

PROCESS FOR EFFECTIVE UTILIZATION OF LOW GRADE CHROMITE OVERBURDEN

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ABSTRACT

In India, 5 million t of chromite overburden is generated each year in addition to the 140 million t that has already been accumulated over the several years of mining. Up to now, this ore has not been commercially exploited due to low percentage (0.6-0.8%) of nickel present. In this study the reduction kinetics of chromite overburden is investigated at high temperatures (1000-1400 °C) with aim to develop a process for cost effective utilization of the overburden. Chromite overburden predominantly consists of iron oxide and chromite minerals along with minor constituents such as silicates and nickel oxides. The overburden samples from Sukinda chromite mines, India are used in the current study. The effect of various critical parameters such as temperature, time, reductant and lime flux on the reduction behaviour is examined. It is observed that the Fe recovery to metal increases with increase in temperature. It is also observed that about 80% of the total Fe, Cr and Ni values are recovered in the form of metal nuggets at 1400 °C and clear slag metal separation was achieved during reduction at optimized flux conditions. The results of bench scale experiments are discussed in this paper.

1 INTRODUCTION

The lateritic nickel ore also known as overburden of chromite mines is the only source of nickel available in the Sukinda Valley of Orissa, India. This overburden has a nickel content that ranges from 0.5 to 0.9 wt%. Up to now, this ore has not been commercially exploited due to low percentage of nickel present. Many pyro and hydro metallurgical methods have been tried mainly to extract nickel from these lateritic ores¹⁻⁵⁾ but these methods are costly and have high energy consumption. The overburden material also has appreciable iron (45-55 %) and chromium (5-20%) contents in it. Therefore, in the present study, the direct reduction of chromite overburden using coal is studied in order to extract all the valuable Fe, Cr and Ni metal values present in the overburden. The various reduction process parameters are established at lab and their effect on recoveries of Fe, Cr and Ni values to metal is discussed.

2 EXPERIMENTAL

2.1 Materials

The nickeliferous chromite overburden from R.O.M of Sukinda chromite mines, Orissa, India is studied. The cumulative size analysis and weights retained in different size fractions for the overburden ore is given in **Figure 1**. It can be seen from Figure 1 that the d_{80} (80% passing) of the particles in the ore is about 98 μm . The overburden ore is subjected to X-ray diffraction (XRD) analysis in order to know the mineral phases. The XRD pattern for raw overburden is shown in **Figure 2**. It can be seen from Figure 2 that Goethite and chromite are the predominant phases in the overburden ore. The chemical analysis of the overburden ore, reductant coal (anthracite), quartz, flux (lime) and bentonite (as binder) is given **Table 1**. Anthracite coal and the fluxes are used in powdered form having average particle size of about 55 μm . The raw materials are mixed at different ratios and agglomerated by using disc pelletizer to form green pellets feed for reduction process.

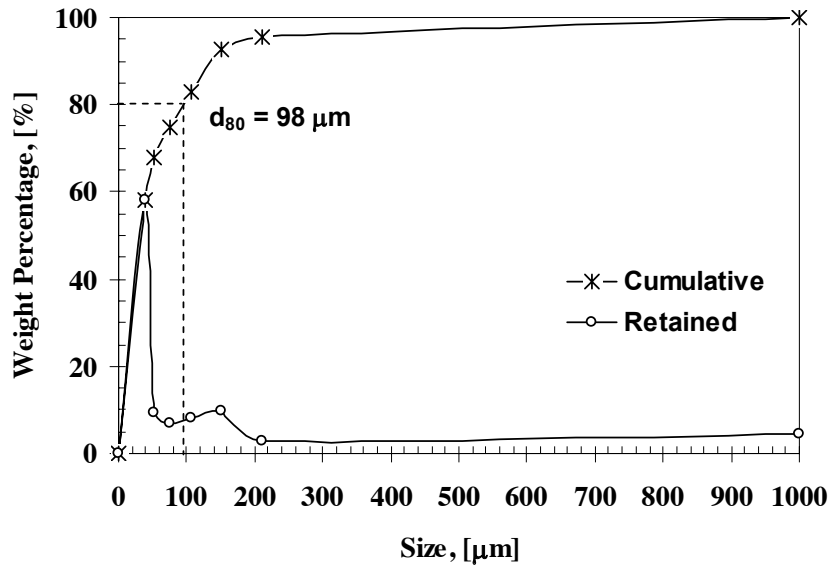


Figure 1: Cumulative size analysis and weights retained in different size fractions for the nickeliferous chromite overburden

