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RECOVERY OF CHROMITE FINES BY FROTH FLOTATION

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Chromite fines generated during communition of the low grade Landi-Raud chromite ore for the gravity processing, have been recovered by Froth flotation. A concentrate assaying 47% Cr_2O_3 with a recovery of 61% has been obtained by using a fatty acid anionic collector during the flotation process on a deslimed feed.

Key words: Flotation, Flocculation, Desliming, Scrubbing, Activation.

INTRODUCTION

Chromite mining in Pakistan has been concerned mainly with the production and export of high grade material. Since the start of chromite mining at the begining of this century at places such as the famous Zhob Valley Igneous complex and later discoveries at a number of sites in North Western Frontier Province, little attention has been paid to the utilization of low grade chromite ores. With the world-wide depletion of high grade ore and improvements in mineral beneficiation techniques, more attention is being directed to low grade ores previously considered unusable.

Gravity processing has been the predominant technique employed for the beneficiation of low-grade chromite ores. The other methods include high intensity magnetic separation and high tension electrostatic separation. In the case of finely disseminated ores which require fine grinding for libration a substantial amount of values is lost in the fines. These fines can be recovered by a variety of processes including selective floculation, Cross belt separation and flotation. These processes may be used independently or in association with gravity processing of low grade chromite ores.

Studies on the processing of chromite by flotation have been appearing in the relevant literature over the years [1-15]. These studies have been devoted to seek favourable conditions for obtaining optimum results regarding the grade and recovery of chromite. These researchers have reported results on the use of different collectors, activators, modifiers, pH regulators and flocculants as dispersing and depressing agents. They have also attempted to explain the effects of different cations and anions present in the flotation pulp on the flotation response of chromite and the most frequently associated gangue minerals, i.e. serpentine and olivine. One of these authors has reported the effect of aging while another studied the effect of magnetic field on the flotation of chromite. It has also been shown that the ores from different origins behave differently [16-17].

The present study aims at the recovery of chromite fines which were collected from the gravity processing of an indigenous low-grade chromite ore [18]. The test work reported here was undertaken with a view to evolve a viable flotation process keeping in view the conclusion of the earlier research work referred to above in order to improve the overall recovery of the local ore.

Description of sample. Chromite fines used for the present study contain 17-19% Cr_2O_3. The gangue material is principally a mixture of serpentine and olivine with traces of talc and magnesite. The sieve analysis of the fines with their Cr_2O_3 distribution in each fraction and the chemical analysis of the fines is given in the Tables 1 and 2 respectively.

Table 1. Sieve analysis of fines with Cr_2O_3 distribution.

Particles size (microns)	Weight (%)	Cr_2O_3 (%)	Distr. (%)
+ 200	2.40	13.29	1.8
– 200 + 150	1.60	9.50	0.9
– 150 + 100	6.96	8.86	3.5
– 100 + 75	4.52	10.13	2.6
– 75 + 63	4.43	12.66	3.1
– 63 + 53	1.44	12.55	1.0
– 53 + 44	1.07	11.43	0.7
– 44	77.62	19.86	86.5
	100	17.82	100

Table 2. Chemical analysis of fines.

Constituents	Percentage
Cr_2O_3	17.80
SiO_2	20.30
Fe_2O_3	11.50
Al_2O_3	11.30
MgO	31.96
L/I	7.04

Recovery of chromite fines by flotation. A number of laboratory experiments on flotation of chromite were carried out using anionic and cationic collectors. The flotation feed material (fines from the gravity processing) was used as such and also after desliming. The effect of various reagents at different values of pH was also studied.

Flotation of fines without desliming. A number of flotation experiments were carried out at different conditions to optimise parameters. A typical example may be described as follows:

Flotation using anionic collectors. 500 gms of the material was dispersed with 1500 g/ton of sodium silicate in an alkaline pulp at a pH of 11 adjusted by using sodium hydroxide. The gangue minerals were then flocculated by using 250 g/ton of carboxymethyl cellulose. The flotation was carried out by adding 1000 g/ton oleic acid as an anionic collector. A concentrate assaying 25-33% Cr_2O_3 with a recovery of 63% was obtained by cleaning the rougher concentrate. The metallurgical balance showing the grade, recovery and the flotation conditions is given in Table 3.

Table 3.

(a) Flotation Parameters

Pulp density	30% solids
Sodium silicate	1500 g/ton
pH (NaOH).	11
Flocculant (C.M.C.)	250 g/ton
Collector/frother (oleic acid)	1000 g/ton

(b) Metallurgical Balance

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
Clean conc.	44	25.33	62.71
Clean. tail	16	9.81	8.79
R. conc.	(60)	(21.20)	(71.50)
R. tail	40	12.66	28.50
Calculated head	100	(17.78)	100

Flotation using cationic collectors. 500 gms of the fines were subjected to flotation. It was attempted to float the slimes in an alkaline pulp of pH 11 adjusted with lime, 50 g/ton of amine acetale (Armac C) and Dowfroth 200 was used as frother at a dosage of 5 g/ton. The flotation time was 10 min. For the chromite flotation, the pH was lowered to 3 with H_2SO_4. The same reagents in quantities of 30 g/ton of collector and 10 g/ton of frother were used. In the cleaning stage the pH was changed to 5. The cleaner concentrate contained 22.8% Cr_2O_3, representing 60.6% recovery. The flotation conditions and the metallurgical balance of the results are presented in Table 4.

