

Beneficiation of low grade chromite for preparation of charge-chrome

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ABSTRACT

Low grade chromite samples from rejected dumps and over-burdens were taken for beneficiation study to produce a material suitable for charge-chrome preparation. The chromite samples with about 25% Cr_2O_3 in average, are ferruginous, but non-magnetic and contain 30-40% Fe_2O_3 , SiO_2 content is significantly low. Limonite, followed by laterite, is the main gangue material. In general, the fraction between 0.5 mm and 0.045 mm size is richer in Cr_2O_3 than the both +0.5 mm and -0.045 mm fraction. A process involving (i) crushing to -1 mm size, (ii) desliming and rejection of the slime, (iii) sieving at 0.2 mm and (iv) tabling of the -0.2 mm fraction, has been found to be successful to produce a material with Cr_2O_3 content around 44%, raising the Cr_2O_3/Fe_2O_3 ratio from 0.6 to above 2.2. The process is a low cost oriented one and the beneficiated Product satisfies the requirements for chromite used for preparation of charge-chrome.

Introduction

The recent breakthrough in stainless steel manufacturing technology by development of processes like AOD (Argon Oxygen Decarbonisation), VOD (Vacuum Oxygen Decarbonisation) AVR (Alleghary Vacuum Refining) and CLU (Creuset Loere and Uddeholm), where reduced partial pressure of carbon monoxide permits the removal of carbon without oxidation of chromium has made it possible to use lower chromium containing ferro-chromium alloy, commonly known as charge-chrome. Charge-chrome contains 50 - 55% chromium in contrast to minimum 65% in low carbon ferro-chrome, required for the manufacture of stainless steel and other high chromium steels by the conventional arc furnace technology. Similarly for the preparation of charge-chrome chromite containing 40-44% Cr/Fe ratio as low as 1.6 could be used,

while that of normal ferro-chrome needs chrome ore containing minimum 48% Cr_2O_3 and Cr/Fe ratio above 2.8. Thus, it is found that charge-chrome facilitates the utilization of lower grade chromite.

Statistical analysis of the Indian chromite reserve shows that neither the reserve nor its current production is significant compared to the statistics of the other leading producers or users of chromite¹. On the other hand, it is found that all over the chromite mines in the country huge quantities of low grade ores are being left in dumps as rejects with over-burden materials. No serious attempt has yet been made for the utilization of these rejected chromite ores. This is mainly because of the fact that conventional beneficiation process to up-grade the ore to the level of standard requirements for normal uses, generally proves to be uneconomical and consequently neither the mine owners nor the users are interested in beneficiation. However, with the

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possibility of utilization of relatively low grade chromite in the preparation of charge-chrome, it seems that some low cost oriented beneficiation process may be an economical endeavour for up-grading the so far rejected chromite ores. Keeping this in view, in the present investigation, some very low grade chromite samples were taken for laboratory scale beneficiation.

Characteristics of the chromite samples

Four chromite samples from rejected dumps and over-burden materials of a chromite mine, were collected for their beneficiation. All the four samples are non-magnetic, soft in nature and black to brownish black in colour.

The main three characterising constituents, Cr_2O_3 , Fe_2O_3 (total iron) and SiO_2 of the chromite samples are given in Table - 1. It is found that except in the sample No. 1, $\text{Cr}_2\text{O}_3\%$ is very low, and Fe_2O_3 is significantly high. However, SiO_2 is found to be exceptionally low.

TABLE - 1

Partial Chemical Analysis of the Chromite samples (Wt%)

Constituents/ Sl. No.	1	2	3	4
Cr_2O_3	33.60	20.40	23.20	22.40
Fe_2O_3	30.60	40.00	36.40	35.80
SiO_2	1.50	1.90	2.55	1.75

Examination of the polished sections under reflected light shows that limonite and laterite are the main two gangue minerals present. Goethite, magnetite, quartz and serpentine are the other accessory minerals, present in decreasing order. The chromite grains are embedded in limonite/laterite mass. They are often cracked and cracks are filled with gangue minerals. The chromite grains are mostly below 0.2 mm size, but occasionally they range up to 0.5 mm. (Fig. 1 - 4).

