Chemical Beneficiation of Indian Chromites

M. C. SEN and A. B. CHATTERJEE

The authors here deal with some preliminary tests on two samples of Indian chromites for their chemical beneficiation. One was from Nausa-hi, Orissa, and the other from Mysore. The ores contained only a little haematite but no magnetite. Talc was the main gangue material in the former and chlorite was the only gangue in the latter. The first ore (-7 mesh) was reduced at different temperatures using coal, coke, charcoal and coke-oven gas. The second (-7 mesh) ore was reduced at different temperatures with coke-oven gas with or without pre-oxidation.

G REAT stress has been laid on the development of alloy steel in the second Five Year Plan. Alloy steels are used for almost all purposes ranging from low-alloy structurals to high-alloy steels. A project for making high-grade ferro-chrome using low-grade Indian chromites was therefore undertaken in the National Metallurgical Laboratory.

The only source of chromium metal is chromite, a mineral of the spinel group having the formula (Fe.Mg)O.(Cr.Al)₂O₅. Though India has a very big reserve of chromite, most of the ores have very low Cr : Fe ratio to be used for the manufacture of high-grade ferro-chrome for alloy-steel making. In most cases Indian chromites cannot be enriched by ore dressing methods due to the fact that iron is not present in the ore as gangue but in chemical combination in the mineral. The only possible method to concentrate such an ore is to attack the spinel structure chemically to remove as much of iron as possible.

Beneficiation of several chromites from different parts of India has been done by ore dressing methods^{1.9} in the ore-dressing and mineral beneficiation division of the National Metallurgical Laboratory. But all the concentrates obtained, though high in Cr₂O₃ content had Cr : Fe ratios less than 3 : 1. A chromite associated with ferrugenous gangue from the Gunjang chromite mine. Orissa, was successfully concentrated¹⁰ by reducing the gangue to magnetic oxide of iron with coke oven gas at 500-560°C and separating the iron by wet magnetic separation from the crushed calcine. The concentrate assayed 58.5%, Cr₂O₃ having Cr : Fe ratio of 3 : 1 with a recovery of 80.6%.

Investigators abroad have tackled the problem of enriching chromites having low Cr : Fe ratio by various chemical methods^{11,28}, of which the method

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adopted by Lloyd and others¹⁴ and Boericke¹⁵ in America and Hammerberg¹⁶ in Sweden seem to be highly encouraging. Investigations were, therefore, undertaken for chemical beneficiation of Indian chromites on similar lines. The process in short consists of preferential reduction of the FeO in the ore with solid reducing agents namely coke, coal, charcoal or gaseous reduction at various temperatures ranging from 850-1250°C followed by leaching the calcine with dil. sulphuric acid^{14,15}. Alternatively the ore is first oxidised and then reduced which is subsequently followed by magnetic separation of the crushed calcine to separate reduced iron¹⁶.

ORE SAMPLES

Two samples of chromite, one from Nausahi. Orissa, sent by M/s. Serajuddin & Co. ,Calcutta and the other from Mysore sent by Bureau of Mineral Development, Mysore, were investigated for enrichment by chemical methods. Chemical analysis of the ores are given in Table I.

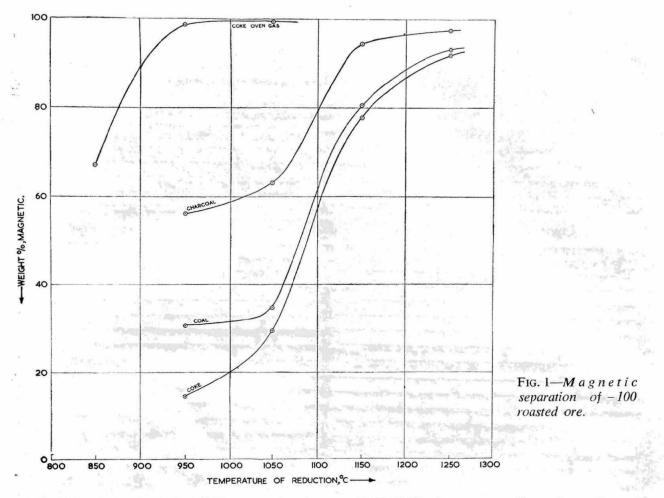
	TABLE I-	Снеміс	L ANA	LYSIS O	F CHRO	MITE
		Percent				
		$\mathbf{Cr}_{e}\mathbf{O}_{n}$	Fe	Soluble Fe	SiO ₂	Cr :Fe ratio
1. 2.	Nausahi ore Mysore ore		11.8* 18.70	1.114	10.0* 6.02	2.92
	* Assayed					

Petrological examination revealed that the gangue material in Nausahi chromite was mainly talc with minor quantities of serpentine and quartz.

