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RECOVERY OF COPPER, NICKEL AND COBALT FROM MANGANESE NODULES BY ARC FURNACE SMELTING

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Abstract

Rolymetallic sea nodule contains multiple metals like copper (1.1%), nickel (1.2%), cobalt (0.08%), manganese (24%), iron (5.4%), silica, aluminum, etc. Of these, cobalt, copper and nickel are of much importance and in great demand world over. India has made remarkable progress in recovering these valuable metals from sea nodules following the hydrometallurgical routes. The present paper describes the attempt for recovering these metals from sea nodules by pyrometallurgical route. A number of experiments were carried out in 50 KVA electric arc furnace for reduction smelting of sea nodule. The smelting produced an alloy rich in Cu, Ni & Co. A typical composition of alloy is: Cu: 12.33%, Ni: 14.05 %, Co: 0.75 %, Mn: 8.23%, Fe: 55.96% and a slag consisting of MnO: 42.61%, SiO_2: 33.51%, FeO: 5.66%, (CaO+MgO): 5.42%, Al_2O_3: 6.1%. The recovery of metals in alloy were Cu: 90-95%, Ni: 95-97% and Co:80-85% with 6 % coke addition at temperature of 1400-1550°C.The alloy obtained may be suitably treated further to recover these metal in pure form by pyro or/and hydrometallurgical routes. The slag contained high Mn/Fe ratio, which was suitable for ferromanganese or ferrosilicomanganese production by smelting in an electric arc furnace.

Introduction

Land based mineral resources are getting depleted day by day; people are looking for alternate resources of minerals. One such alternate resource is sea nodules, which is available in the sea bed world over (1, 2). The nodules are rock concentrates formed by concentric layers of iron and manganese hydroxide around a core. Metal entities such as Cu, Ni, Co, Mo & Zn are accommodated in the complex cage of iron and manganese hydroxides (3). These are often called manganese nodule due to its high Mn content. According to an estimate around 1 trillion of polymetallic sea nodules are lying on the sea bed. The requirement of Cu, Ni, and Co by many mineral resource-starved countries like Japan, India, China, and Korea encouraged the research organizations in their countries to develop processes, which are economical and environmental friendly to recover the valuable metals from the sea nodules. So far, most of metal recovery processes developed for sea nodules are based on hydrometallurgical routes (4). Extensive work on reduction roasting of sea nodules followed by ammoniacal leaching has been carried out at NML, Jamshedpur (5,6). Most of the hydrometallurgical processes inherits the associated problem like handling of large volume of extractants, dilute leach liquor, very specific downstream processes etc. In this connection, a new pyrometallurgical process route based on reduction smelting is being carried out at NML, Jamshedpur to recover copper, nickel, cobalt and manganese.

When carbon is added to the charge, various metallic elements are reduced to different extent, at a given level of carbon addition during smelting. This behavior allows a reasonable degree of separation of metals to take place. The objective of the present study is to separate the valuable metals like Cu, Ni & Co from iron, manganese and the gangue constituents present in the charge. The process involves selective reduction of copper, nickel and cobalt oxide with limited addition of carbon and separation of alloy of Cu, Ni & Co from slag. Temperature and amount of reductant play the important role in such type of smelting operations. Studies were carried out by varying the amount of coke while keeping the temperature range around 1400^{0}C to 1450^{0}C in a two electrode submerged electric arc furnace. After separation of Cu, Ni, Co and part of Fe 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. The present paper describes the studies carried out only for the recovery of Copper, Nickel & Cobalt as alloy.

