A new process for the enrichment of nickel in Sukinda chromite overburden ore

S. BHATTACHARJEE, P. DASGUPTA, D. KAR, R. N. BHATTACHARJEE,
S. GHOSAL and A. R. PAUL

National Metallurgical Laboratory, Jamshedpur, 831007, India

ABSTRACT

Chromite Over Burden (COB) ore from Sukinda valley, Orissa is too lean in nickel concentration to be exploited for the extraction of nickel. The average nickel concentration in the COB ore lies in the range of 0.4-0.6%. An acid leaching route at atmospheric prsssure has been developed for screening out silica as insoluble. Metal values in the leach liquor are retrieved as hydroxides by appropriate manoeuvring of pH. The metal hydroxides are converted to corresponding oxides by calcining at 900°C. The resultant nickel content in the mixed oxide has been consistently found to be 1.6% and above. This product may be directly used as a starting material for the preparation of ferro-nickel.

Key words : Chromite overburden ore, Nickel, Acid leaching, Ferro-nickel

INTRODUCTION

Sukinda valley of Orissa is well known for its rich reserve of chromite ore. Mining of chromite ore generates overburden from the upper layer, which is typical of its own. This overburden, which is also known as Chromite Over Burden (COB) ore, is the only indigenous source of nickel in the country.

The average nickel concentration in the COB ore of Sukinda lies in the range of 0.4-0.7%. The existing deposit of COB ore in the Sukinda valley has been estimated to be around 140 million tonnes[1]. This makes COB ore a highly prospective source of nickel, especially in view of the fact that nickel is a strategic metal and entire nickel demand of our country is met through import.

Two radically different types of nickel ores, namely, sulphide ores and oxide ores have been recognised. Sulphide ores occur as layers and lenses of mafic and ultramafic rocks while oxide ores occur due to the weathering and laterization of the parent metal bearing rock[2]. COB ore of Sukinda valley comes under the

second category. the oxides. The primary mineral phases in the COB ore are quartz, goethite and limonite in association with other minor phases like magnetite, hematite. chromite etc.

Early exploits of nickel were mostly from sulphide ores except till 1943 when Freeport Sulphur Company for the first time tried to harness the lateritic oxide ores for the purpose of extracting nickel[3]. It was a daunting task at that time since the nickel content in the starting material was even less than 1.5%. Caron's process of ore pre-reduction followed by ammonia-ammonium carbonate leaching was adopted. Nickel[3] was extracted as $NiCO_3$/ $Ni(OH)_2$. Freeport's Enterprise was, however, aborted because of technical non-viability.

Parallel developments were made on acid leaching of the lateritic oxide ore. Sulphation of oxide ores was attempted by several workers. Both high and atmospheric pressure leaching routes were attempted. Freeport Sulphur Company put up another plant at Moa Bay, Cuba in which lateritic oxide ores with a nickel content of about 1.3% was subjected to high pressure sulphuric acid leaching[3]. Extraction of nickel was excellent and almost selective thus requiring less amount of sulphuric acid. The process was, however, plagued with severe corrosion problem.

Atmospheric pressure acid leaching of nickeliferrous laterites received popular attention because of a number of apparent advantages that include ease of operation, less corrosion and low energy consumption. However, atmospheric pressure acid leaching has the disadvantage of being non-selective with high acid consumption. Acid leaching of lateritic ores under atmospheric pressure was attempted by Rice and Strong[4] in the early seventies but did not receive much favour at that time. Decade of eighties saw a spurt of research in this area. A number of inorganic and organic acids were investigated as probable lixiviants for COB ore[5]. Among the inorganic acids, rate of extraction was highest for HCl. Pre-roasting of the COB ore at about 360°C decomposes the goethite phase to hematite. Shukla and Das[6] studied the effect of this transformation on the leaching behaviour of Sukinda COB ore. Shukla and co-workers further carried out a comparative study on the leaching of COB ore in HCl and H_2SO_4[7]. Under similar reaction conditions HCl produce better extraction than H_2SO_4. Pre-roasting of the ore increased the extractability. Panagiotopoulos and co-workers worked on the atmospheric pressure sulphuric acid leaching of serpentinic[8] and low-grade hematitic laterites[9]. Acid leaching of Australian nickeliferrous laterites at atmospheric pressure was carried out by Canterford with reference to leaching temperature, acid strength, ore mineralogy, pre-roasting temperature etc.[10,11].