Table 4.

(a) Flotation Parameters

Pulp density	30% solids
For slime flotation	
pH (Lime)	11
Collector Amine Acetate	50 g/ton
Conditioning time	5 min.
For chromite flotation	
pH Rougher (H_2SO_4)	3
Collector (Amine Acetate)	30 g/ton
Frother (Dowfroth 200)	10 g/ton
pH (cleaner)	5

(b) Metallurgical Balance

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
Clean. conc.	48	22.80	60.60
Clean. tail	10	21.52	11.90
R. conc.	(58)	(22.58)	(72.50)
R tail	14	10.13	7.85
Slimes (Froth)	28	12.66	19.65
Calculated head	100	(18.06)	100

In another experiment 500 gms. of the fines were scrubbed with H_2SO_4 at a pH of 2. After 20 minutes the pulp was diluted and chromite floated with amine acetate using Dowfroth 200 as frother. The concentrate obtained was poor with respect to its grade. It was observed on the other hand that the rougher tail was perfectly clean, yellow green in colour apparently free from chromite. This observation indicated that gangue minerals other than serpentine were not depressed and floated with the chromite resulting in a poor grade concentrate.

500 grams of the fines were scrubbed with HF at pH 2. After 20 min. the pulp was diluted and chromite floated with amine acetate using Dowfroth 200 as frother. The concentrate obtained assayed 28.53% Cr_2O_3 at a recovery of 50%.

Flotation of fines after desliming

Flotation using anionic collectors. 500 grams of the fines were conditioned with 1000 g/ton of sodium silicate and thoroughly deslimed by decantation. The deslimed pulp was activated with HF at a pH of 5 for 5 min. Small increments of oleic acid, totalling 70 g/ton of fines were used to collect the chromite. The rougher concentrate was cleaned in one stage using HF to pH 3.5-4. The cleaner concentrate contained 46% Cr_2O_3, representing 50% recovery.

The flotation parameters and the metallurgical balance are summarized in Table 5.

Table 5.

(a) Flotation Parameters

Pulp density	25% solids
Sodium silicate	1000 g/ton
Deslime collector (oleic acid)	70 g/ton
Conditioning time	5 min.
Activator HF to pH 5 (rougher)	
H.F. to pH 3.5-4 (cleaning)	

(b) Metallurgical Balance

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
Clean. conc.	21	46.00	50.15
Clean. tail	19	8.52	8.14
R. conc.	(40)	(28.20)	(58.56)
R. tail	30	8.86	13.83
Slimes	30	17.73	27.62
Calculated head	100	(19.26)	100

In another experiment the fines were scrubbed with H_2SO_4 at a pH of about 2. After 15 min the pulp was diluted and then deslimed thoroughly. The deslimed pulp was subjected to flotation using HF as an activator and oleic acid as collector.

A concentrate assaying 47% Cr_2O_3 with a recovery of 61% was achieved. The flotation conditions and the metallurgical balance of the test are detailed in Table 6.

The result of the flotation test has indicated that there is a fair amount of improvement (10%) in the recovery if desliming is preceded by scrubbing with H_2SO_4 instead of dispersion of slimes by sodium silicate.

Flotation using cationic collector. 500 gms of the fines were dispersed with 1000 g/ton of Na_2SiO_3 and thoroughly deslimed in a bucket. The sands were scrubbed in a scrubber with H_2SO_4 at pH 2. After 20 min the pulp was diluted and chromite floated with amine acetate (Armac-C) using Dowfroth 200 as frother. The rougher concentrate was cleaned 3 times. The 3rd cleaner concentrate assaying 36.8% Cr_2O_3 with a recovery of 64% was obtained. The results of the test and the flotation parameters are presented in Table 7.

Table 6.

(a) Flotation Parameters

Pulp density	25% solids
Acid scrubbing (H_2SO_4 to pH 2)	15 min.
Deslime collector (oleic acid)	50 g/ton
Conditioning time	5 min.
Activator HF to pH 5 (rougher)	
H.F. to pH 4 (cleaning)	

(b) Metallurgical Balance

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
Clean. conc.	24	47.0	61.20
Clean. tail	6	14.0	4.56
R. conc.	(30)	(40.40)	(65.76)
R. tail	36	7.60	14.87
Slimes	34	10.50	19.37
Calculated head	100	(18.43))	100

Table 7.