Experimental: Materials and method

The sea nodules were supplied by National Centre for Antarctic and Ocean Research (NCAOR), Goa. Nodules were crushed down to 5-10 mm size fraction. The size of other raw materials viz. coke and quartz were made to 5 mm. The charge mix was prepared by manually mixing the calculated amount of raw materials. Smelting was carried out on 20 Kg scale in an electric arc furnace. The furnace consisted of Mag-carbon brick-lined rectangular vessels with power rating of 50kVA and the top was lined with refractory material. There were two electrodes suspended through the top into the hearth. The electrodes were connected to the bus-bars via a water-cooled clamp connection. The electrodes and clamp formed part of a moveable electrode arm. Each mechanical arm was electrically isolated from the electrical connections (electrode and clamp) and was used to control the current and voltage ratio by adjusting the arc length i.e. moving the arm up or down. A tap hole was provided to tap out the molten mass after the completion of experiment. In a typical experiment, the furnace crucible was preheated with initial arc between electrodes on small amount of coke. The charge was added slowly in initial stage and after formation of a molten pool further addition of charge material was done. During melting period the furnace current and voltage were kept at 500 Amps and 45 volts respectively. After complete melting, another 10 minutes was provided for proper separation of slag and alloy. Thereafter the alloy and slag was tapped in a preheated clay bonded graphite crucible. On cooling, the slag and alloy were separated and ground to 100 mesh size to prepare representative samples of slag & alloy for analysis. The major elements were analysed by standard wet methods and trace elements analysis was done with an AAS (Perkin Elmer Analyst 400).

Results and Discussion

The chemical compositions for the raw materials are given below.

Table - 1: Composition of Manganese Nodule

Consttituents	% (mass)	Consttituents	% (mass)
Cu	1.2	S	0.2
Ni	1.2	P	0.007
Co	0.15	Mo	0.02
Mn	24	SiO_2	15.5
Fe	7	Na_2O	0.92
Zn	0.09	Al_2O_3	3.5

Table - 2: Chemical composition of coke and quartz

Coke		Quartz	
Fixed carbon	77.0 %	Silica	92.0 %
Ash	16.60 %	Al_2O_3	1.53 %
Volatile matter	2.35 %	Fe (T)	3.35 %
Moisture	3.80 %	L O I	0.37 %

From the Ellingham diagram it is evident that the oxides of Cu, Ni & Co tend to get reduced to respective metallic state with carbon at lower temperature (about 800°C) whereas the oxides of Fe, Mn & Si needs higher temperature i.e. in the range of 1350 - 1600°C to get reduced. Therefore, it is thermodynamically favored that with limited amount of coke and maintaining temperature around 1400°C will result in the reduction of Cu, Ni & Co oxides along with some of iron. The resulting slag contains almost all the manganese with remaining amount of iron and silica. The basic reactions taking place during smelting are described as follows (7, 8):

$2MnO_2$ '! $Mn_2O_3 + \frac{1}{2} O_2$	(1)
$Fe_2O_3 + C$ '! $2FeO + CO$	(2)
$FeO + CO$ '! $Fe^0 + CO_2$	(3)
$Fe_2O_3 + CO$ '! $2FeO + CO_2$	(4)
$FeO + CO$ '! $Fe^0 + CO_2$	(5)
$CuO + C$ '! $Cu^0 + CO$	(6)
$CuO + CO$ '! $Cu^0 + CO_2$	(7)
$CoO + CO$ '! $Co^0 + CO_2$	(8)
$NiO + C$ '! $Ni^0 + CO$	(9)
$NiO + CO$ '! $Ni^0 + CO_2$	(10)
$Co_2O_3 + C$ '! $2 CoO + CO$	(11)
$CoO + C$ '! $Co^0 + CO$	(12)