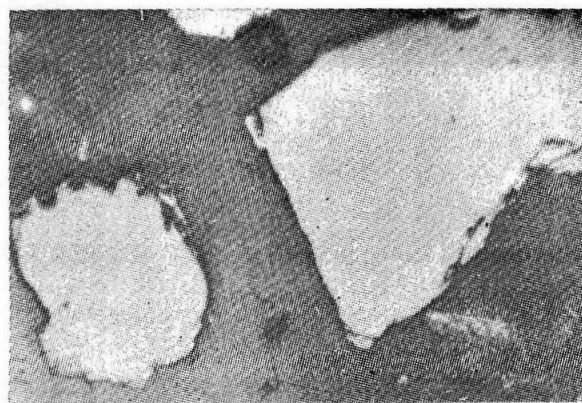


FIG. - 1. Photomicrograph Common chromite grains. Reflected light. X 175

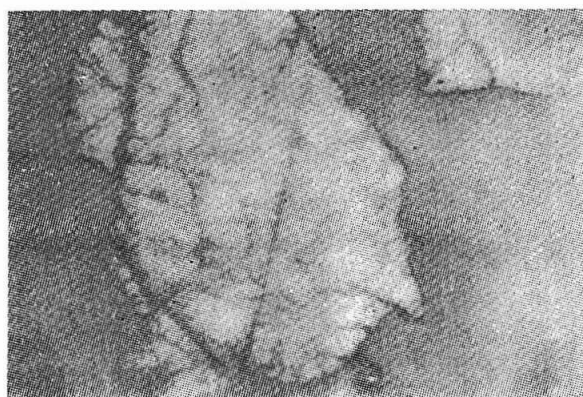


FIG. - 2. Photomicrograph. Cracked chromite grains; cracks are filled with gangue materials. Reflected light. X 175

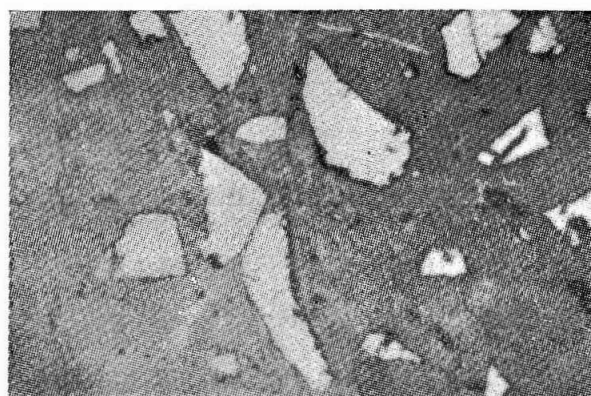


FIG. - 3. Photomicrograph. Fine chromite grains in lateritic mass. Reflected light. X 175.

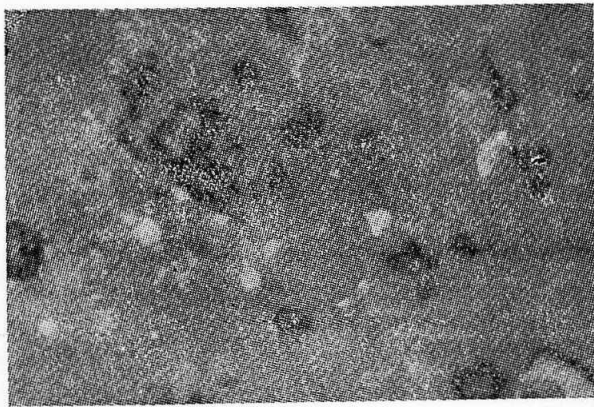


FIG. - 4. Photomicrograph. Limonite with remnants of primary iron oxides white globules are goethite. Dark specks are pores. Reflected light X 175.

