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Recovery of Cu, Ni, Co and Mn from Sea Nodules by Direct Reduction Smelting

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ABSTRACT

Polymetallic nodule contains various metals like copper, nickel, cobalt, manganese, iron, lead, zinc, aluminum, etc. Of these, copper, nickel and cobalt are of much importance and in great demand world over. In fact, due to their extensive technological use these three metals are fast depleting from the earth surface. Hence a world-wide research is progressing on sea nodules as an alternative future source of these metals. India is entirely dependent on imports to meet its requirements of cobalt and nickel both of which are most strategic in nature. In this respect, India has made remarkable progress in recovering these metals from sea nodules. The recovery process so far developed in India is based on either purely hydrometallurgical or pyro-hydrometallurgical routes. The processes generate very dilute leach solution, the downstream processing of which is very difficult. Generation of concentrated leach solution from sea nodule would make the process simpler and economical which may not be possible by direct leaching process. Therefore, it has been planned to explore direct smelting of sea nodules to recover copper, nickel and cobalt along with part of iron in the form of alloy followed by individual metal recovery through matte formation and dissolution. Initial studies on direct reduction smelting of Indian sea nodule were conducted using coke as reductant in lab scale experiments. Various parameters like smelting temperature, reductant concentration, holding time etc. have been optimized to obtain an alloy of suitable composition. At a smelting temperature of 1400 ^{o}C, recovery of 90-92% Cu, 92-95% Ni and 80-85% Co is obtained in the form of alloy in a recrystallized alumina crucible which can be further treated to recover these metals in pure form. The iron content in the alloy varies significantly with coke concentration. The slag generated after smelting can be directly treated for production of standard grade Fe-Si-Mn without blending.

Key Words: Sea Nodule; reduction smelting; Cu; Ni; Co; Mn

INTRODUCTION

Polymetallic sea nodules, better known as manganese nodules, contain valuable metals like copper, nickel, cobalt, manganese & others and are available in plenty in the ocean beds. Available estimates show that nickel and cobalt availability in the manganese nodules is about five and forty times higher, respectively, than that in land-based resources as cited by Das (1989).

Attempts were made to process polymetallic nodule almost forty years back, as an aftermath of the oil crisis. Several oil companies visualized large scale ocean mining, where their expertise on high-sea operations will be useful. This led to formation of several consortiums. Soon, the fluctuating metal prices, the ease of oil crisis, and the lack of a viable mining technology resulted in slowing down, and in most cases, stoppage of metallurgical activities. An excellent review of several processes developed during seventies was prepared by Monhemius (1980) and the similarities and the differences were discussed. The requirement of Cu, Ni and Co by many resource-starved countries like India, Japan, China, and Korea encouraged the research organizations in these countries to develop processes which are economical and environmental friendly. The sea nodules are rock concentrates on the sea bed sediments formed by concentric layers of iron and manganese hydroxide around a core. Metal entities such as Cu, Ni, Co, Mo and Zn are accommodated in the complex cage of iron and manganese hydroxides. Nickel and copper oxides, are distributed and associated with the manganese oxide phase. Cobalt is present as cobaltic oxide, is associated with iron oxide phase. Mineralogical studies of sea nodule have been reported in detail by (Heimendahi, Hubred, Fuerstenau and Thomas 1976). Sea nodules are highly porous due to their inherent morphological structure and, therefore, are associated with high free moisture content. These are often called manganese nodule due to its high Mn content. So far, most of metal recovery processes developed in India for processing sea nodules are hydrometallurgy based, which inherit the associated problem like handling of large volume extractants, dilute leach liquor, very specific downstream processes etc. In this connection, a process to recover Cu, Ni and Co based on reduction smelting is being carried out at NML, Jamshedpur, India. The proposed flow-sheet for this route is shown in figure 1.

