# Some observations on the processing of the polymetallic sea nodules at the National Metallurgical Laboratory

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There is now no doubt that the deep sea bed nodules occuring in the oceans are the potential source of major metals of importance to mankind. So for as India is concerned, it has very small deposits of nickel, comparatively less of copper and no cobalt. The annual requirements of nickel and cobalt are met with large import of these metals involving heavy foreign exchange. Copper is also imported to a certain extent as indigenous production is not able to meet the growing demand of this metal. So far as manganese is concerned, the present situation is that, limited resources of good grade manganese ores are available which can not sustain the ferro-manganese industry for long. Under the above circumstances alternate resources of these metals are necessary for the major requirements of various industries. One of the major resource of the above metals is the polymetallic sea nodules from the Indian Ocean which is of great strategic importance to India.

The National Institute of Oceanography, Goa has surveyed[1] the prospecting areas of polymetallic sea nodules in the Indian Ocean and identified the target areas. It is now accepted that the first generation mining area site will have an area of about 30,000 sq. Kilometers and nodule abundance of greater than 6 Kgs. per square meter, preferably over 10 Kgs. per square meter. It should contain more than 2.47% Ni + Cu + Co and reserves of about 60 million tonnes. NIO has classified and identified the target areas as follows :

Marginal $>$2.47% Ni + Cu + Co, Central Indian Basin. Sub - marginal —1.63% to 2.47% Wharton Basin, South West Australia Basin, Mozambique Basin, Scychalles-Somali Basin and West of Lakhshadweep.

A commercial establishment of a future plant processing 3 million tonnes of the nodules per year has been assured on this basis(1). However the results of various analysis show much lower content in respect of the total values of the valuable metals.

The NML has been involved in the analysis of a large number of samples, preparing standand samples from the very beginning of this project work in connection with selection of the mining site in the Indian Ocean. Apart from the analysis of a large mumber of samples, extensive studies have been undertaken in respect of the characterization of the sea nodules for understanding the mineralogical and the morphology of the sea nodules which can help in the selection of the appropriate process studies for recovery of the valuable metals from the nodules.

**Characterisation studies :**

Studies were done by the simultaneous DTA and TG techniques with 499 S. T. A. model apperatus. It was noted that the DTA curve has a sharp endothermic peak at about 140°C followed by smaller endothermic peaks at 440°C and 618°C. The predominant manganese mineral appeared to be vernadite/manganese-manganite with sharp endothermic peak at 140°C. The endothermic peak at 440°C may be due to the decomposition of Goethite (Hydrated iron oxide).

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The TG curue showed the initiation of weight loss at about 70°C and the constancy of weight took place from about 230°C.

According to X - ray diffraction analysis, the following phases were detected in sea nodule samples using Cu $K\alpha$ radiation operating the unit at ratings 35 KV, 20 MA current.

(1) $(MnFe)_5H_2(PO_4)_4 \cdot 4\ H_2O$

(2) 5 CaO, $3Al_2O_3$ (3) $Fe_2O_3H_2O$

(4) CaO $MnO_2$ (5) Ca $SiO_3$

(6) $CaAl_2\ Si_2O_8$ (7) Todorokite

From the above X-ray phases, the first compound appeared to be more as compared to others.

Analysis done by transmission electron microscopy, revealed that Mn mineral is orthorhombic or monoclinic with nearly 90°. The correlation between selected area electron diffraction and field images show the crystal to be thin plated flattened on (001). The basic crystal morphology is fibrous (narrow platelets) instead of parallel as reported by various workers & elongated parallel to b-axis of the monoclinic system. Todorokite appears to be major manganese mineral.

**Extractive metallurgy of deap sea-nodules :**

Since the sea nodules contain significant quantity of free moisture (30—40%) and the valuable metals are in their oxide form distributed in maganese dioxide lattice, the physical methods of beneficiation are not possible. The various processes based on pyro and hydrometallurgical routes which have been developed and are reported in the literature are summarised[2] below :

A. Pyrometallurgical : smelting with flux to produce high manganese slag and a metal alloy.

B. Hydrometallurgical :

(a) Hydrochloric acid leaching.

(b) High pressure sulphuric acid leaching-modified Moa Bay Process.

(c) Atmospheric pressure sulphuric acid leaching.

(d) Sulphur dioxide leaching.

(e) High temperature reduction roast ammoniacal leaching.

(f) Aqueous reduction/ammoniacal leaching—Kennecott Cuprion Process.

Among the processes cited above, the pyrometallurgical processes have not been found favour due to the high water content of the nodules. The hydrometallurgical processes based on chloride or sulphate routes will bring the manganese in the solution alongwith undesirable impurities. Apart from the solution purification all the managanese in solution is undesirable, since the major requirement for manganese is in the from of Fe-Mn, Si-Mn and $MnO_2$ and other manganese based chemicals. It is, therefore, important that any hydrometallurgical process that will reject manganese in the tailings will be most suited. The residue can be treated as and when necessary to produce the most desired manganese based products. On this account two ammonia based processes viz. (a) Reduction roast-ammonia leaching (b) Direct ammonia leaching in presence of Cuprous ions and carbon monoxide have been tried.

(1) Reduction roast-ammonia leaching process :

The reduction roast ammonia leaching process which is commercially being used for the treatment of lateritic nickel ores was applied to the sample of the polymetallic sea nodules. Nodules of different sizes were crushed, dried and ground to—60mesh. The nodules were then subjected to roast reduction in a tubular electric furnace with fuel oil as reductant. The calcine was then leached with ammonia ammonium carbonate solution in presence of air and with agitation. The factors studied in roast reduction were the effect of temperature, amount of fuel and quantity of additives in roast reduction. The kinetics of leaching and the concentration of leachant were studied in detail. The results of the experiments gave high extraction of copper, nickel and cobalt rejecting manganese in the residue. The recoveries were in the order of 99.5%, 95.0% and 78.5% for copper, nickel and cobalt respectively.