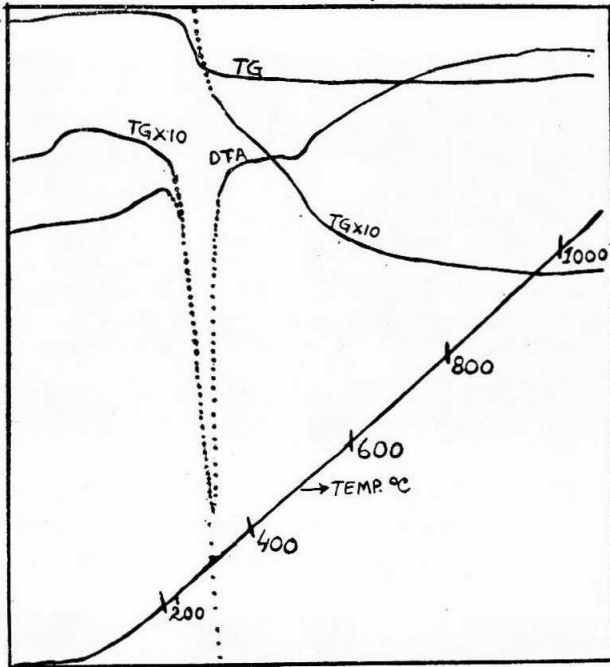


FIG - 5. DTA/TG Curves of the chromite ore

Combined DTA/TG of the chromite samples was carried out in the Netsch Simultan Thermo Analysis, Model 429 with potentiometric recorder up to 1000°C at a heating rate of 10°C/minute. DTA curves show two endothermic peaks, one at 340°C and the other at 530°C with corresponding loss in TG (Fig. - 5). The

first peak is due to limonite/Lepidocrocite². The second peak is identified to be of laterite. It is observed that basically all the four samples are identical in character, only with difference in quantity of impurities SiO₂ content is appreciably low and for up-grading the ore it requires particularly the removal of iron.

Fractional characteristics.

The chromite samples were crushed in a Roll-crusher and were reduced to - 1 mm size. As the S. No. 1 shows better liberation than the others, in some experiments, this sample was crushed to - 3 mm size only. Sieve analysis of the 4 individual samples and of a composite sample prepared from equal amount of material from each of the samples. is shown in Table - 2. From the sieve analysis, it is found that S. No. 1 produces minimum of - 0.045 mm material, while S. No. 3 produces both - 0.045 mm and + 0.5 mm fractions higher than those of the other samples.

TABLE - 2
Sieve Analysis (all crushed to - 1 mm)

Size in mm Sl No.	1	2	3	4	Composite (1-4)
- 1+0.5	8.3	6.7	11.2	6.4	10.3
- 0.5+0.212	22.0	18.8	17.6	17.3	17.4
- 0.212+0.106	27.6	24.4	15.8	21.6	21.9
- 0.106+0.045	16.4	16.3	18.8	21.3	16.9
- 0.045	25.7	33.8	36.6	33.4	33.5

Both Cr₂O₃ and Fe₂O₃ of some selected fractions of the samples are reported in Table - 3 A and B. From Table-3A it is found that except in S. No. 3, in all the samples, the three fractions lying between 0.5 mm and 0.045 mm size are richer in Cr₂O₃ than both +0.5 mm and -0.045 mm fractions and most of the Cr₂O₃ content is present in these fractions. From Table - 3 B, it is found that the fractions lying between 0.5 and 0.045 mm are poorer in Fe₂O₃ content than the - 0.045 mm fraction and total iron content in these fractions is significantly low. In case of sample No. 3, although a signi-

TABLE — 3 A
Cr₂O₃ distribution in different size fractions.