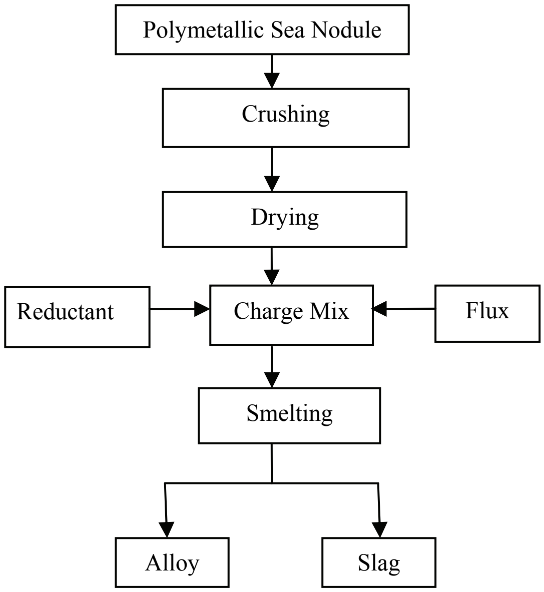

Figure 1- Flow sheet for reduction smelting of polymetallic sea nodules

After removal of Cu, Ni and Co as alloy from sea nodule smelting, the slag generated contains high manganese, which is a good starting material to produce Ferro-manganese or Ferro-silico-manganese from it. The present paper throws light on the lab scale studies carried out for the recovery of Copper, Nickel, & Cobalt as alloy by reduction smelting of polymetallic sea nodules in a recrystallized alumina crucible.

MATERIAL PREPARATION

Growth of the nodules takes several thousand years and the changing environment over their period of development makes the nodule composition non-uniform within individual nodule as well as from other nodules. Material preparation, hence, assumes great importance in homogenizing the nodule composition. In order to homogenize, the nodules, after drying (air/oven), are crushed and ground to suitable size and then mixed thoroughly in a mixer. Along with sea nodule other raw material required are commercial grade quartz, suitable binder and coke. These raw materials were crushed down to minus 100 mesh size fraction. The mixed nodule powder along with quartz, coke and suitable binder is then pelletized to suitable size (10-12 mm). The pellets prepared above are dried in an oven to remove the free moisture. Finally it is subjected to reduction smelting in an electric resistance furnace.

EXPERIMENTAL

The smelting experiments were carried out with charge mix pellets prepared in the disc pelletizer by mixing the calculated raw materials with respect to reductant and flux requirement. Smelting was carried out on 500 Gms scale in an electric resistance furnace. The charge was kept in a recrystallized alumina crucible as shown in figure 2 inside the furnace with lid covered on top of the crucible. Temperature was raised slowly in steps from room temperature to the smelting temperature region. After attaining the desired temperature, the smelting temperature was hold for various time periods to complete all the chemical reactions and, proper alloy and slag separation to take place. On cooling, the slag and alloy metal were separated by gravity as shown in figure 3. A representative sample of alloy and slag was collected by cone and quartering method for chemical analysis. This representative sample of alloy and slag was ground to 100 mesh size for chemical analysis. The major elements were analyzed by standard wet methods and trace element analysis was done with AAS technique using Perkin Elmer Analyst 400.

Figure 2 – Photograph of recrystallized alumina crucible

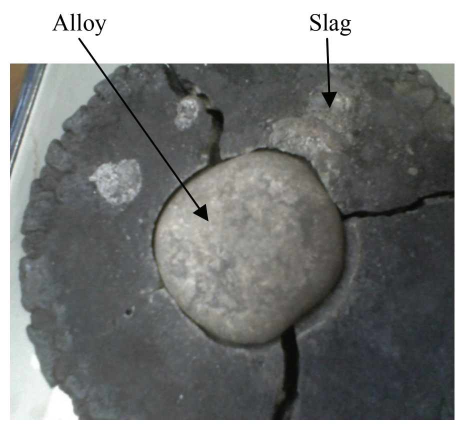

Figure 3 – Photograph of Alloy and slag from recrystallized alumina crucible experiment

RAW MATERIAL COMPOSITION

The chemical compositions for all the raw materials are as follows

Table 1 – Chemical composition of coke and quartz

Coke	Average Content (wt %)
Fixed carbon	77.00
Ash	16.60
Volatile matter	2.35
Moisture	3.80

Quartz	Average Content (wt %)
Silica	92.00
Al_2O_3	1.53
Fe (T)	3.35
L O I	0.37

Table 2 – Composition of Polymetallic Sea Nodule

Sea Nodule	Average Content (wt %)
Ni	1.15
Co	0.08
Cu	1.10
Mn	24.30
Fe	5.36
SiO_2	13.14
Al_2O_3	4.50
MgO	2.70
CaO	0.54
Na_2O	1.02
S	0.31
P	0.01