At the temperature range of 600 – 950°C the oxides of Co, Cu & Ni are reduced to the metallic state, Co^0, Cu^0, Ni^0 along with some iron, followed by melting at around 1400-1500°C to separate alloy from slag. Under the controlled conditions, the manganese is not reduced to Mn^0 but remains as Mn^{2+} in the slag. The Co, Cu, Fe & Ni form a metal alloy that settles at the bottom of the furnace. The reduction is performed by coke and slagged by silica. On complete melting, metal alloy separates from the oxide-silicate slag by gravity. As the total copper, nickel and cobalt content in nodules is only 2-3% by mass, the selective reduction of such small quantity of metals is quite difficult and hence, some amount of iron was also allowed to reduce along with copper, nickel and cobalt oxides. As mentioned above, the temperature & amount of reductant (coke) are two variables which determine the degree of reduction for manganese nodule smelting. Moreover, this process needs to operate at a temperature above the liquidus temperature of the alloy containing the Cu, Ni, Co and Fe. Of these elements, Fe has the highest melting point of around 1540ºC. For present purposes an operating temperature somewhere between 1400 and 1500ºC was maintained and quantity of coke in charge mix was varied. Numbers of experiments were carried out varying the amount of coke addition and the effect of coke on reduction smelting of nodule is given in figure 1.

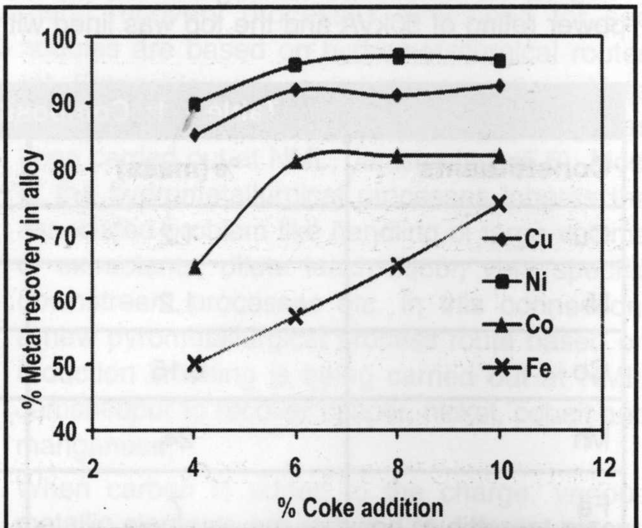

Fig. 1: % recovery of different metal with the variation of coke in charge

The recoveries of Cu, Ni, Co and Fe increased when coke addition was increased from 4% to 6%. Thereafter, the Cu and Ni recovery remained almost constant in the range of 90-95% and 95-97% respectively. The cobalt recovery, which also improved very fast with 6% coke addition, was found to be slightly increased with further addition of coke in the charge. Therefore, it was considered that maximum recoveries of Cu, Ni and Co were obtained with addition of 6% coke.

One main concern was the reduction of manganese oxide to metallic manganese and its loss into alloy as per reactions given in equations 15 and 16 because they are feasible at the temperatures of 1420 and 1220^{0}C respectively (10, 11). An increase in Mn content of alloy was found with increasing coke. This has been depicted in fig. 2. MnO reduction also depends on its activity in slag and the surrounding reducing conditions (12). To decrease the MnO activity in slag by facilitating reaction 18, a fixed quantity of SiO_2 as quartzite (4%, by mass) was added in the charge.

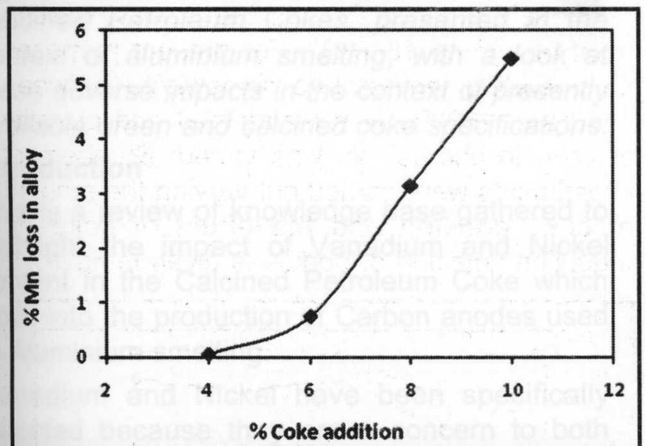

Fig. 2: Manganese loss into alloy with the variation of coke in charge

$3Mn_2O_3$ '! $2Mn_3O_4 + ½\ O2$	(13)
Mn_3O_4 '! $3MnO + ½\ O2$	(14)
$2MnO + 2C$ '! $2Mn + 2CO$	(15)
$2MnO + 8/3\ C$ '! $2/3\ Mn_3C + 2CO$	(16)
$MnO + CO_2$ '! $MnCO_3$ (carbonation)	(17)
$2MnO + SiO_2$ '! Mn_2SiO_4	(18)

