On the Flotation of a Low Grade Chromite Ore

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Abstract

This study is concerned with the processing of low grade chromite ores, Ingassena Hills by froth flotation techniques. For this purpose, representative samples were taken from four different mines. Mineralogical examinations indicated that, the major minerals are chromite and serpentine. Olivine, iron oxides and talc have been identified as minor minerals. Adequate degree of liberation of chromite was obtained by grinding the ore to minus 177 μ m.

Froth flotation was used to upgrade that particular chromite ore. Oleic acid was used as collector. Several operating parameters influencing the floatability of both high grade chromite and serpentine were investigated. These include the concentrations of the collector and depressant, pulp pH and conditioning time. From an ore feed grading 20.27% Cr₂O₃, a chromite concentrate of 28.71% Cr₂O₃ with recovery of 94.54 % could be obtained by flotation at collector dosage of 0.300 kg /t , neutral pulp (pH 9), conditioning time, 2min, and pulp density, 20%.

مستخلص

هذا البحث يهتم بمعالجة ، خامات الكروميت المنخفض الدرجة من جبال الانقسننا حيث تم الفحص المعدني وتحديد الخصائص المعدنية والفيزيائية قبل التركيبي و دراسة امكانية معالجة خام الكرومايت بواسطة التطويق الرغوى. لهذا الغرض، أخذت عينات ممثلة من عدة مناجم مختلفة و تبين من الفحص المجهرى لتلك العينات ان معدني الكروميت و السيرينتين هما المعدنان الرئيسيان ويصاحبهما قليلاً من معادن الاوليفين والتلك

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واكاسيد حديدية . وتم تحديد حجم التحرر لمعدن الكروميت عن الشوائب وقابلية العينات للطحن , وجد أنه يمكن بطحن الخام لأقل من 177 ميكروميتر الحصول على درجة تحرر عالية (83.4 %) لمعدن الكرومايت عن الشوائب المصاحبة للخام. استخدمت طريقة الفصل بالتعويم الرغوى لمعالجة ذلك الخام و تم دراسة العوامل المختلفة المؤثرة على كفاءة الفصل مثل، تركيز المجمع و المهبط ، وزمن التهينة و درجة الاس الهيدروجيني علي عينات عالية الدرجة من الكرومايت والسيربنتين . وبتطبيق ظروف التشغيل المثلى تم الحصول على ركاز يحتوى على 28.71% اكسيد الكروم و نسبة استرجاع 94.54% من خام يحتوى على 20.27% اكسيد الكروم عند تركيز المجمع 300 جرام لكل طن، وزمن التهينة دقيقتان و درجة الاس الهيدروجيني الطبيعى (9 pH) و نسبة المادة الصلبة إلى الماء فى الخليط 20 %.

1. Introduction

Chromium is one of the most versatile and widely used elements. Its main uses are in the metallurgical, chemical, and refractory industries are well known. Chromium is an essential element in the production of a wide variety of stainless steels, tool and alloy steels, nickel-chromium heating elements, and plating metals. Its widespread use in the metallurgical industry is attributed to its capability of enhancing properties such as resistance to corrosion or oxidation, creep and impact strengths, and hardness.

In the Sudan, Chromite ore deposits occur in the Ingassana hills in the Blue Nile region and other occurrences had been reported at Hamissana-sol Hamed in the northern Red Sea Hills, the Nuba Mountains in southern Kordofan, J.Rahib northwest Sudan and J.El Tawil in central Butana in southern Sudan. However, the Ingassana chromite ore is considered as one of largest chromite ore deposits in Sudan.

Low-grade deposits and the fines resulting in the mining operations can not be exported and are unmarketable. Therefore, beneficiation of low grade and fine disseminated ores is becoming more important in recent years due to the shortage of high grade ore reserves. Although gravity methods are well known and widely used for the concentration of chromites, such techniques fail to recover the size fractions below approximately 100 μm . Recovery from the fine size fractions is particularly important in finely disseminated ores.

Flotation offers an alternative concentration process for the separation of the fine materials and the avoidance of chromium losses. In general, earlier results of flotation of lower-grade chromite ores were inferior to those obtained by tabling [Ralph H. Nafziger, 1982]. There are two general types of methods for separating chromium ore (chromite) values from associated gangue minerals by froth flotation techniques. In the first method chromite ore which has been deslimed is subjected to flotation at a pH of 1.5 to 5.5 with a long chain fatty acid collector as reported by Havens, R., 1946. The selectivity of the process is enhanced by the inclusion of a soluble fluoride ion containing compound such as hydrofluoric acid, sodium fluoride or sodium silicofluoride in the flotation medium.

