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NICKEL, COBALT AND COPPER RECOVERY FROM SEA NODULES BY DIRECT SMELTING PROCESS

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Abstract

A direct smelting process has been developed at CSIR-National Metallurgical Laboratory, to recover all four valuable metals such as Ni, Co, Cu and Mn. Initially sea nodules containing 1.1% Cu, 1.15% Ni, 0.76% Co, 22.3% Mn, 5.5% Fe and 13.1% SiO_2 was smelted in presence of coke to produce an alloy rich in Ni, Co, Cu and Fe. Various parameters such as amount of coke, quartz, smelting temperature and holding time etc. were optimized on different scale between 0.5-20 kg scale. Under optimized condition, the alloy of composition : 16.% Cu, 18.4% Ni, 1.2% Co 57.0% Fe and 3.6% Mn was produced on 20 kg scale using 7% coke with more than 90% metal recovery. The process was further up-scaled to 250 kg where similar recovery was achieved with 8% coke and 1 h holding time. The alloy and slag was further processed to recover different value added products.

Introduction

With the rapid depletion of land based mineral resources for nickel, copper and cobalt, several countries have explored the possibility of using deep sea manganese nodules. Although the accretion rate is very slow, only a few mm in a million years, however the present reserve of these nodules is substantial. Therefore, this can be an attractive resource due to the presence of significant amount of nickel, copper and cobalt.

India is completely dependent on imports to meet its requirements of cobalt and nickel and has launched an ambitious programme of sea bed exploration of minerals for some of these strategically important metals with a view to explore them for the national needs. The Indian program of work considers the manganese recovery option in addition to recovery of Cu, Ni & Co for better process viability & environmental consideration. Three process namely (i) combined pyro-hydrometallurgical process of reduction roasting and ammoniacal leaching, (ii) direct leaching process in ammoniacal medium with dissolved sulfur-dioxide as aqueous reducing agents and (iii) High temperature reductive sulphuric acid leaching, have been developed and extensively tested in India.

The direct reductive acid leaching process was developed by Hindustan Zinc Limited, Udaipur. Starch was used in the process as reductant during leaching. The separation process is based on selective sulphide precipitation followed by solvent extraction and electrolysis. The other two processes are based on ammonia leaching, developed at the Institute of Materials and Minerals Technology, Bhubaneshawar (IMMT-B) and National Metallurgical Laboratory, Jamshedpur (NML). The IMMT-B process constitutes [1] direct ammoniacal leaching in presence of sulphur dioxide followed by demagnetization and solvent extraction to produce pure metal by electrolysis. The process is tested up to 500kg scale in order to prepare a pre-feasibility report. NML developed a process based on reduction roasting-ammonia leaching followed by metal separation using solvent extraction technique to produce pure metal by electrolysis. The process was tested on 100kg scale per day [2].

The above processes generate very dilute leach liquor as a result downstream operation requires very large equipments and higher energy. The ammoniacal leaching process also generate huge quantity of residue containing high moisture & sulphate / ammonia, which was further treated by NML to develop a process for the recovery of manganese as Fe-Si-Mn by electrothermal reduction-smelting route. However, due to low Mn/Fe ratio, standard grade Fe-Si-Mn alloy was produced by blending with high grade Mn-ore or by pre-smelting to remove iron. To obviate the above gap areas, direct reduction smelting of sea nodules was explored to recover Cu, Ni, and Co in the form of alloy and Mn as Fe-Si-Mn from Mn-rich slag by further smelting. The alloy containing high percentage of Cu, Ni, Co was subjected to matte formation followed by pressure leaching to generate concentrated leach liquor, which was suitably treated to recover metal by selective hydrothermal reduction / SX. The major advantages of the process are (a) enriched Cu, Ni, and Co alloy produced is only about 5.5-6.0% of the input sea nodules weight, (b) concentrated leach solution of Cu, Ni and Co with reduced volume is generated by pressure leaching of alloy/matte and (c) with partial removal of iron in the alloy, the Mn rich slag generated in direct smelting of sea nodules is highly suitable for production of standard grade Fe-Si-Mn. Sridhar et al [3] reported prereduction roasting followed by smelting to produce Cu-Ni-Co alloy with about 85% metal recovery. Earlier, bench scale study on direct reduction smelting was reported by our group [4]. In the present paper, systematic syudy on direct reduction smelting of sea nodules was reported both on bench scale as well on pilot scale to recover Cu-Ni-Co in the form of alloy, which was further processed to recover individual metal.