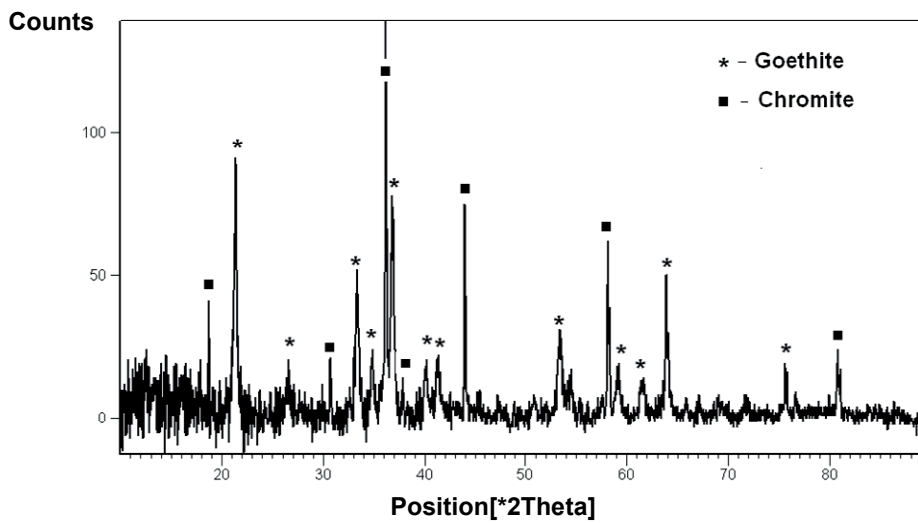


Figure 2: X-ray diffraction analysis of overburden material

Table 1: Chemical analysis of raw materials

Item	Chemical analysis, wt (%)						
	Fe(t)	Cr ₂ O ₃	CaO	MgO	SiO ₂	Al ₂ O ₃	NiO
Chromite overburden	46.0	14.9	0.06	2.5	4.03	6.7	0.8
Lime	2.9	-	64.6	0.9	1.9	0.05	-
Quartz	0.28	-	-	-	99.4	0.4	-
Bentonite	7.7	-	1.05	1.7	58.0	5.5	-
Proximate analysis, wt (%), wet basis							
Anthracite coal	FC		VM		Moisture	Ash	
	73.5		12.5		10.0	4.0	

2.2 Reduction Experiments at Lab

A horizontal tubular furnace is used to conduct the isothermal reduction experiments at various temperatures in the range of 1000-1400 °C. Throughout the reduction experiments argon gas having 99.0 % purity is purged at rate of 5.0 lpm through the furnace in order to maintain the inert atmosphere within furnace during reduction. The rest 1.0% in gas were impurities such as nitrogen and moisture. The green pellets are produced by agglomeration of overburden ore, quartz, lime, binder (bentonite) and reducing agent (coal) for carrying out the reduction process. The weighed pellets were placed in the alumina crucible and inserted in the hot zone of tube furnace. The green balls were subjected to various temperature and time during the reduction process. After each experiment, the crucible was taken out of the furnace and the weight of the reduced products is noted and subsequently subjected to chemical analysis. The effect of various operating parameters such as time, temperature, reductant and flux on the reduction process is examined primarily to establish the recoveries of the Fe, Cr and Ni metal values.

3 RESULTS AND DISCUSSION

3.1 Effect of temperature and time

The dried green pellets prepared with stoichiometric carbon (18.4g) and silica (3.0g) and 4.7g CaO (lime flux) are subjected to various temperatures in the range of 1000 °C to 1400 °C for different duration. The % Fe-metallization is estimated as the ratio of metallic Fe to total Fe content in the reduced pellets obtained after reduction experiment. The variation of percentage Fe metallization at different temperatures and time is shown in **Figure 3**.