The resulting slag contains high manganese along with iron and silica. The Mn/Fe ratio is more than 7 in the slag and hence it can be subjected to ferromanganese or silicomanganese production after adjusting the charge basicity by addition of flux (quartz, dolomite etc. as required). The typical composition of alloy and slag obtained after smelting with 6% coke is given in Table 3 & 4 respectively.

Table -3: Chemical composition of alloy from sea nodules smelting

Element	%	Element	%
Cu	12.33	Mn	8.23
Ni	14.05	Fe	55.96
Co	0.75	Si	0.31

Table -4: Chemical composition of slag from sea nodules smelting

Constituents	%	Constituents	%	Constituents	%
MnO	42.61	CaO	1.01	Cu	0.10
FeO	5.66	MgO	4.41	Ni	0.05
SiO_2	33.51	Al_2O_3	6.10	Co	nf

Conclusions

1. Smelting of sea nodules with 6% coke yields 92% Cu, 95% Ni and 81% Co recovery.
2. Smelting produces manganese rich slag, which has suitable Mn/Fe ratio for ferromanganese or silicomanganese production.

References

1. Fuerstenau DW, Herring AP and Hoover M (1973). "Characterization and extraction of metals from sea floor manganese nodules," *Trans. AIME* 254, p. 205–211.
2. Fuerstenau DW and Han KN (1983). "Metallurgy and processing of marine manganese nodules," *Miner. Process. Technol. Rev.* 1, pp. 1–83.
3. Jana, RK, Singh, DDN and Roy SK (1997). "Some physicochemical characteristics of Central Indian Ocean nodules and their effects on extractive metallurgical schemes." *NML Tech. J.* **39**, p. 93–103.

4. Agarwal, HP and Goodrich, JD (2003). "Extraction of copper, nickel and cobalt from Indian Ocean Polymetallic Nodules," *Can. Jour. of Chem. Engg.*, Vol. 81, pp 303-306
5. Saha AK and Akerkar DD (1987). "Fuel oil reduction of polymetallic manganese sea nodules of Indian Ocean for extraction of nickel, copper and cobalt," *NML Tech. J.* 29 pp. 3–8.
6. Jana, RK, Pandey, BD and Premchand (1999). "Ammoniacal leaching of roast reduced deep-sea manganese nodules," *Hydrometallurgy*, Vol. 53, No. 1, p. 45-56
7. Monhemius, AJ (1980). "The extractive metallurgy of deep sea manganese nodule," *'In' Topics in non ferrous extractive metallurgy'*: Ed. R. Burkin. Society of chemical industry, London, 42-69
8. Habashi, F, Handbook of Extractive Metallurgy, Volume 1, Part II, p. 421-438
9. Jones, RT, Hayman, DA, and Denton, GM (1996). "Recovery of cobalt, nickel and copper from slag, using DC-Arc furnace technology," *International Symposium on Challenges of Process Intensification,* 35th Annual Conference of Metallurgists, Montreal, Canada
10. Elyutin, VP (1961), "Production of ferro-alloy.Electrometallurgy," 2nd Edition, p. 113-114
11. Riss, M, Khodorovsky, Y, (1967)."Production of ferroalloys," Mir Publishers, Moscow, p. 138
12. Kubaschewsky, O, Evans, EU and Alcock, CB (1979). "*Metallurgical Thermochemistry,*" 5th ed., Pergamon Press, Oxford.