Experimental

Sea nodules containing 1.15% Ni, 1.1% Cu, 0.076% Co, 22.3% Mn, 5.36% Fe,13.1% SiO_2, 3.19% Al_2O_3, 7.03% MgO, 0.54% CaO, 1.76% Na_2O+K_2O, 24.5% LOI, were crushed down to minus 20 – plus 10 mesh size fraction; commercial grade quartz & coke were crushed to minus 5 mesh size fraction. Factsage (6.1 version) was used for thermodynamic calculations. The authors have used FACT53, oxide and SGSL data bases of the software to predict equilibrium of slag, alloy and gaseous products. The smelting experiments were carried out with charge mix, by mixing the desired amount of reductant and fluxing material. Initial smelting experiments were carried out on 500 g scale using recrystallized alumina crucible, in a resistance furnace. Smelting on 20 kg scale was done using 50 kVA two phase AC arc furnace with double electrode in graphite brick-lined rectangular vessels. These electrodes were suspended through the top into the hearth of 50 kVA furnace. 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, which were used to control the current and voltage ratio by adjusting the arc length i.e. moving the arm up or down. Before the start of the sea nodules smelting the furnace was preheated for few minutes and charge materials were added gradually. After complete melting of the charge, it was hold for 10 minutes. Thereafter, the molten metal and slag was discharged through a tap hole to a pre-heated crucible. After complete cooling, the metal and slag were separated and weighed.

Both metal and slag samples were ground to fine powder and analyzed for their chemical composition.

Results and Discussion

The X-ray diffractogram of the bulk sample of sea nodules indicated most of the mineral phases were either amorphous in nature or very poorly crystalline. The identified peaks confirmed the presence of quartz only. However, X-ray diffraction on individual layer deposit of nodules and EDAX analysis revealed the presence of todorokite as the major phases of manganese. The only iron oxide phase indicated was goethite. The major components in the sea nodules were reported earlier also to be present in the form of complex/individual oxide [5, 6]. From the Ellingham Diagram [7] it is evident that in presence of carbon as reductant Cu, Ni and Co could be selectively reduced by controlling reduction temperature during smelting and carbon in the charge. Higher oxides of manganese and iron will reduce to their lower oxides and need higher temperature to get reduced to their metallic state. Theoretical calculations were done using the thermodynamic software Factsage, to determine the composition and temperature for selective reduction of Cu, Ni and Co. Table I represent theoretical alloy composition at different carbon composition during smelting of sea nodules at 1400 ^{o}C in presence of additional 4% quartz. Actual smelting result under similar experimental condition conducted in a recrystallise alumina crucible was found good co-relation between the theoretical and experimental alloy quantity and composition. Recrystalise alumina crucible used to avoid carbon pick-up and to optimise coke requirement during smelting of sea nodules.

Table I. Comparisons between experimental and theoretical alloy quantity and composition obtained for sea nodules smelting on 500 g scale at 1400 ^{o}C in recrystallise alumina crucible.

Constituents	4% Carbon		6% Carbon	
	Theoretical, %	Experimental %	Theoretical,%	Experimental,%
Cu	29.8	29.9	10.88	12.2
Ni	31.2	33.1	11.4	12.9
Co	2.06	2.01	0.75	0.89
Mn	0.35	1.24	21	17.1
Fe	36.6	29.7	52.9	55
Alloy wt.(g)	18.5	16.12	50.5	45.0