According to Rao and others²⁹ the Mysore chromite is fine-grained and greyish black. The chromite is black and opaque and the gangue is composed of chromite, probably kammererite, a chromoferrous variety. The spinel grains assayed 56.30°_{\circ} Cr₂O₂, 30.96°_{\circ} FeO, with Cr : Fe ratio of

* The screens referred to in this report are from Tyler Standard sieve series. No responsibility is taken for the results except in so far as they apply to the samples tested.

Dr. A. B. CHATTERJEE, Sr. Scientific Officer, and Mr. M. C. SEN, Sr. Scientific Assistant, National Metallurgical Laboratory.



1.60. This obviously indicates that ore dressing methods are not suitable to enrich the ore to a concentrate having Cr: Fe ratio of 3 : 1 or more.

The ore was stage-crushed to -7 mesh and representative sample of requisite quantity for each experiment was taken by coning and quartering.

REDUCTION WITH SOLID REDUCING AGENTS

For each test the following materials were thoroughly mixed and moistened with 5% water and pellets were made under a pressure of 5000 lbs/sq. in. in a hydraulic press :—

-7 mesh chromite	100 gms.
-7 mesh reducing agent	
(coal, coke or charcoal)	20 gms.
Dextrine	2%

The pellets after drying at 110°C were taken in a covered crucible and placed in an electric muffle furnace raised to the desired temperature and kept for four hours.

REDUCTION WITH COKE OVEN GAS

Approximate analysis of the coke oven gas used in this investigation is given in Table II.

TABLE II-ANALYSIS OF COKE OVEN GAS

$\begin{array}{c} \text{Constituent} \\ \text{CO}_2 \end{array}$	% by volume 3.8
$CnHm^*$ O_2	212 0.7
CO H ₂	9.7 51.0
$\underset{N_2}{\overset{CH_4}{\operatorname{SH}_4}}$	23.0 9.6
	100.0

* Saturated higher hydrocarbons

For each experiment 200 gms. of -7 mesh chromite was packed in a silica tube having arrangements for passing coke oven gas through the ore bed. Hot junction of a chromel alumel thermocouple was embedded in the centre of the chromite bed for measuring the temperature of the charge. The silica tube was placed inside electric tubular furnace and gas was passed through the charge, via a flow meter for 4 hours after the desired temperature was attained.

LEACHING OF CALCINE

For leaching, 6 gms. of calcine crushed to -100 mesh and 9 c.c. of dil. H₂SO₄ (1 : 2 by vol) were

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taken in a small pyrex tube and kept inside a lead lined cast iron vessel provided with a lid. The vessel with the lid closed was placed inside an electric furnace and kept for 4 hrs. at a temperature of 105°C. The tube was taken out and the contents were filtered off and residue dried after it was washed free of leach solution.

BENEFICIATION OF NAUSAHI CHROMITE

Pellets were made using coke, coal and charcoal and dextrine. The pellets were then calcined at different temperatures namely 950, 1050, 1150 and 1250°C. The calcines were crushed to -100 mesh and passed through magnetic separator. The ore, as it is, was also reduced with coke oven gas at 850, 950 and 1050°C and was then passed through magnetic separator after crushing to -100 mesh. Results of magnetic separation are given in Fig. 1.

Though reduction of FeO was efficient in all cases, magnetic separation failed to improve the Cr : Fe ratio, probably due to non-liberation of reduced iron from the oxide of chromium at this grind. Magnetic separation with calcines ground finer than -100 mesh was not tried due to practical difficulties.

The ore reduced at 1050°C with coke oven gas, was leached with dil. H_2SO_4 (1 : 2 by vol) at 105°C

and was filtered. The residue assayed 53.15% Cr₂O₃ having Cr : Fe ratio of 8.12 : 1 with a recovery of 80.6%.

BENEFICIATION OF MYSORE ORE

Results of experiments with Nausahi ore clearly indicated that coke oven gas was capable of reducing the FeO of the ore at a much lower temperature, and as such the Mysore ore was reduced invariably with coke oven gas and without prior oxidation of the ore.