Present paper describes a new process for the chemical enrichment of nickel content in high silica Sukinda COB ore. The process is based on the dissolution of the COB ore through atmospheric acid leaching and retrieving the metal

values through precipitation as hydroxide. A nickel value of 1.6% or above qualifies the final product as a starting material for producing ferro-nickel.

EXPERIMENTAL

Digestion experiments for optimising the leaching parameters were carried out in a three-necked Borosil flask under refluxing condition and constant agitation. In each batch 500 g of the COB ore was used. The extractability of different sieve fractions was performed in open beakers. 1 g of each fraction was subjected to acid digestion in the proportion, 5 ml HCl, 5 ml HNO_3, 10 ml H_2SO_4 and 20 ml H_2O kept over a hot plate for a period of two hours with occasional stirring. Total analyses of the sieved fractions were carried out by dissolving 1 g of each fraction in $HCl-HNO_3-HClO_4$ tri-acid mixture using standard protocols. SiO_2 was determined by standard HF digestion of the residue. All the metal analyses were performed using GBC 908 AA Atomic Absorption Spectrometer. All the reagents used were of AR grade with 18MΩ ASTM Grade 1 distilled water was used for making the solutions.

RESULTS AND DISCUSSION

Table 1 gives the complete chemical analysis of the COB ore used in the present study. As a prerequisite for the acid leaching of COB ore. The ore must be ground to a fine size to make more and more surface area available for acid attack. However, grinding of the ore has a cost, which increases sharply with finer size requirement. This warrants an optimisation, as the final techno-economics of the process should be influenced by the grinding cost.

To arrive at an optimum particle size following exercise was carried out. 1 kg ore of -10 mesh ore was passed through sieves of different sizes and their percentages were calculated. Percentages of different fractions as recovered from 1 kg of -10 mesh ore are shown in Table 2.

It may be observed from Table 2 that -10 mesh COB ore was a well distributed matrix. All the sieve fraction collected were analysed for their principal components, namely, LOI, SiO_2, Fe, Ni, Co, Cr and Mn and the results have been shown in Table 3. It is evident from Table 3 that grinding to finer sizes leads to the liberation of metal values and silica percentage goes down considerably. There has been an enrichment of all the metals in -200 mesh fraction. However, it was also interesting to find that metal values did not vary significantly in fractions B, C and D. Thus, it may be inferred that grinding upto -44 mesh size should be sufficient as far as metal liberations are concerned.

To look into this observation more critically leaching experiments were carried out with all the sieved fractions under similar reaction conditions. 1 g of each fraction was digested with 5 ml HCl, 5 ml HNO_3 and 10 ml H_2SO_4 under

identical conditions. The leach liquor in each case was analysed for the metal values and the percentage extractability was calculated on the basis of analytical data for each metal in each fraction given in Table 3. The percentage extractability of each metal in each fraction is given in Table 4.

Table 1 : Complete chemical analysis of the COB ore

Element/Radical	Content %
LOI	5.15
SiO_2	55.39
Fe_2O_3	34.41
NiO	0.93
CoO	0.05
Cr_2O_3	2.01
MnO	0.57
ZnO	0.01
Na_2O	0.16
CaO	0.35
MgO	0.74

Table 2 : Sieve analysis of -10 mesh COB ore

Label	Sieve fraction, mesh	Weight, g	Weight, %
A	-200	165	16.5
B	+200 to -100	265	26.5
C	+100 to -60	186	18.6
D	+60 to -44	145	14.5
E	+44	214	21.4
	Loss	25	2.5
	Total	1000	100

Table 3 : Chemical analyses of different sieve fractions

Element (%)	Sieve fractions				
	A	B	C	D	E
LOI	7.73	5.29	5.59	5.76	5.7
SiO$_2$	43.98	48.62	55.32	58.92	58.90
Ni	1.1	0.756	0.747	0.766	0.701
Co	0.062	0.031	0.036	0.042	0.051
Cr	1.27	1.21	1.07	1.33	0.96
Fe	32.48	20.16	19.04	20.16	20.16
Mn	0.65	0.43	0.46	0.5	0.47

Data in Table 4 make some interesting observations. On increasing the fineness of the ore particles, one expected a higher extraction. However, for all the metals reported, fraction B had shown maximum extractability though fraction A was of highest fineness. The leachant combination of HCl, HNO$_3$, H$_2$SO$_4$ and water was adhoc in nature and no attempt was made at this stage to optimise the leachant combination. The objective of this study was to find out the metal extractability of different sieve fractions under similar reaction conditions. It was not readily explainable why the extractability was less in fraction A. It was further interesting to note that metal extractability of fractions B, C and D did not differ much. This strengthens our earlier contention that a grinding upto -44 mesh was sufficient for the leaching of the COB ore and there was no need to go for expensive finer grindings.