Inorder to optimise carbon, the coke containing 77.2% fixed carbon was varied between 2.5% to 15% in the charge and smelted at 1400 ^{o}C. Alloy formation was not observed for smelting experiment with 2.5% coke. However, alloy weight increased with further increase in the coke percentage. The alloy composition and metal recovery obtained with different coke percentage is incorporated in Table II. Smelting with 5% (w/w) coke produced a copper and nickel rich alloy containing very low iron (0.21%) and manganese (0.014%). Due to low iron recovery, the cobalt in the alloy was also found very low (0.09%). There was a sharp decrease in the concentration of copper and nickel with increase in coke percentage from 5% to 6.25%. The copper and nickel in the alloy decreased from 44.6 and 47.7% to 17.4 and 18.2% respectively with increase in coke from 5% to 6.25%. With the same increase in coke, the cobalt concentration in the alloy increased from 0.1% to 1.08%.

Table II. Metal recovery in the form of alloy obtained during smelting of sea nodules with varying coke addition.

% coke, (w/w)	Alloy wt. (g)	Alloy Composition, %					Metal Recovery, %				
		Cu	**Ni**	**Co**	**Fe**	**Mn**	**Cu**	**Ni**	**Co**	**Fe**	**Mn**
2.5	0	0	0	0	0	0	0	0	0	0	0
5.0	9.33	44.6	47.8	0.09	0.21	0.014	75.7	77.5	2.21	0.07	0
6.25	27.7	17.4	18.2	1.08	51.7	4.64	87.6	87.7	78.7	53.5	1.06
7.5	34.0	14.9	15.9	0.96	58.4	5.02	92.1	95.1	85.9	74.2	1.41
10	39.4	13.2	14.0	0.83	62.1	6.21	94.8	95.9	86.1	91.3	2.01
15	44.4	11.8	12.3	0.76	54.6	12.8	96.7	97.2	88.8	90.4	4.66

The iron concentration in the alloy increased from 0.2% to 51.7% with increase in coke percentage from 5% to 6.25% and there is a marginal increase in the iron in the alloy with further increase in coke up to 10% (Table II). With 15% coke, iron in the alloy decreased due to incorporation of more manganese in to alloy. The manganese concentration in the alloy increased from 0.01% with 5% coke to 12.7%with 15% coke.

It was observed that recovery of all metals increased with increase in coke during smelting (Table II). Copper and nickel recovery increased from 75.7% and 77.5% to 96.7% and 97.2% respectively with increase in coke from 5% to 15% in the charge. The cobalt, iron and manganese recovery was found almost nil at 5% coke, but increased to 88.8%, 90.4% and 4.66% respectively using 15% coke during smelting.

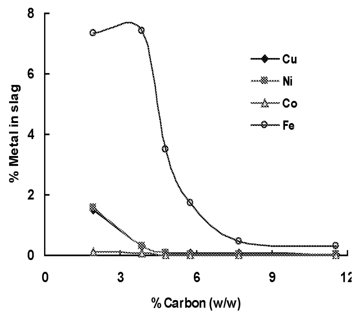


Fig. 1 : Metal distribution in slag obtained from smelting of sea nodules at different %ge of coke addition.

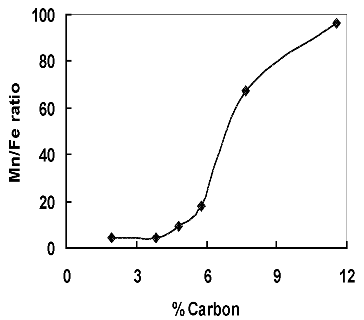


Fig. 2 : Mn/Fe in slag obtained during smelting of sea nodules at different %ge of coke addition.

The trend in metal content in the slag with increase in the coke during direct smelting of sea nodule in alumina crucible using muffle furnace is represented in Fig. 1. Percentage of metal in the slag gradually decreased with increase in the coke in the charge. There was a sharp decrease in the percentage iron from 7.4% to 3.5% with increase in the coke from 5% to 6.25%, thus removing almost 50% of iron from the system making the slag ideal for production of high grade Fe-Si-Mn. With further increase in coke, iron in the slag gradually decreased. With manganese composition remaining almost similar above 30%, the Mn/Fe ratio in the slag increased with increase in coke (Fig.2). The Mn/Fe ratio of 10 with 6.25% coke, increased to about 10 fold with 15% coke in the charge during direct smelting of sea nodules (Fig.2). The slag with such high ratio of Mn : Fe would be suitable for ferromanganese production.