(a=Material %, b=Cr₂O₃ %, c=Cr₂O₃ distributions % and ND=not determined)

Size in mm Sl. No.	1*			2			3			4		
	a	b	c	a	b	c	a	b	c	a	b	c
+ 0.5	24	23.8	17	6.7	ND		11.2	17.5	9	6.4	ND	
- 0.5 + 0.212	16	46.6	19	18.8	30.2	28	17.6	16.65	13	17.3	ND	
- 0.212 + 0.106	22	45.8	30	24.4	38.4	46	15.8	19.2	14	21.6	36.0	35
- 0.106 + 0.045	13	35.2	14	16.3	28.2	22	18.8	35.8	30	21.3	35.0	33.3
- 0.05 (Calculated)	25	26.9	20	33.8	ND		36.8	21.5	34	33.4		ND

* S. N. 1 crushed to - 3 mm.

TABLE — 3 B
Fe₂O₃ distribution in different size fraction

(a=Material %, b=Fe₂O₃ %, c=Fe₂O₃ distribution %, ND=not determined)

Size in mm Sl. No.	1*			2			3			4		
	a	b	c	a	b	c	a	b	c	a	b	c
+ 0.5	24	25.6	20.1	6.7	ND		11.2	24.0	7.4	6.4	ND	
- 0.5 + 0.212	16	17.0	8.9	18.8	20.6	9.7	17.6	27.0	13.1	17.3	ND	
- 0.212 + 0.106	22	18.2	13.1	24.4	24.4	14.9	15.8	25.0	10.9	21.6	19.4	11.7
- 0.106 + 0.045	13	29.4	12.5	16.3	33.6	13.7	18.8	24.6	12.7	21.3	30.0	17.9
- 0.045	25	55.6	45.4	33.8	ND		36.6	35.6	55.9	33.4	ND	

* S. No. 1 crushed to - 3 mm.

ificant amount of Cr₂O₃ goes with the - 0.045 mm fraction, more than 50% of the iron is also present in this fraction.

Beneficiation

Desliming and sieving at 0.5 mm.

From the fractional analysis of the samples it becomes evident that - 0.5 + 0.045 mm fraction is the best grade ore and removal of both + 0.5 mm and - 0.045 mm fraction is necessary in up-grading the chromite samples. For this purpose desliming of the material and then sieving (in wet condition) at 0.5 mm looks to be the best method. In Table - 4, analysis of the products derived by desliming and sieving at 0.5 mm of different samples are shown. From Table - 4 it is found that, except in S. No. 3, very high amount of Cr₂O₃ is confined to the

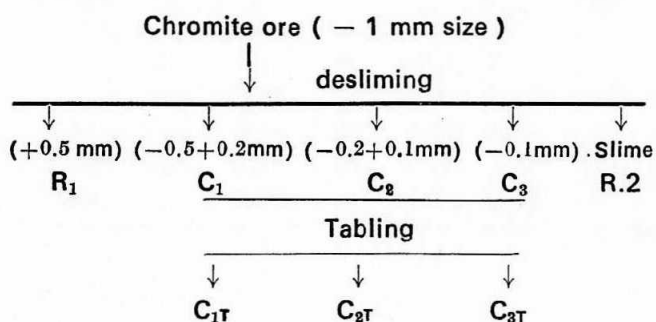
fraction derived from desliming and sieving at 0.5 mm. Particularly in S. Nos. 2 and 4 almost the entire amount of Cr₂O₃ remains in this fraction. It is also found that Fe₂O₃ content decreases significantly in this fraction. However, in none of the samples, except in S. No. 1, Cr₂O₃ value of this fraction goes above 40%. This suggests that further treatment of this fraction is necessary.

TABLE — 4
Characteristics of the product derived by desliming and sieving at 0.5 mm

Sl. No.	Product%	Cr ₂ O ₃ %	Cr ₂ O ₃ Distr %	Fe ₂ O ₃ %	Fe ₂ O ₃ distr %
1	62.8	42.0	78	18.4	37.7
2	57	35.0	98	25.0	35.6
3	42	31.2	56.5	27.0	31.9
4	53	38.4	91	26.0	38.6

Tabling

Considering the low quality of the product derived by desliming and sieving at 0.5 mm, it was thought that further tabling of the material might produce the desired result. Accordingly different size fractions were processed in a standard laboratory size wilfley table. The entire process may be summarized in the following form :



From the processing of individual samples, according to the procedures shown above, it is

found that generally the product C_{1T} is of relatively low Cr₂O₃ value. Although in both cases, Cr₂O₃/Fe₂O₃ ratio is higher than 1.7, the product C_{2T}+C_{3T} is of much higher quality than the product C_{1T}+C_{2T}+C_{3T}.