Table 4 : Percentage extractability of metals in each sieved fraction

Element (%)	% Extractability in fraction				
	A	B	C	D	E
Ni	68.20	75.39	70.95	71.80	78.45
Co	46.77	61.29	55.55	61.90	54.90
Cr	19.68	20.66	23.27	22.93	29.17
Fe	83.43	91.07	90.02	90.57	77.77
Mn	58.46	66.51	63.04	66.01	61.96

Process for Nickel Enrichment

COB ore of Sukinda valley is a high silica matrix. Present nickel enrichment process consists of primarily three stages. In the first stage the ore is subjected

to acid digestion which solubilizes the metal values and screens out the silica. In the second stage the leach liquor that consists of salts of Ni, Co, Cr, Fe and other trace metals is neutralised with an appropriate alkali to precipitate the hydroxides of Ni, Co, Cr and Fe. In the third stage the metal hydroxides are calcined at a higher temperature to achieve the desired grade of nickel. Fig.1 gives the schematic diagram of the proposed enrichment scheme.

Stage I   : Digestion with acid/ Combination of acids, HCl, HNO and H_2SO_4.

Stage II   : Neutralisation with alkali, Na_2CO_3, NaOH.
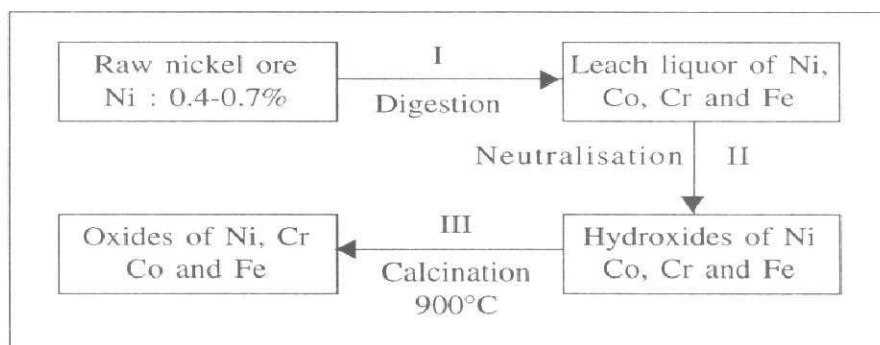
Stage III : Calcination at 900°C

Fig.1 : Schematic diagram of the nickel enrichment scheme

Optimisation of leaching parameters :

Leaching parameters for the optimum leaching of nickel from Sukinda COB ore were identified as, HCl, HNO_3 and H_2SO_4 concentrations, reaction temperature, amount of water added and digestion time. A large number of experiments (about 40) were carried out in the laboratory to optimise these parameters. The parameters as optimised are given below.

Under the optimised conditions the extraction of nickel from the COB ore was slightly more than 80%.

Neutralisation of the leach liquor :

The leach liquor contains salts of Co, Fe, Cr and traces of Al, Mn and Zn. These metals were precipitated using an appropriate neutralising agent. Both Na_2CO_3 and NaOH were used. However, use of Na_2CO_3 is recommended as washing the precipitate, which is a very crucial step for obtaining the product grade, is easier with Na_2CO_3 than NaOH. NH_4OH cannot be used as part of the nickel and cobalt get solubilised and the product yield goes down.

Table 4 : Optimised parameters with reference to the extraction of Nickel

Parameters	Optimised values
COB ore	500 g
Fineness	-44 mesh
HCl concentration	50 ml 12N
HNO_3 concentration	50 ml 14N
H_2SO_4 Concentration	100 ml 36N
H_2O	500 ml
Digestion time	3 hours
Temperature	100°C

Calcination of the hydroxides :

Metal hydroxides produced during the neutralisation process must be converted into the corresponding oxides to achieve the desired grade of nickel. Though it has been shown in the schematic diagram that the hydroxides were calcined at a temperature of 900°C, a thorough study was carried out to find out the optimum calcination temperature. The results of calcination temperature optimisation for a typical metal hydroxide have been given in Table 5. It is evident from Table 5 that calcination of the hydroxides is a need-based requirement. If the starting material has a higher grade of nickel it may not be at all necessary to calcine the product if the desired nickel percentage is 1.6% and a mere demoisturisation at 110°C should be sufficient, as may be seen from Table 5. However, most of the COB ores are very poor with respect to nickel concentration and calcination at a higher temperature appears to be a necessary step. This may be mentioned again at this stage that washing of the metal hydroxide precipitate is an extremely crucial step for achieving the product purity. Presence of sodium salts has a tendency to deteriorate the product purity to a great extent.