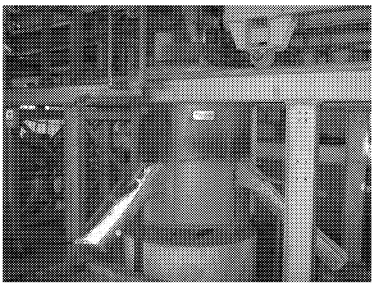
Based on the data generated on 0.5 kg in recrystallise alumina crucible further scale-up experiments were carried out on 4 kg scale using graphite crucible and on 20 kg scale using a graphite brick lined 50 kVA electric arc furnace (EAF) with variation of coke and quartz. For optimisation of direct smelting of sea nodules on 20 kg scale, the coke percentage was varied from 6-8%. The alloy weight obtained for each experiment with variation of coke is incorporated in the Table III. The alloy quantity increased with increase in coke in the charge. With 6% coke and 20 minutes holding time, the alloy weight obtained was 980 g which increased to 1078 g with increase in coke to 8%. Experiment with 7% coke produced 1031 g alloy of composition: 18.2% Cu, 19.35% Ni, 1.28% Co, 53.9% Fe and 4.08% Mn (Table III) which corresponds to a metal recovery of 85.1% Cu, 86.7% Ni, 86.8% Co, 51.8% Fe and 0.94% Mn of the input metal present in sea nodule. However, metal recovery increased when holding time increased from 20 min. to 30 min. With 7% coke and 30 min. holding time, 90.5% Cu, 92.0% Ni and 86.6% Co recovery was achieved (Table-III). Under this condition iron and manganese in the alloy is 56.7% and 2.84%, which corresponds to recovery figure of 60.0% and 0.73% respectively. The smelting result was validated with three repeat experiments, which was found to yield almost similar recovery of Cu, Ni and Co. (Table III).

Table III. Copper, nickel and cobalt recovery in the alloy obtained during smelting of sea nodules on 20 kg scale in graphite lined 50 kVA arc furnace with varying coke and holding time in presence of 4% additional quartz.

% coke	Holding time	Alloy wt. (g)	Alloy Composition, %					Metal Recovery, %				
			Cu	Ni	Co	Fe	Mn	Cu	Ni	Co	Fe	Mn
6	20	980	18.1	19.4	1.24	54.3	3.72	80.4	82.5	80.0	49.7	0.82
7	20	1031	18.2	19.4	1.28	53.9	4.08	85.1	86.7	86.8	51.8	0.94
8	20	1078	17.4	18.6	1.17	56.9	3.42	85.6	87.3	83.0	57.2	0.83
7	30	1145	17.4	18.5	1.15	56.7	2.84	90.5	92.0	86.6	60.0	0.73
7	30	1177	16.5	17.9	1.19	56.2	3.45	88.5	91.6	84.3	53.7	0.83

Pilot Scale Smelting of Sea Nodules

Based on the optimization experiments on 20 kg scale, further scale-up experiment on 250 kg scale was carried out in a graphite brick lined 150 kVA electric arc furnace (Fig. 3). As optimized on 20 kg scale, 7% coke and 4% quartz were added during pilot scale smelting. With 7% coke the alloy and slag weight obtained with 20 minutes holding time were 9.45 and 137 kg respectively. However some unmelted / sintered mass found at the furnace bottom. The alloy of composition : 17.6% Cu, 19.3% Ni, 1.15% Co, 54.9% Fe and 2.4% Mn was obtained which corresponded to metal recovery of 60.5% Cu, 63.4% Ni, 57.2% Co, 36.8% Fe and 0.41% Mn. The melted slag collected through tap hole with composition: 0.65% CuO, 0.51% NiO, 0.049% CoO, 5.7% FeO and 41.7% MnO have percentage metal distribution of 21.4% Cu, 19.2% Ni, 26.7% Co, 43.3% Fe and 97.0% Mn. Incomplete reduction due to less holding of the melted charge resulted in low recovery of different metals. Therfore, further experiments were conducted with variation coke from 6-10% maintaining 1 h holding time.