The flotation process is typically conducted by adding 0.5 to 5.0 pounds fatty acid, 0.1 to 10.0 pounds soluble fluoride ion and 1.0 to 11.0 pounds sulfuric acid per ton of ore to the aqueous treatment medium containing the chromite ore. A typical product obtained by such a process from an ore containing 25.2% Cr_2O_3 is a recleaner concentrate containing 41.0% Cr_2O_3 and 2.5% SiO_2 with a chromium recovery of 77.0%. In the

second technique as shown in [U.S. Pat. No. 3,473,656] chromite ore flotation is achieved with an undeslimed ore at a pH of 11.5 using a long chain fatty acid collector. The pH of the pulp is adjusted with NaOH with the pulp being dispersed by sodium silicate using carboxymethylcellulose as a flocculating depressant for silicate gangue minerals. Typically during processing, three pounds of sodium silicate, from 1.0 to 3.0 pounds of tall oil and from 0.25 to 0.50 pounds of carboxymethylcellulose per ton of ore, are added to a processing solution.

From an ore containing 18.13% Cr_2O_3 and 23.98% SiO_2 , a flotation concentrate was obtained containing 52.16% Cr_2O_3 and 3.72% SiO_2 with a chromium recovery of 80.0%. Also, L. Wenz, (1955 cited in E. J. Poyor, 1965) reported studies on a Turkish ore containing 30% Cr_2O_3 , associated with oxide and sulphides and gangue minerals are chiefly serpentine and olivine. When grounded to-100 μm the serpentine dominated the fines, chromite the medium particles and olivine the coarse. Strongly alkaline pulp (pH+10) was used, with sodium oleate and oleic acid (lb/ton) to float the serpentine. The pulp was then rendered acid (pH3) and chromite was floated with.3/4lb./ton of fatty acid-amine collector. Olivine, which only floats in a neutral solution under these conditions, remained in the final tailing, the concentrate grade being 45% Cr_2O_3 .

Further studies by the U.S. Bureau of Mines showed that lower-grade chromites could be selectively concentrated by flotation in the presence of slimes.

Preconditioning with fuel oil permitted flotation of the chromite from the flocculated siliceous-gangue slimes. Recoveries of up to 91 per cent

were realized with products containing up to 45 per cent Cr_2O_3 by mass [Hunter, and Sullivan, 1960]. The Cr/Fe ratios ranged from 2.17 to 2.46. Oleic acid was used for flotation.

Sodium fluoride and sulphuric acid yielded better results than dilute hydrofluoric acid when these reagents were added to free the 'flocs' from the siliceous gangue. A process developed for one ore does not usually yield optimum results for another ore of different origin. It is thought that differences in the composition of the gangue materials, as well as in the composition of the chromium spinels, are responsible for these variations in flotation behavior.

Fundamental research is required to alleviate this problem. Investigations involving the flotation of a pure chromite and a pure serpentine using sodium oleate as the collector showed [Sagheer, 1966] that the chromite can be collected at collector concentrations of between 0.3 and 1000 mg/l.

2. Experimental

2.1 Materials

2.1.1 Chromite Ore Sample

A chromite ore sample about (250 kgs) of low grade ore was collected from Chickay mines, at the Ingassana Hills. A high grade chromite ore samples (10Kg) and a similar pure serpentine sample were selectively collected to investigate their flotation characteristics. Lumpy Samples, about 10 kg low grade chromite ore were taken from chickay and Romallic mines. Firstly, thin and polish sections have been made for mineralogical analysis.

2.2 Methods

2.2.1 Preparation of Samples

The low grade sample (20 kg) was crushed through Jaw crusher and Roll crusher, coned, quartered and divided into lots of 1kg samples for the mineralogical and chemical analysis. Table 1 shows the results of the chemical analysis.

Table (1): Results of Chemical Analysis of a chromite Ore Sample (By Using AAS)

Loc.	CaO%	MgO%	Fe%	Cr ₂ O ₃	SiO ₂	Al ₂ O ₃	L.O.I	S%	Cr/Fe
Ch.	0.022	13.08	6.00	24.89	24.177	ND	7.33	ND	2.9
Ro ₁₄₃	0.034	13.56	5.80	24.31	14.108	ND	17.79	ND	2.5

2.2.2 Characterization of Single High Grade Minerals

Both the chromite and serpentine samples were obtained from the Gam Chromite Mine, Ingassana hills, Sudan. Chromite and serpentine samples were purified by hand sorting, magnetic separation and panning, washed with triple distilled water. After drying, the sample was ground to pass 250µm sieve by an agar mortar. Density of chromite and serpentine were determined to be 4.6 and 2.6 g/cm², respectively.