Final product :

The final product after the calcination was essentially a mixed oxide of Fe, Ni, Cr, Co and other trace elements like, Al, Mn, Zn, Na, Ca etc. Complete analysis of a typical final product is given in Table 6.

X-ray diffraction of the final product (not shown here) indicated that it consisted of two phases, (-Fe_2O_3 and nickel ferrite, $NiFe_2O_4$. It was observed that the final product was weakly magnetic in nature which supported the formation of weakly magnetic $NiFe_2O_4$ phase. It could be possible that the final product consisted of a magnetic and a non magnetic phase. (-Fe_2O_3 constituted the

Table 5 : Effect of heat treatment on the metal hydroxides
obtained from leach liquor

Sample	Temperature °C	Ni, %	Co, %	Fe, %
$O_3 4R_1$	110	1.68	0.063	56.0
$O_{34}R_1$	300	1.66	0.077	58.2
$O_{34}R_1$	500	1.81	0.084	63.8
$O_{34}R_1$	700	1.91	0.088	67.2
$O_{34}R_1$	900	1.95	0.086	69.4

Table 6 : Complete analysis of the final product

Element/Radical	Content %
LOI	0.11
SiO_2	0.13
Fe_2O_3	92.12
NiO	2.54
Cr_2O_3	1.75
CoO	0.14
Al_2O_3	1.21
MnO	1.42
ZnO	0.38
Na_2O	0.67

nonmagnetic fraction while $NiFe_2O_4$ made for the magnetic fraction. This opened up the possibility of further nickel enrichment by separating the magnetic and non-magnetic fraction through magnetic separation. A study was carried out to ascertain the extent of $NiFe_2O_4$ formation through measurement of saturation magnetisation. It was calculated from chemical analysis that in a typical final product, assuming all the nickel were converted into $NiFe_2O_4$, the percentage of $NiFe_2O_4$ would have been 9.37%. The same product yielded a saturation magnetisation value of 4.5 emu/g. Considering the standard saturation magnetisation value of $NiFe_2O_4$ 50 emu/g, the amount of $NiFe_2O_4$ in the product should have been 9.04%. The nearness of the $NiFe_2O_4$ percentage data obtained from two completely independent methods vindicated our contention that the entire nickel was converted into $NiFe_2O_4$ and the final product consisted of a magnetic and a non-magnetic phase. Thus, in principle it is possible to enrich the nickel content further by separating the magnetic phase

Merits and strengths of the present process :

The present process is attractive because it is essentially a low energy consumption process. The existing nickel exploitations from lateritic oxides, whether by acidic or alkaline route, are all energy intensive processes. Also these processes need to crush the ore to a very fine size (about -200 mesh). The present process can handle ores of -44 mesh size quite easily. The leaching temperature is only 100-110°C. Calcination at a higher temperature is only a need-based operation and will depend on the quality of the starting material and percentage extraction of nickel. Even if calcination is required, a much smaller mass compared to the starting material needs to be handled and going upto 900°C may not be necessary. Reagents used in the present process are inexpensive and known to have no toxic effects on the operator provided general laboratory safety norms are adhered to. The process is marked with operational simplicity involving essentially digestion, precipitation and filtration. The process will generate valuable by-products, which has a steady market within the country. The process does not envisage any waste and effluent disposal problem thus making it environment friendly.

CONCLUSION

Conclusions of the present study may be listed as follows :

1. COB ore of Sukinda valley may be leached with an appropriate combination of HCl, HNO_3, H_2SO_4 and water. Extractability of nickel is more than 80%.

2. An ore size of -44 mesh is sufficient for acid digestion.

3. Neutralisation of the leach liquor is carried out with Na_2CO_3 and NaOH.

4. Washing of metal hydroxide precipitate is extremely crucial for achieving the desired product grade.

5. Calcination of the hydroxide precipitate at higher temperature enhances the nickel content in the final product. However, calcination is not a necessary step and will depend on the quality of the starting COB ore and extractability of nickel.

6. The process is not energy intensive and generates valuable by-products that have ready market in the country.

7. The process is environment friendly and does not encounter waste and effluent disposal problems.

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