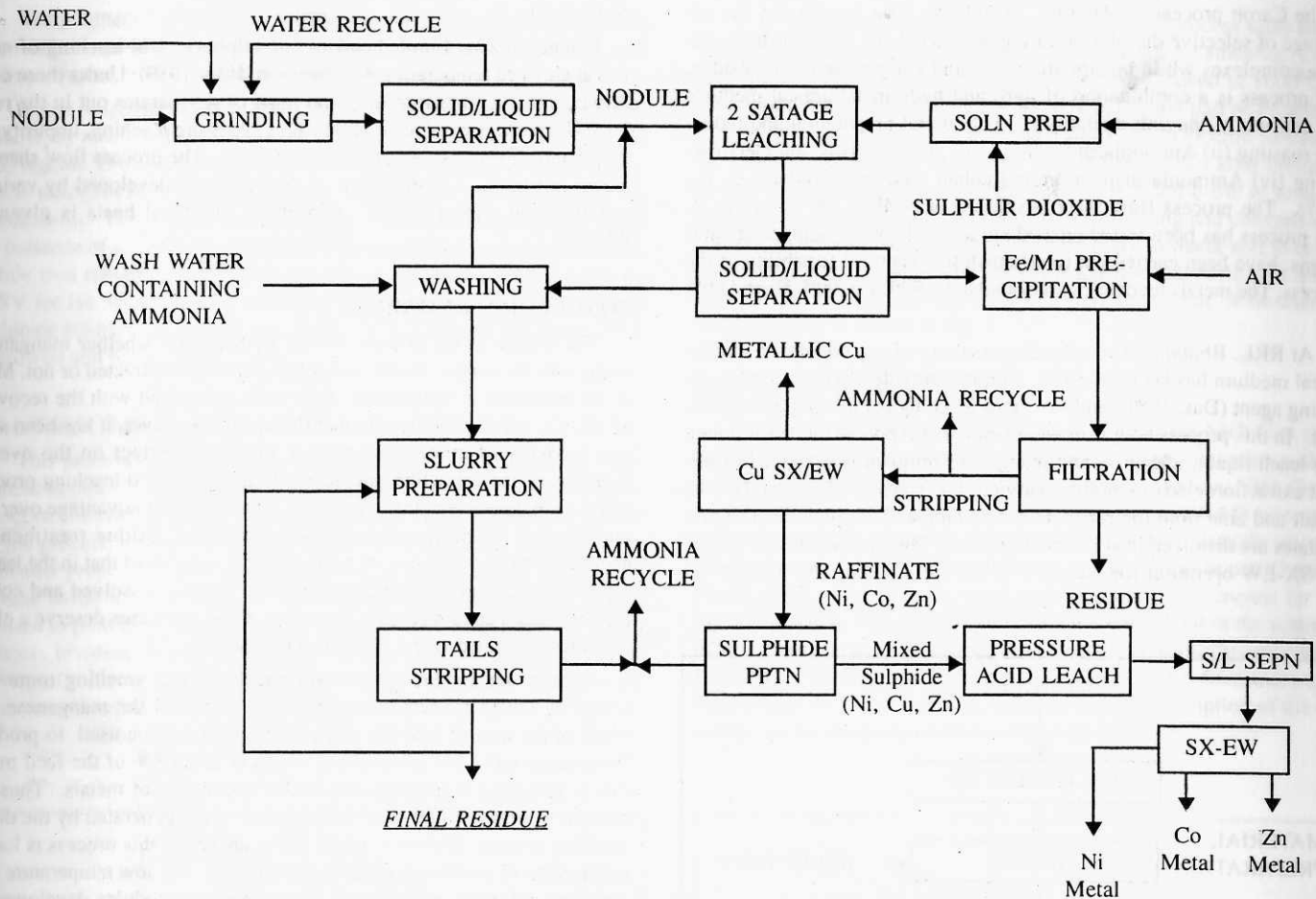


Fig. 5 : Flowsheet of RRL(B) Process

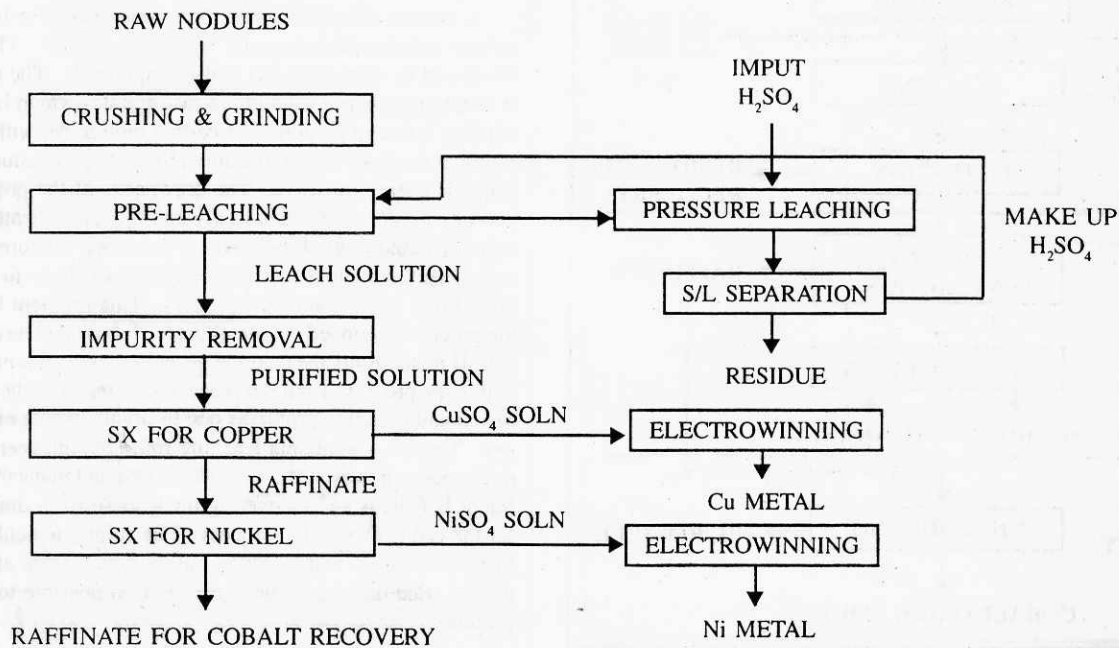


Fig. 6 : Flowsheet of HZL Process

TABLE-2
COMPARISON OF THE PROCESSES DEVELOPED BY VARIOUS METALLURGICAL CONSORTIA AND IN INDIA

Process	Material Preparation	High temp. pretreatment	Leaching method and metal recovery(%)	Metal separation	Develop-mental stage	Remarks
1.Kennecott Copper Corporation	Crushing And grinding	None	Ammoniacal lixiviant in presence of cuprous ions and carbon-monoxide. Recovery: Cu-90, Ni-90, Co - 90	SX-EW and H ₂ S precipitation	Pilot plant	Moisten nodules can be used; selective for Cu, Ni and Co; Manganese is not recovered; CO is health hazardous.
2.Deepsea Ventures	Crushing And grinding	None	Hydrochloric acid leaching. Recovery: Cu-98, Ni-98, Co-98 Mn-98	SX-EW	Pilot Plant	Moisten nodules can be used; manganese recovered; high acid consumption; chlorine evolution and corrosiveness
3.Metallurgie Hoboken-Overpelt	Crushing And grinding	None	Hydrochloric acid leaching. Recovery: Cu-98, Ni-98, Co-98, Mn-98	H ₂ S precipitation	Pilot Plant	Moisten nodules can be used; chlorine utilised at the end of the process; manganese recovered; high acid consumption and corrosiveness