RESULTS AND DISCUSSION

The basis towards smelting of sea nodules is the well-studied Ellingham Diagram (Ray, Sridhar and Abraham 1985). From the diagram it is evident that with carbon at lower temperature (600 – 950^0C), the higher oxides of manganese and iron are reduce to their lower oxide forms respectively and the oxides of Ni, Co & Cu tends to get reduced to respective metallic state. The oxides of Fe, Mn & Si needs somewhat higher temperature i.e. in the range of 1300 - 1550^{o}C to get reduced to their metallic state. Therefore, it is thermodynamically favorable that with required amount of reductant and maintaining the optimum temperature in the range mention above will result in the reduction of Cu Ni, & Co oxides along with some of iron & manganese in an alloy form. The resulting slag contains almost all the manganese with remaining amount of iron and silica. The basic reaction taking place during smelting (Ray, 1985; Habashi 1997; Haynes, 1985) is described as follows:

$$MnO_2 + CO \rightarrow MnO + CO_2 \quad (1)$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (2)$$

$$CuO + CO \rightarrow Cu + CO_2 \quad (3)$$

$$CoO + CO \rightarrow Co + CO_2 \quad (4)$$

$$NiO + CO \rightarrow Ni + CO_2 \quad (5)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (6)$$

Higher oxide of manganese and iron are reduced to their lower state oxides as in reaction 1 & 2, which break the internal structure of the nodule. This leads to subsequent reduction of copper Nickel, and Cobalt to their metallic state as in reaction 3 – 5. Iron is also reduced to either the Fe^{2+} state or possibly to Fe (reaction 2 and 6). It is desirable to reduce iron only to Fe^{2+} state because Fe may alloy with Ni metal. Formation of FeNi alloy retards and often prevents solubilization of the Ni values associated with the alloy formation.
In this process, at the temperature range of 600 – 950^0C the oxides of Cu, Ni, &Co are reduced to the metallic state, along with required amount of the iron and some manganese in the temperature range of 1300 - 1550^{o}C to form alloy and separate from slag as shown in figure three.

$$MnO_2 + C \rightarrow MnO + CO \quad (7)$$

$$MnO + SiO_2 \rightarrow MnSiO_3 \quad (8)$$

$$2\,MnO + SiO_2 \rightarrow Mn_2SiO_4 \quad (9)$$

$$2\,Mn + O_2 \rightarrow 2MnO \quad (10)$$

$$Fe_2O_3 + C \rightarrow 2FeO + CO \quad (11)$$

$$CuO + C \rightarrow Cu + CO \quad (12)$$

$$NiO + C \rightarrow Ni + CO \quad (13)$$

$$CoO + C \rightarrow Co + CO \quad (14)$$

Under the controlled smelting parameters, the manganese is not reduced to Mn but remains as Mn^{2+} in the slag. The Cu, Ni, Co & Fe form a alloy that settles at the bottom of the crucible by gravity. The reduction while carrying out smelting is performed by using coke and unreduced oxides at that temperature are slagged by using silica. Reaction 7 is for the reduction of Mn^{4+} to Mn^{2+}. Reaction 8 & 9 are the slag formation reactions and reaction 10 is reoxidation of Mn to Mn^{2+}. Reaction 3 to 6 and 12 to 14 shows the various steps for Ni, Co, Cu and Fe reduction to the metallic state. After complete reduction, metal alloy separates from the oxide-silicate slag by gravity. As mentioned above, the temperature, reaction time & amount of reductant are three variables which determine the degree of reduction for manganese nodule smelting. In present study the temperature was kept constant at 1400^{o}C and quantity of reductant in charge mix was varied. Numbers of experiment were carried out by varying the amount of reductant addition, reaction time and at a fixed temperature.

Figure four shows weight corresponds to alloy amount obtained in smelting experiment with using coke in recrystallized alumina crucible. At 2 % carbon, the weight of alloy obtained is 0 Gms, further increasing the % carbon to 3.85, the alloy weight came 9.33 Gms on 500 gms Sea nodule basis and after that it increases with increasing % carbon while doing the smelting studies.

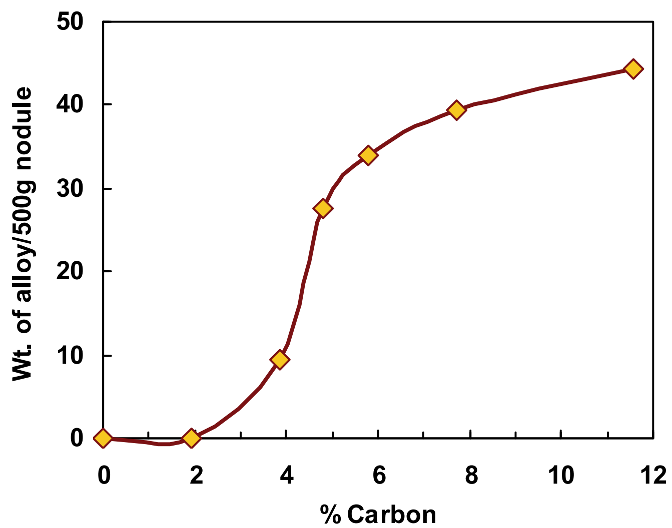

Figure 4 – Weight of alloy obtained with the variation of % carbon in charge in recrystallized alumina crucible