Processing of composite sample

A composite sample, prepared from equal amount of material from each of the samples was processed according to the procedures described. The results of the experiments are summarised in Table - 5. It is found that a product (C_{2T}+C_{3T}) with Cr₂O₃ value ranging from 43 to 44.6% can be achieved by the process adopted Cr₂O₃/Fe₂O₃ ratio of the product is between 2.2 and 2.4. When processed separately, total of product C_{2T}+C_{3T} is found to be 25 to 27% of the original ore. When the product C₁ and C₂ are processed together, the yield is found to be slightly higher with a slightly lower Cr₂O₃ value.

TABLE - 5
Analysis of product derived by desliming, sieving and tabling of composite samples

Product (Ref. 4.2)	Product Wt %	Cr ₂ O ₃		Fe ₂ O ₃		Cr ₂ O ₃ / Fe ₂ O ₃	
		Wt%	Distr. %	Wt%	distr. %		
R ₁	10	20	8	18.5	5.2		
R ₂ (Calculated)	34.7	13.6	19	61.8	59.5		
C ₁	17.8	29.0	20.7	22.0	11.0		
C ₂	21.0	35.0	29.5	21.5	12.6		
C ₃	16.5	34.0	22.5	26.0	12.0		
C ₁ +C ₂ +C ₃	55.3	32.8	73	22.76	35.3		
Trial - I							
C _{2T}	14.66	45.0	26.5	17.3	7.1		
C _{3T}	10.21	44.0	18.0	20.6	5.9		
C _{2T} +C _{3T}	24.9	44.5	44.5	18.7	13	2.4	
Trial - II							
C _{2T}	16.67	45.0	30.1	19.4	9		
C _{3T}	10.27	42.6	17.6	22.0	6.3		
C _{2T} +C _{3T}	27.0	44.1	48.2	20.3	15.3	2.2	
Processing							
C₂ and C₃							
1 together	C _{2T} +C _{3T}	29.5	43.0	51.4	19.0	15.7	2.3

TABLE — 6
Chemical analysis of the Composite samples (Wt. %)

Sample	Cr ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	MgO	LOI	Cr ₂ O ₃ /Fe ₂ O ₃
1. Original	25.2	34.4	20.4	1.5	0.9	6.8	10.7	0.74
2. Beneficiated product	44.0	18.0	17.8	1.0	0.95	11.0	7.2	2.44

Characteristics of the beneficiated product

Chemical analysis of the composite sample and that of beneficiated product (C_{2T}+C_{3T}) are shown in Table - 6 as product characterization. It is found that in the beneficiated product both Cr₂O₃ and MgO increase significantly, while Fe₂O₃, Al₂O₃ and LOI decrease. Consequently Cr₂O₃/Fe₂O₃ increases from 0.73 to 2.44.

Discussion

It is found that soft and ferruginous but non-magnetic low grade chromite ore can be up-graded by a combined process of desliming, sieving and tabling to a level suitable for preparation of charge-chrome. The process is simple and economical and includes the following unit operations.

All reduced to — 1 mm size.

Desliming and rejection of the slime.

Sieving (wet) at 0.2 mm.

Tabling of the —0.2 mm fraction.