The ground samples were kept in plastic bags for experiments. The size, chemical and mineralogical compositions of the samples, determined by chemical analysis and microscope methods, are given in table (2).

Table (2): Chemical, Physical and Mineralogical Properties of High Grade of Chromite and Serpentine Samples

Property	Chromite	Serpentine
%100 passing size, μm	250	250
Specific gravity	4.6	2.7
Cr_2O_3 , %	57.6	1.2
Fe_2O_3 , %	19	12
SiO_2 , %	3	47
MgO , %	8.5	29
CaO , %	0.2	2.5
Mineralogical composition	Chromite, hematite, magnetite, olivine	Serpentine, chlorite, smectite, hematite, calcite

2.2.3 Mineralogical and Chemical Properties

The mineralogical properties of ore sample were examined by ore microscopy, while chemical analysis was conducted by wet chemical assaying methods, AAS, and XRF.

2.2.4 Liberation Characteristics Study

The liberation characteristics between chromite and associated gangue was performed as follows; the particles of both chromite and serpentine minerals as well as the locked particles were counted under microscope.

$$\text{Degree of liberation} = \frac{\text{Liberated Particals}}{\text{All Particals}} \times 100 \quad (1)$$

2.2.5 Ore Sample Preparation for Final Tests

Low grade Sample was prepared for flotation tests by stage crushing and grinding down to liberation size (0.177mm particle size). The ground sample was subjected for sieve analysis as show in table (3).

Table (3): Particle –Size Distribution of Chromite Ore as Feed for Flotation Tests

Particle size(mm)	Weight%	Cum.O.size %	Cum.U.size %
-0.177+ 0.076	41.42	0	100
-0.076 + 0.038	13.7	41.42	58.58
-0.038	44.9	55.1	44.9
Total	100	--	--

2.2.6 Flotation Tests

For each test, a certain weight of ore sample (chromite / serpentine / chromite ore) was transferred to the flotation cell, then a measured quantity of tap water according to the required pulp density was added. The sample was wetted for 5 minutes, and then the pulp pH was adjusted by H₂SO₄ or NaOH. Then the depressant (sodium silicate) dosage was added if required and conditioned for preset period. The collector (oleic acid) dosage was then added and conditioned afterwards, and then the frother was added and conditioned, for 1 minute. Finally the air is open and the froth was collected until the froth is barren. Both froth and the sediment were filtered, dried, weighted and analyzed.

3. Results and Discussion

3.1 Mineralogical Characteristics

The examination of Thin and polished sections revealed that the main minerals were chromite $[(Fe,Mg)O.(Al,Fe,Cr)_2O_3]$, Serpentine $[(Mg,Fe)_3Si_2O_5(OH)_4]$, talc $[Mg_3 Si_4 O_{10} (OH)_2]$, and chlorite. Intercrystalline enhedrall and subhedrall chromite crystals are filled with unhedrall and frequently fractured serpentine crystals (Figure (1)). Traces of olivine can be determined as fine grains within the serpentinite matrix as well as trace quantities of iron oxides, antigorite $(Mg,Fe)_3Si_2O_5(OH)_4$, asbestos and talc-carbonate. These micrographs gave also the grain size of the these components.

Figure (1): Highly Disseminated and Refractory Chromite. The Chromite Crystals were Subjected to Restoration and Dislocation in a Serpentine Ground Mass Thin Section (XN, 4x10)

The results revealed from investigation of thin and polish sections and chemical analysis, indicated that the ore contains approximately 45% - 72% of serpentine, 26% - 40% of chromite and traces of talc, olivine, asbestos and iron oxides. Grain size range from 1 to 0.02mm.

3.2 Flotation characteristics of high grade chromite

Figure (2) shows the chromite flotation recoveries as a function of various concentration of oleic acid at different pH values. The flotation results revealed that increasing the oleic acid concentration up to 3kg/t causes higher recovery. Because the pH of the medium is an important factor in flotation, its effect was investigated. The higher flotation recoveries were attained at pH 9; 11, and this may be due that ions Al^{3+} and $RCOO^-$ were predominant in the solution [Sobieraj, and Laskowski, , 1973; Shibata and Fuerstenau, 2003].

Figure (2): Flotation recoveries of chromite as a function of various concentrations of oleic acid at pH 11; pH 9; pH 2.5

The flotation of a high grade chromite using oleic acid as the collector showed, that the chromite can be collected at collector concentrations of between 0.2 and 2 kg/t.