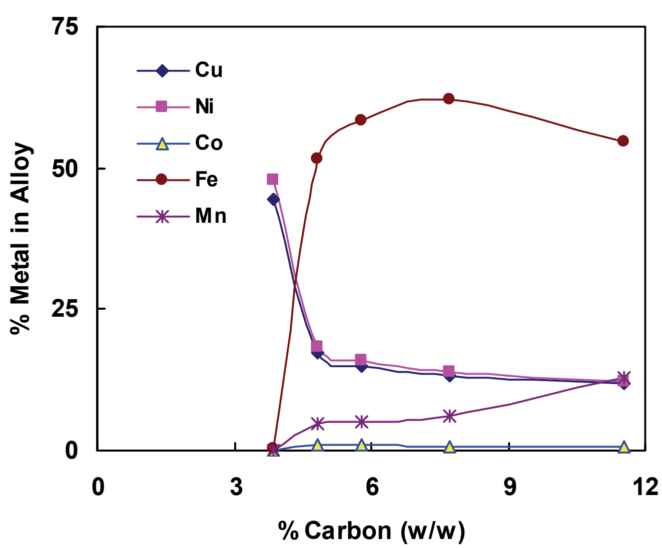

Figure 5 – % of metal in alloy with the variation of carbon in recrystallized alumina crucible

Representative sample of alloy and slag was collected by cone and quartering method for chemical analysis. Chemical analysis shows different % of metal composition in alloy by varying the carbon content in the reduction smelting studies as shown in figure 5. In this figure % of copper and nickel in alloy composition decreases with the increase in carbon %, but there is reverse trend in case of cobalt, iron and manganese. There is % increase of Co, Fe and Mn with the increase in carbon % addition. As the amount of reductant is increasing, more iron and manganese will reduce. Cobalt reduction follows the same pattern as of iron.

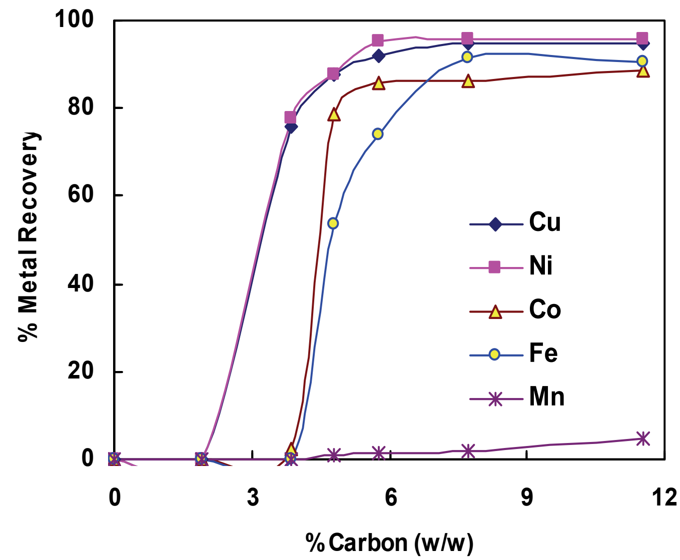

Figure 6 – % Metal recovery with the variation of % carbon in alumina crucible

The recoveries of Cu, Ni, Co, Mn and Fe in the alloy are depicted in figure 6, which shows that at 3.85% carbon addition recovery of 72% Cu, 75% Ni, 2.2% Co, 0.10% Mn and 0.54% Fe was achieved in alloy. Maximum recoveries of Copper Nickel, and Cobalt, along with iron in alloy were obtained with addition of 5.7% carbon. After that with further increase in carbon % addition, there is decrease in the recovery of Cu Ni, & Co as recovery of Mn and Fe increases. Further addition of carbon has not much role to increase the recoveries; rather it led to decrease the recoveries of Cu, Ni, & Co.