To keep the energy consumption at the minimum possible level, it was not attempted to get very fine grinding. It is found that as the ores are quite friable, grinding in a Roll mill is enough to reduce the material to - 1 mm size. At this level, although complete liberation is not achieved, the desired quality is attainable. In the laboratory, desliming of the material was carried out manually as well as by using centrifugal classifier. The latter can be adopted for plant scale operation. The quantity of recovered product is about 30% of the ore with around 50% Cr₂O₃ recovery, although looks to be low, is quite significant from the fact that the material taken is of very low grade and the process is

low cost oriented. The composite ore sample assays only about 25% Cr₂O₃. It may be pointed out that in India, the estimated reserve of 33.725 million tonnes of chromite does not include the type of material taken for the present investigation³. These are either lying as rejected materials or in overburden of the working faces. In present mining practice, these are mined and then dumped to reach the quality grade ores. Thus even recovery of 30% is beneficial, provided the process is economical.

The beneficiated material satisfies the requirement for chromite used for preparation of charge-chrome. Besides, it is found that in the beneficiated product total Cr₂O₃+Al₂O₃ is above 60%. So, this product also satisfies the specification for the U. S. National stockpile chrome ore which requires minimum Cr₂O₃+Al₂O₃ content to be 58%³.

As it is well known, these beneficiated fine products can not be used as such for metallurgical purpose including charge-chrome. However, various means of agglomeration like pelletisation, sintering and briquetting are known to be employed for chromite fines and concentrates. In India also, briquetting process for fine chromite has been developed and practised^{4,5}. And so, there should not be any apprehension about the possibility of utilizations of the fine concentrate.

In the present industrial context, the increase in production of ferro-alloys is quite natural. Production of ferro-chrome in India which was 1,900 tonnes in 1972, reached the level of 31,300 tonnes in 1981⁶: And with the changing technology in steel making, it is understandable

that charge-chrome is going to replace the ferro-chrome gradually but definitely. Thus, it is observed that low cost - oriented beneficiation of very low grade chromites from rejected dumps and overburdens for the purpose of its utilization in preparation of charge-chrome is a practical proposition,

Acknowledgement

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Discussion

M. Nawaz, Indian Metals & Ferro-Alloys, Bhubaneswar

1. From which mines samples were drawn ?
2. Will the suggested process be applicable to all ferruginous but non-magnetic ores ?
3. What is the reason for improvement in Cr_2O_3 content in the -0.5 to -0.45 mm fraction ?

Answer

1. Samples belong to Sukinda Valley, Orissa.
2. There is a need for examination of the associated materials since the characteristics vary from deposit to deposit, However / the process should be applicable to soft friable, ferruginous but non-magnetic ores.
3. During crushing most of the limonite and laterite get crushed to very fine size to -45 micron. In $+0.5$ mm liberation is not perfect and gangue materials are present. Consequently -0.5 mm to -0.045 is the best.

N. Chatterjee, Alloy Steels Plant, Durgapur

1. Does this process of beneficiation give rise to dephosphorisation of the ore? If so to what extent ?

Answer

We have not examined dephosphorisation.

A. K. Tripathy, R. R. L., Bhubaneswar

1. What is the ratio for Cr/Fe required for charge chrome plant ?
2. Your beneficiation process involves grinding -5 mm size and there is considerable loss in recovery of chromite. How would it compare with a process developed by RRL for removal of Fe by reduction with C followed by leaching with acid of low grade ferruginous chromite ores to improve the chromium iron ratio ?

Answer

1. Chromium iron ratio required is 1.6. We have achieved 2.2.
2. The chromite taken for study is only from rejects and the party sponsoring the project feels that even recovery of 45-50% Cr_2O_3 will be more economical than a high cost process involving fine grinding, hydro-cyclone, reduction, followed by leaching etc. Whether the RRL process is economical is to be examined thoroughly.

B. Banerjee, N. M. L., Jomshedpur

1. Are the photomicrographs shown are of the ore pieces or of their ground product and the grain size shown does it represent the liberation size of chromite grain? If so what is the technique adopted to measure grain size from polished section?

Answer

1. Photographs show ground product in polished section. As shown in the photograph, under $-5\ \mu\text{m}$, some grains are completely liberated but not all.