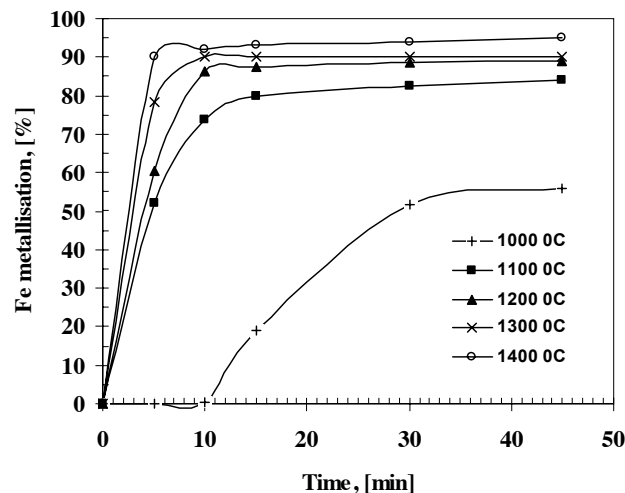


Figure 3: Effect of variation in reduction temperature and time on % Fe-metallization

It can be seen from Figure 3 that, at a given temperature and with increase in time the % Fe-metallization has increased upto certain time and after that remained constant indicating completion of the reduction reaction. It is also observed that the time required for achieving a given extent of Fe-metallization has minimized with increase in temperature. Thus for achieving minimum 50% of Fe-metallization the time required for the reduction process at 1000 °C is about 30 min whereas the same degree of Fe-metallization is achieved in only 5 min at 1100 °C. The highest degree of Fe-metallization, which is greater than 90% is achieved in 10 min at 1400 °C and increase in further time did not have any effect on improving the Fe-metallization due to completion of reaction. Clear slag and metal separation is observed at temperature of 1400 °C. It is worthwhile to mention here that the standard method for estimating the metallic Iron in a reduced product containing both its metallic and oxides compounds is well established. By contrast, there is no instituted method in order to differentiate between metallic Chromium and metallic Ni with their respective oxide forms in a reduced product. Considering this difficulty, all the studies are carried out at high temperature of 1400 °C in order to estimate the Fe, Cr and Ni recoveries since clear slag and metal separation is achieved. The

physical separation of slag and metal products obtained at high temperature range (about 1400 °C) was practical using physical separation. The metal and slag are analysed after separation in each reduction experiment at 1400 °C.

3.2 Effect of CaO

CaO in the form of lime is used as flux in the present reduction process. The optimum amount of lime is established at 1400 °C and 45 min reduction duration by varying the CaO/100 g of overburden ore in the range of 3 to 6 g by maintaining stoichiometric requirement of carbon (18.4g) and silica (3.0g) in the charge. The effect of variation in CaO content in the charge on recovery of Fe, Cr and Ni values to metal is shown in **Figure 4**.

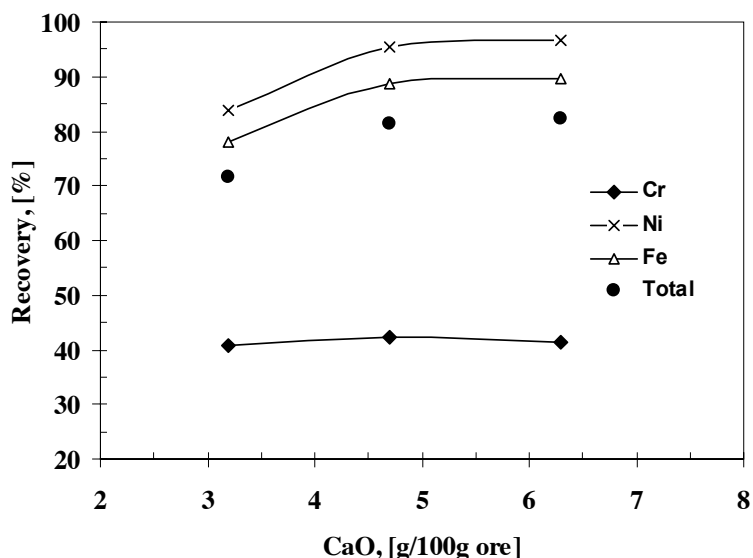


Figure 4: Effect of variation in CaO content on recovery of Fe, Cr and Ni to metal at 1400 °C and 45 min