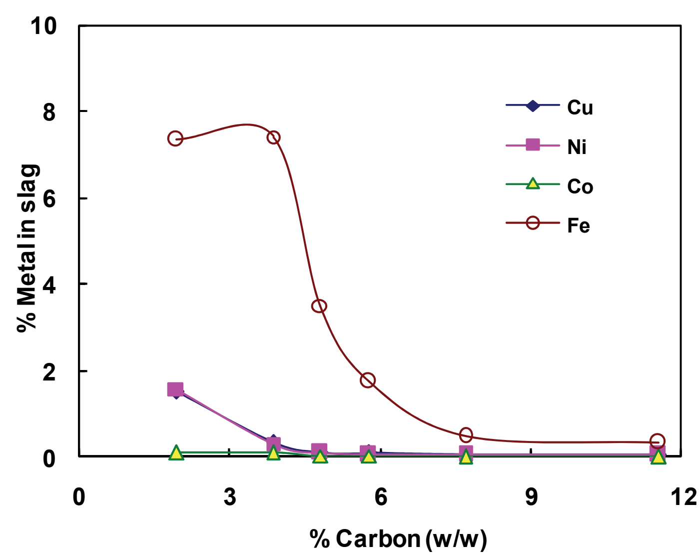

Figure 7 – % metal in the slag with the variation of carbon in alumina crucible

Figure 7 shows the % of different metal that came to slag phase instead of going to alloy phase. Metal in slag is decreasing with increase in carbon %. At 5.7 % carbon we get minimum % of Cu, Ni, & Co entrapped in the slag phase.

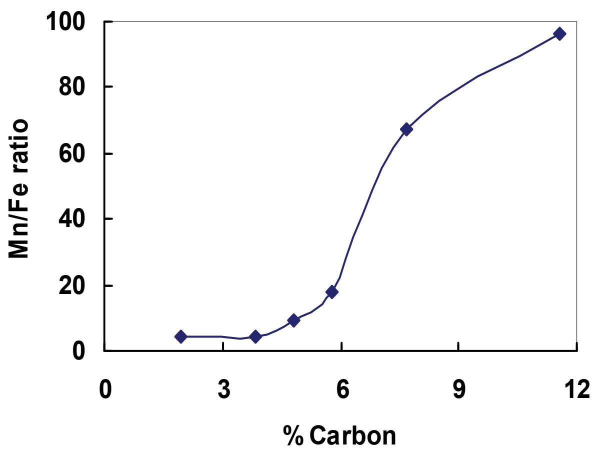

Figure 8 – Effect of carbon on Mn/Fe ratio in slag

Figure 8 shows that the Mn/Fe ratio in the slag is increasing with increase in carbon% addition during smelting. It can be seen that addition of carbon more than 5 % brings down the MnO and FeO content of the slag. This may be due to more reduction of MnO and FeO to their metallic state that would bring more Mn and Fe in alloy metal as shown in the figure 3 & will disturb the Mn/Fe ratio in the slag. At 5.7% Carbon, we have Mn/Fe ratio of around 16 as shown in figure 8. We need a part of iron in the alloy and rest will go to the slag phase to have proper Mn/Fe ratio of slag. There is a desire to have a favorable ratio of Mn/Fe in slag to further recover manganese, iron and silicon either in the form of ferro-manganese or silico-manganese alloys. Hence we have to have a compromise for the recovery of Cu, Ni & Co along with Fe and Mn in the alloy phase. If we increase the amount of reductant , there is increase in the recovery of Cu, Ni, Co, Fe and Mn in the alloy as shown in the figure 3, but this will hinder or add further downstream process steps to recover in there metallic form. Hence there is a tradeoff to be played between recovery of Cu, Ni, Co along with Fe and Mn in the alloy phase. The recoveries of, Cu, Ni & Co in smelting alloy metal are 92%, 95% and 82% respectively at 5.7 % carbon addition seems to look optimum as we have to further down process the alloy to recover copper, nickel, cobalt in the metallic form.
The resulting slag contains high manganese along with iron and silica. The Mn/Fe ratio is more than 7 and hence it can be subjected to ferromanganese or silico-manganese smelting (Riss, 1967; Breg, 2000) after adjusting the charge basicity by addition of flux (quartz or dolomite as required).
Further research is going on, to study the behavior of different % of quartz addition, different holding time at various temperature on the recovery of different metal values from direct smelting of sea nodules in a recrystallized alumina crucible.
The typical composition of alloy and slag obtained after smelting with 5.7 % carbon is given in Table 3 & 4 respectively.

Table 3– Chemical composition of alloy from sea nodules smelting

Element	Wt %
Ni	15.92
Co	0.96
Cu	14.89
Mn	5.02
Fe	58.40
Si	0.11

Table 4 –Chemical composition of sea nodules smelting slag

Slag	Wt %
MnO	42.15
FeO	2.56
SiO_2	27.54
CaO	0.78
MgO	4.41
Al_2O_3	2.74
Cu	0.069
Ni	0.045
Co	0.006

CONCLUSION

Reduction smelting of sea nodule with 5.7 % carbon yields maximum recoveries of Cu Ni, & Co in the alloy form and those are 92% 95%, & 82 % respectively.
Smelting produces manganese rich slag, which has suitable Mn/Fe ratio for ferromanganese or silico-manganese production.

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