(2) Direct ammonia leaching of sea nodules :

The development of direct ammonia leaching process consists in the leaching of ground sea nodules with ammonia-ammonium carbonate solution in presence of cuprous ions and carbon monoxide. The bench scale work in the range of 20 to 300 gms of sea nodules was undertaken and the results were highly encouraging. The recoveries of copper, nickel and cobalt were in the order of over 95%, 95% and 78% respectively in the ammoniacal medium.

Various parameters such as the concentration of ammonia, additive agent, solid to liquid ratio etc. were studied and a flow sheet has been developed. Based on the above flowsheet the process is being scaled up to treat 1 Kg/hr nodules using continuous leaching and counter-current decantation system. Experiments are also being done to recover manganese values from the residue.

**Recovery of metallic values from the ammonical solutions obtained by leaching the polymetallic sea nodules in reduction roast ammonia leaching and direct ammonia leaching processes :**

Leaching solutions generated in the above two processes were furthur processed for the recovery of nickel, copper and cobalt by solvent extraction and electro-winning techniques. Bench scale shake out experiments were carried out in separating funnel with LIX-64 N in kerosene using both synthetic as well as actual leach solutions. Copper and nickel were co-extracted leaving cobalt in the raffinate. The loaded organic was scrubbed for removal of ammonia extracted with the base metals, by treatment with ammonium bicarbonate solution followed by very dil $H_2SO_4$ . After the removal of ammonia, nickel was selectively stripped with dilute sulphuric acid whereas copper was stripped with concentrated sulphuric acid from the loaded organic, thus regenerating LIX-64N for further extraction.

Effect of various parameters viz; organic to aqueous ratio, shaking time on loading and stripping, sulphuric acid conc. in stripping of nickel, have been studied to work out the number of stages in extraction as well as stripping. To recover metals from the stripped solutions, their compositions were adjusted to prepare the electrolytes for electrowinning of the metals. Open type non-diapharagm cells were used, using stainless steel and copper sheets as cathodes in nickel and copper electrowinning respectively, while anodes were made up of lead sheets. Various parameters such as effect of current density, time on current efficiencies were studied. Cobalt was recovered from the reffinate in a novel process of adsorption of cobalt on lignite followed by desorption with sulphuric acid, thereby producing cobalt sulphate solution from which cobalt can be recovered. Alternately cobalt was recovered from the raffinate as basic carbonate of cobalt by distillation of ammonia which was absorbed in water and recycled. The precipitated basic carbonate of cobalt was calcined to get cobalt oxide.

**Recovery of manganese values from the residue :**

The residue from the direct ammonia leaching process contains manganese as manganese carbonate which is eminently suitable for recovery of manganese values in various forms. Preliminary studies have indicated the possibility of producing electrolytic manganese and dioxide and also the pure manganese carbonate or nitrate or the various oxides of manganese used in many electronic applications.

Alternately possibilities are also explored to calcine and blend the residue with good grade manganese ores for smelting to produce ferromanganese of acceptable grades. It is also worth mentioning that in the leaching of the residue with $H_2SO_4$, all nickel, copper and cobalt remaining undissolved in the residue in ammonical leaching also gets dissolved and is easily recoverable by treatment with $BaS/H_2S$ in the production of EMD/EMM. The recoveries of all the four metals viz. Ni, Cu, Co and Mn are thus over 90% and the process therefore appears to be highly economical.

**Scale up operations and future programme :**

The direct ammonia leaching process has proved to be highly successful for recovery of various metal values economically. Attempts are made systematically to scale up the operations to continuous leaching and counter current decantation as well as solvent extraction and electrowinning of the metals. These scale up operations are done with a view to ultimately develope the design data for modification of the three main pilot plants of the laboratory in order to carry out large scale trials for obtaining data for setting up a commercial plant. The three pilot plants are the nickel and the manganese pilot plants and the 500 KVA submerged arc furnace.

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**Discussion :**

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*Question 1* : What is the rate of formation of sea nodules on the sea bed ?

*Author* : The formation and growth of manganese sea nodules is favoured under slow rates of sedimentation. However, it is observed that fresh nodules are formed at the rate of 10 million tonnes a year.

*Question 2* : What is the total deposits of manganese nodules in Indian Ocean ?

*Author* : The total deposits of manganese nodules in the Indian Ocean are in the order of 0.15 trillion tonnes.

*Question 3* : Please give the analysis of rich/high metallic content of the nodules ?

*Author* : Nodules having as high as 37% Mn, 1.55% Ni, 1.36% Cu and 0.9% Co have been found, but the average contents of the metals in Indian Ocean nodules are Mn 15.57%, Ni 0.43% Cu 0.2% and Co 0.18%. However, the target area for the first generation sight in the central Indian Basin would have 2.47% Ni + Cu + Co.

*Question 4* : Which process is the best possible one to win the three metals Cu, Ni & Co ?

*Author* : It is very difficult to give a conclusive answer to this question on the basis of the available published information, since no attempt has yet been made to produce the metals on commercial scale. However, it is possible to compare the various processes developed. It appears that the Kennecott Cuprion Process based on ammonia leaching technology to recover Ni, Cu and Co as electrolytic metals has several advantages over the other processes and the process has been thoroughly tested on the pilot plant scale.

**References :**

1) National Institute of Oceanography, India, Document on "Exploration and Exploitation of Marine Minerals, Part 'B' Manganese Nodules, October 1981.

2) Topics in non-ferrous extractive metallurgy-edited by A. R. Burkin, 1980.