The total recovery is obtained as a ratio of total weight of Fe, Cr and Ni reported in metal to initial weight of Fe, Cr and Ni values present in the charge before reduction. It is observed from Figure 4 that, with increase in the CaO content the total recovery of Fe, Cr and Ni values to metal has increased. Increase in CaO imparts fluidity to slag at high temperatures enabling improved diffusion reactions and slag metal separation thus resulting in improved total recovery. Therefore, the increase in the total recovery was more prominent during initial CaO addition from 3 to 4.7g increasing the total recovery from about 70 to 80%. With further increase in the CaO upto 6.3g, the total recovery was more or less stagnant. The recovery of chromium as expected was the least (40%) even at increased CaO addition due to refractory nature of chromite and requirement of higher temperatures of greater than 1400 °C for complete reduction. It is also observed that more than 90% of Ni and about 80% of the Fe is recovered in metal at optimized conditions of 4.7 g CaO (or 7.5 g lime) per 100 g of overburden.

3.3 Effect of carbon (coal) addition

Anthracite coal is used as carbon source for reduction process of low grade chromite overburden. The carbon content in the charge was varied from 20% less than stoichiometry (14.7g) to 20% excess (22g) in order to understand the effect of carbon addition on the total metal recoveries at 1400 °C. The theoretical requirement of carbon for reduction of Fe, Cr and Ni oxides in 100 g overburden is 18.4 g. The effect of variation in carbon per 100 g overburden ore on the recoveries of Fe, Cr and Ni at 1400 °C is shown in **Figure 5**. It can be seen from Figure 5 that the total recovery in metal have climbed upto 80% with increase in carbon from 14.7g to 18.4g (theoretical requirement) and hovered at 80% indicating no further significant effect of carbon addition on overall recoveries. Carbon when available in less proportion than minimum theoretical requirement (less than 18.4g) it is expected that the reduction process will starve for carbon required for gasification and result in decreased total

recoveries. Therefore, highest degree of total recoveries (80%) is achieved at theoretically expected carbon levels of about 18g. The least recovery of chromium (40%) obtained during the reduction process is not surprising due to refractory nature of chromite. It is also observed that more than 90% of Ni and about 80% of Fe is recovered in metal at optimized 18.4 g carbon (25g coal) per 100 g of overburden. Therefore, the suitable charge mix established from bench experiments is 25g coal, 3.0g quartz, 7.5g lime and 1.0g bentonite as binder per 100 g of overburden ore.

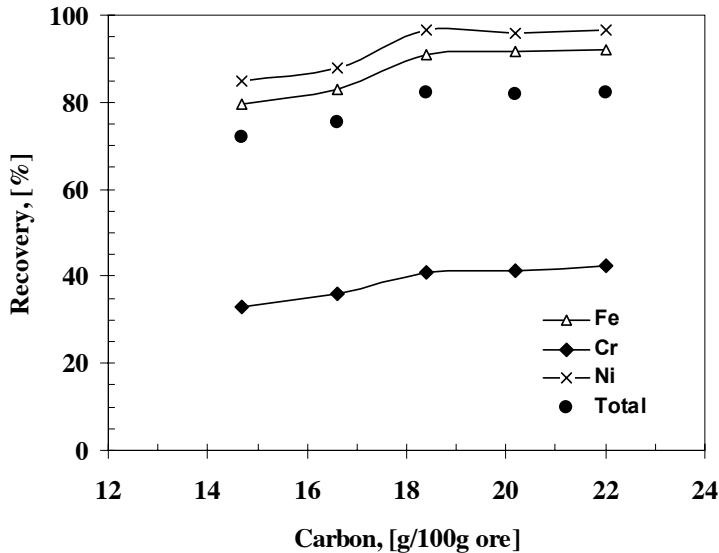


Figure 5: Effect of variation in carbon on recoveries of Fe, Cr and Ni to metal at 1400 °C and 45 min

3.4 Composition of reduction products

The Fe-Cr-Ni metal and slag nuggets obtained at 1400 °C and 45 min reduction duration are shown in **Figure 6**. It is observed from Figure 6 that a typical Fe-Cr-Ni metal nugget is about 10mm in height and width and has no micro-pores because of melting. The characteristics of having no micro-pores provide it a strong residence for reoxidation. The chemical composition of the metal nuggets and slag obtained at 1400 °C and 45 min reduction time is given in **Table 2**. It can be seen that, the Fe-Cr-Ni metal nuggets contain high metallic values of Iron about 88%, chromium up to 7-8% and 1.4 % Ni thus recovering the maximum Fe, Cr and Ni values present in the chromite overburden. The Fe-Cr-Ni metal nuggets could be potentially used as substitute raw material in SS and alloy steel making.