(a)

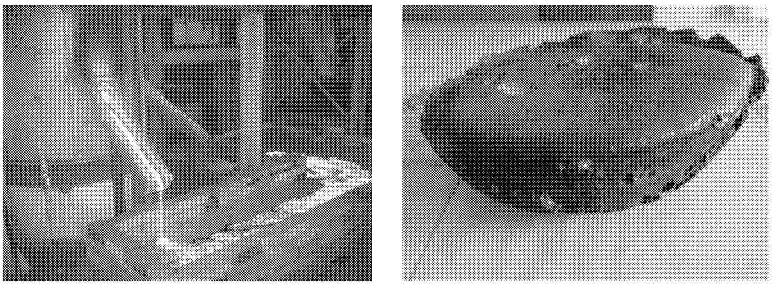
(b)

Fig. 3 : (a) 150 kVA electric arc furnace with (b) control pannel

Table IV. Copper, nickel and cobalt recovery in the alloy obtained during pilot scle smelting of sea nodules on 250 kg scale in graphite lined 150 kVA arc furnace with varying coke.

% Coke	Holding time, min	Slag wt. (kg)	Alloy wt. (kg)	Metal recovery, %				
				Cu	Ni	Co	Fe	Mn
6	60	149	10.5	73.3	75.6	74.6	39.5	0.54
7	60	143	14.6	87.1	89.9	86.1	59.6	0.97
8	60	145	15.3	89.8	90.9	87.8	61.6	1.31
10	60	142	19.1	90.8	93.2	89.5	72.7	5.04
8	60	142	14.9	90.4	91.7	87.8	58.8	1.18

Alloy quantity increased from 10.5 kg to 19.1 kg with increse in coke from 6% to 10% in the charge during smelting on 250 kg scale in presence 4% quarz (Table IV). With 6% coke, the alloy of composition : 19.2% Cu, 20.7% Ni, 1.35% Co, 52.9% Fe and 2.87% Mn was obtained which corresponded to metal recovery figure of 73.3% Cu, 75.6% Ni, 74.6% Co, 39.5% Fe and 0.54% Mn. With increase in coke to 8% and maintaining similar holding time (1 h) during smelting, the alloy (Fig. 4) quantity obtained was 15.3 kg of composition: 16.1% Cu, 17.0% Ni, 1.09% Co, 56.9% Fe and 4.77% Mn which corresponded to metal recovery of 89.8% Cu, 90.9% Ni, 87.8% Co, 61.6% Fe and 1.31% Mn (Table IV). There was a marginal increase in Cu (90.8%), Ni (93.2%) and Co (89.5%) recovery with further increase in coke to 10%. Iron and manganese recovery in the alloy was increased to 72.7% and 5.04% respetvively, which is not desiredrable. Therefore considering 8% coke is appropriate for getting optimum recovery; one repeat smelting campaign was conducted to validate the recovery result. Metal recovery of 90.4% Cu, 91.7% Ni, 87.8% Co, 58.8% Fe and 1.2% Mn was obtained with the repeat smelting trials using 8% coke (Table IV).



(a) (b)

Fig. 4 : Slag tapping during smelting of sea nodules in 150 kVA arc furnace (b) Cu-Ni-Co rich alloy obtained from sea nodule smelting on 250 kg scale

Conclusion

As an alternate process on direct reduction smelting of sea nodules is developed at CSIR-NML to recover Cu, Ni and Co in the form of alloy with about 90% recovery, achieve good result. Using 8 % coke & 4 % quartz, 90.4% Cu, 91.7% Ni, & 87.8% Co recoveries were achieved on pilot scale. As a part of iron was recovered in the alloy, the process generate a slag rich in manganese with Mn/Fe ratio of about 10, from which standard grade Fe-Si-Mn was produced. The metal rich alloy was further processed to recover Cu, Co and Ni in pure form.

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