Two series of experiments on reduction were carried out with this ore. In the first series -7 mesh ore was reduced at 800, 850, 900, 950, 1000 and 1050°C with coke oven gas. In the second series -7 mesh ore was first oxidised at 850°C and then reduced at 800, 850, 950, 1000 and 1050°C with coke oven gas. In both the cases the products from these two series of experiments were crushed to -100 mesh and leached with dil. H₂SO₄ (1 : 2 by vol.) at 105°C and residues were filtered off free of leach solution. Results of these experiments are shown in Fig. 2.

Reduction of preoxidised ore with coke oven gas at 800, 850, 900, 950, 1000 and 1050° C followed by magnetic separation of calcines crushed to -100

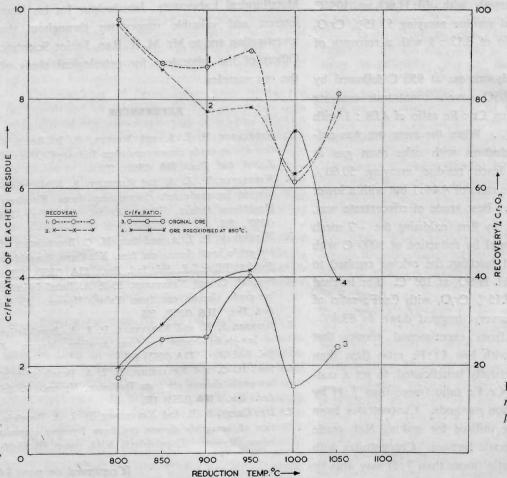


FIG. 2—Leaching of reduced ore under pressure.

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mesh could not separate any reduced iron from oxide of chromium in the magnetic fraction.

SUMMARY AND CONCLUSIONS

Two chromites, one from Nausahi, Orissa assaying 5.3% Cr₂O₃ having Cr : Fe ratio of 2.92 : 1and another from Mysore assaying 49.11% Cr₂O₃ having Cr : Fe ratio of 1.80:1 were tested for chemical beneficiation. The ores contained only a little of haematite but no magnetite. Talc was the main gangue in the former and chlorite the only gangue in the latter ore.

Reduction with coal, coke, charcoal and coke oven gas showed that rate of reduction of FeO in the mineral was slow at lower temperatures but increased rapidly between 1050 and 1150°C with the solid reducing agents and between 850 to 950°C with coke oven gas, thereafter the rate slowed down considerably in all the cases.

Reduction of the -7 mesh Nausahi ore at 1050° C with coke oven gas followed by leaching of calcine crushed to -100 mesh with dil. H₂SO₄ at 105° C gave a concentrated residue assaying 53.15% Cr₂O₃ having Cr : Fe ratio of 8.12 : 1 with a recovery of 80.6%.

Reduction of Mysore ore at 950°C followed by leaching with dil.H₂SO₄ gave a concentrate assaying 55.46% Cr₂O₃ having Cr : Fe ratio of 4.08 : 1 with a recovery of 90.6%. When the same ore was oxidised prior to reduction with coke oven gas at 950°C it gave a leach residue assaying 50.60% Cr₂O₃ having Cr: Fe ratio of 4.44:1 but with a lower recovery of 78.3%. Best grade of concentrate was, however, obtained by first oxidising the -7 mesh ore at 850°C followed by reduction at 1000°C with coke oven gas and leaching the calcine crushed to -100 mesh with dil. H₂SO₄ at 105°C. The leached residue assayed 53.15% Cr₂O₃ with Cr: Fe ratio of 7.30:1 but the recovery dropped down to 63.4%

It is evident from experimental results that Indian chromites with low Cr:Fe ratio (less than 3:1) may be successfully beneficiated, to get a concentrate higher in Cr:Fe ratio (more than 3:1) by chemical beneficiation methods. Concentrates from this process can be utilised for making high grade ferro-chrome in electric furnace. Concentrates with very high Cr:Fe ratio (more than 7:1) may also be

obtained by this process and can be used for sweetening the ores, having Cr:Fe ratios less than 3:1.

The cause of sudden drop in recovery of Cr_2O_3 at a reduction temperature of 1000°C was not fully understood at this stage and has to be further investigated in fuller details.

Leach solution can be utilised for leaching more calcine by crystallising out $FeSO_4$. $7H_2O$ from the solution and making up the pH concentration with requisite quantity of H_2SO_4 .

Industrial application of this process will open out a new field for utilising low grade Indian chromites which are simply dumped near the mine site for successful preparation of ferro-chrome, a ferroalloy which has to be imported from outside for alloy steel making.

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