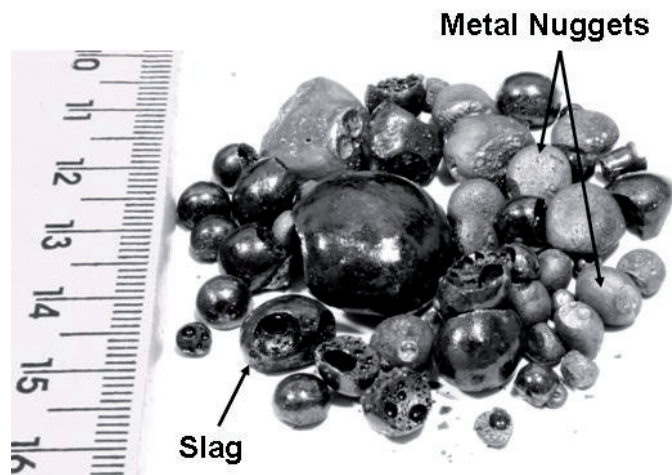


Figure 6: Fe-Cr-Ni metal and slag nuggets obtained at 1400 °C and 45 min reduction time

Table 2: Chemical compositions of the slag and metal nuggets at 1400 °C temperature and 45 min time

Metal Nuggets	Fe (t)	Cr	Ni	Si	C	S
	87.5	7.2	1.4	0.9	2.7	0.15
Slag	Cr₂O₃	SiO₂	Al₂O₃	CaO	Fe(t)	MgO
	24.8	20.4	17.8	12.2	12.4	4.0

4 CONCLUSIONS

The reduction process of low grade chromite overburden of Sukinda chromite mines is investigated with objective of recovering maximum Fe, Cr and Ni values present in the overburden. The effect of various operating parameters in reduction process is estimated in lab experiments. It was found experimentally that 25g coal, 3.0g quartz, 7.5g lime and 1.0g bentonite as binder per 100 g of overburden ore was suitable charge mix for obtaining more than 80% of total (Fe-Cr-Ni) recovery to metal at 1400 °C. More than 90% of Fe and Ni metal values are recovered in the form of metal nuggets. The slag and metal nuggets obtained were easily separable. The Fe-Cr-Ni metal nuggets obtained have high metallic values of iron about 88%, chromium up to 8% and 1.4% nickel thus recovering the maximum Fe, Cr and Ni metal values present in chromite overburden. Based on the experimental results, it is found that a coal based reduction process to produce Fe-Cr-Ni nuggets could be a suitable method for effective utilization of low grade chromite overburden.

5 REFERENCES

- [1] Chander, S. and Sharma, V. N., "Reduction roasting/ ammonia leaching of nickeliferous laterites", *Hydrometallurgy*, 1981, **7**, pp 315-327.
- [2] Sukla, L. B. And Das, R. P., "Leaching behaviour of Sukinda lateritic nickel ore with sulphuric acid", *Miner. Process. Extract. Metall.*, 1986, **95**, pp 53-55.
- [3] Panda, S. C., Sukla, L. B. and Rao, P. K., "Extraction of nickel through reduction roasting and ammonical leaching of lateritic nickel ores", *Trans. Ind. Inst. Metals.*, 1980, **33**, pp 161-165.
- [4] Stella, A. L. And Ioannis, G. Z., "Beneficiation of a Greek serpentinitic nickeliferous ore Part II. Sulphuric acid heap and agitation leaching", *Hydrometallurgy*, 2004, **74**, pp 267-275.
- [5] Hwa, Y. L., Sung, G. K. and Jong, K. O., "Electrochemical leaching of nickel from low-grade laterites", *Hydrometallurgy*, 2005, **77**, pp 263-268.