(a) Flotation Parameters

Pulp density	25% solids
Sodium silicate	1000 g/ton
Deslime	30 g/ton
scrubbing with H_2SO_4 to pH 2	
Collector (amine acetate)	
Frother (dow froth 200)	10 g/ton

(b) Metallurgical Balance

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
3rd Clean. conc.	35.75	36.80	64.14
3rd Clean. tail	3.25	20.30	3.22
2nd Clean conc.	39.00	35.40	67.36
2nd Clean tail	3.00	8.70	1.27
1st clean. conc.	42.00	33.50	68.63
1st clean. tail	6.00	5.66	1.67
R. conc.	(48.00)	(30.00)	(70.30)
R. tail	12.00	5.00	2.93
Slimes	40.00	13.75	26.82
Calculated head	100	(20.50)	100

CONCLUSION

The results of the laboratory flotation tests described have pointed out the possibility of obtaining a concentrate assaying 47% Cr_2O_3 with a recovery of 61% from the gravity fines containing 17-19% Cr_2O_3 by anionic flotation with preliminary desliming of the material (cf. Table 6).

Although the grade of the concentrate is fairly high, the recovery is only moderate. This is probably due to the loss of fine chromite during desliming as indicated by the quantity of material less than 44 microns in Table 1. At the same time it has also been observed that a recovery of 61% is only possible if scrubbing is carried out with sulphuric acid followed by desliming of the pulp. The intense agitation during scrubbing probably helps in cleaning the mineral surface and the subsequent desliming removes the slimes resulting in reagent adsorption and flotation of chromite.

The presence of slimes in the flotation pulp has a deleterious effect on both recovery and grade. This may be explained by the non-availability of free chromite mineral surfaces for the adsorption of the collector. It is, therefore, imperative that the slime coatings from the mineral be removed as much as possible prior to the flotation of the chromite mineral.

The removal of free slimes may be effected either by successive desliming or by selective flocculation. But the slimes coatings on the mineral surface may be held strongly and may not be removed by these methods. It is seen that desliming of the fines after scrubbing with H_2SO_4 resulted in better grade and recovery (47% and 61%). The dispersion of slimes with sodium silicate gave the same grade as scrubbing with H_2SO_4 but the recovery in the latter case was 10% higher. This shows that during dispersion with sodium silicate the strongly held slime coating has been removed only partially exposing a part of the mineral surface to activation by HF resulting in lower recovery. In the meantime it has been reported that the point of zero charge (pzc) of chromite is around the pH of 7 [19-21]. The sodium silicate [22-23] added to the pulp to disperse the slime yields charged ions such as $(SiO(OH)_3$, $(SiO_2(OH)_4^{4-}$, $(Si_2O_3(OH)_4)^{2-}$ and $(Si_4O_8\ (OH)_4^{4-}$ besides other ionic species resulting from the dissolution of gangue minerals and the ground chromite particles. At negative zeta potential values of the system, the slimes remain dispersed. As the pH of the system moves towards acidic side, i.e. towards positive zeta potential values, the negatively charged ions in the pulp tend to be adsorbed on the chromite surface which is progressively acquiring a positive charge. Under the dynamic conditions prevailing in the flotation cell, the surface of the mineral particles appears to be partially covered with the adsorbed specise resulting in low collector adsorption and hence low recovery.

Hydrofluoric acid has been shown to exhibit good selectivity in activation of chromite mineral, resulting in better flotation. It seems that HF could be adsorbed strongly and preferentially on the chromite surface to give the extremely insoluble CrF_2 ions, leading to formation of a water repellent coating. Hydrofluoric acid also attacks the magnesium and ferrous sites on the surface of olivine and serpentine with the formation of soluble magnesium and ferrous fluorides, thus providing a clean chromite surface devoid of the adhering gangue minerals. The acid also attacks the silicon sites at pH<4 with the formation of fluosilicic acid, thus impeding the formation of a collector coating on the surface of olivine and serpentine [24].

The presence of Ca^{2+} ions does not seem to have any effect on the flotation of chromite in the acidic pH range. According to Havens [1] sulphuric acid has the added advantage of removing soluble calcium salts from the pulp and thereby preventing interference with the mineral concentrating treatment.

Tables 3 and 4 show the response of chromite to flotation with anionic and cationic collectors respectively. It is seen that the anionic collector gives slightly inferior results in the rougher flotation as compared to the cationic collector. This situation is reversed in the cleaner flotation. Although the difference in grade and recovery is not substantial, it is difficult to explain why it happened so. Probably the cleaning pH was not correct. It is, therefore, not possible to conclude whether the anionic collector is more selective or the cationic.

Gravity processing of the chromite ore [25] results in the production of a chromite concentrate assaying 44% Cr_2O_3 with a recovery of 65%. By combining the results obtained by gravity processing and flotation, a concentrate assaying 44.6% Cr_2O_3 with a recovery of 81.10% could be achieved as is indicated in the combined metallurgical balance, Table 8.

Table 8. Metallurgical balance of the combined gravity and flotation circuit

Products	Weight (%)	Cr_2O_3 (%)	Distribution (%)
Gravity concentrate	45.40	44.00	65.32
Gravity middling	12.00	23.00	9.02
Flotation concentrate	10.23	47.00	15.72
Flotation tails + slimes + gravity tail	32.37	9.4	9.94
Calculated head	100	(30.58)	100

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