4.INCO	Crushing	Smelting to alloy	Sulphuric acid leaching of alloy. Recovery: Cu-90, Ni-95, Co 95	SX-EW	Pilot scale	High temperature process and hence energy intensive; manganese can be recovered as Fe-Mn or Fe-Si-Mn
5.Reduction-Roast-Ammonia Leaching (NML, India)	Crushing And grinding	Low temperature reduction roasting	Ammonical leaching. Recovery : Cu-95, Ni-95, Co-60	SX-EW	100 kg/day	Selective leaching for Cu, Ni and Co; residue treatment needed for manganese recovery. Process is commercialised for lateritic nickel ore.
6.SO ₂ Ammonia Leaching (RRL-B, India)	Crushing and grinding	None	Ammonical leaching with SO ₂ under pressure. Recovery: Cu-95, Ni-95, Co-85, Mn-30	SX-EW and H ₂ S precipitation	100 kg/day	Moisten nodules can be used, separate treatment for cake and residue needed for manganese recovery, SO ₂ is health hazardous
7.Sulphuric acid Pressure Leaching (HZL, India)	Crushing and grinding	None	Sulphuric acid leaching under oxygen pressure. Recovery : Cu-95, Ni-95, Co-80, Mn-6, Fe-7	SX-EW and H ₂ S precipitation	Lab. Scale	Moisten nodules can be used; iron and manganese impurities in leach liquor; separate residue treatment needed for manganese recovery.

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