3.3 Flotation of Serpentine

Fig. 3 shows the serpentine flotation recoveries as a function of various concentration of oleic acid at pH 2.5; 6; 9; 11. The flotation results revealed that increasing the oleic acid concentration increase of serpentine floatability. The effect of medium pH was also investigated. The results of which are represented in Fig.3. The maximum flotation recovery using oleic acid was 94.6 %, which obtained at pH 11 when Al^{3+} and $RCOO^-$ are predominant in the solution. The flotation recovery using oleic acid was 59.7 %, which obtained at pH 9. Flotation results show that the recovery increased with increasing collector concentration. From the above results it is clear that, both chromite and serpentine minerals have similar flotation characteristics.

Figure (3): Flotation Recoveries of Serpentine as a Function of Various Concentrations of Oleic Acid at pH 11; pH 9; pH 6; pH 2.5.

3.4 Influence of pH

As shown in fig.4, chromite float will in the presence of 200g/t oleic acid at pH region greater than 10. Fig.5 reveals that chromite float well at pH greater than pH_{pzc} , (PH 7 to 9.5) [Palmer B. R., Fuerstenau M.C., Aplan F.F., 1975.]; this considered an evidence of the flotation by chemisorption.

The decrease of flotation recovery in the acidic pH range was attributed to adsorption of less surface active oleic acid (neutral acid, $\text{HOL}_{(\text{aq})}$) [Somasundaran and Wang, 2006].

Figure (4): Effect of pH on Recoveries of Chromite and Serpentine at Oleic Acid Conc. 200g/t.

Among the various ions that can be present in the pulp, Al^{3+} ions exert the most influence on the flotation behaviour of chromites. These ions cause depression in the pH range 4.5 to 8 and activation between pH 10 and 12 [Sobierag and Laskowski, 1973]. At pH from 2.5 to 6, there no difference in the floatability between chromite and serpentine. The results depicted of (Fig.5), is agree with that reported by Havens, 1946.

Figure (5): Effect of pH on Recoveries of Chromite and Serpentine at Oleic Acid Conc. 600g/t.

3.5 Effect of Depressant Concentration

Figure (6) revealed that the sodium silicate 4kg/t has no significant depressing effect on chromite flotation. However, at pH 11, sodium silicate has some what marked depressing action at 200g/t of oleic acid. It is expected, that a high grade concentrate could be obtained by applying several cleaning stages.

Figure (6): Flotation Recoveries of Chromite as a Function of Various Concentrations of oleic acid in sodium silicate conc. 0 Kg/t; 4Kg/t at pH 9, 11

As silicate concentration increases the flotation recovery of chromite decreases at pH between 9 to 11, which indicates the increase of adsorption of silicate at this pH range. studies of the distribution of various silicate species as a function of pH have shown that silicic acid, Si(OH)_4 , and the monosilicate ions SiO(OH)_3^- , predominate in the pH range 9 to 10.

Figure (7): Reveals that the Floatability of Serpentine Decreased as a Result of the Addition of Sodium Silicate. It also Appears from fig. (8) that, at pH 11 the Flotation Recovery Decreased from 58.5% to 27.55% as a Result of Addition of 4kg/t Sodium Silicate

It is stated that, if the mineral surface is covered with highly polymerized silicate, it would be difficult for anionic collectors to adsorb on the surface of mineral and consequently the mineral surface will be strongly depressed. If the mineral surface is covered with monomer silicates or colloidal amorphous silica particles of large size, the coverage will be incomplete and attachment becomes weaker. Therefore, it is less difficult for the oleate to adsorb onto the surface and make the surface hydrophobic.

Figure (7): Flotation recoveries of serpentine as a function of various concentrations of oleic acid in sodium silicate conc. 0 Kg/t; 0.25Kg/t ; 4Kg/t at pH 11.

Figure (8): Flotation Recoveries of Serpentine as a Function of Various Concentrations of Sodium Silicate.

Using of sodium silicate (4kg/t) as depressant indicated a somewhat similar effect on flotation behavior of both minerals at pH 11, 400g/t oleic acid, while increasing oleic acid concentration more than 400g/t increased that difference their floatability markedly (Figure(9)).

Figure (9): Flotation recoveries of Serpentine and Chromite as a Function of Various Concentrations of Oleic Acid in Sodium Silicate Conc. 4Kg/t at pH 11.

3.6 Influence of Conditioning Time

Studies to date have revealed that conditioning time plays a very important role in serpentine flotation. Tests conducted to determine the

influence of conditioning time on flotation behavior of high grade samples yielded some what surprising results. It can seen from figure (10) that the flotation recovery of serpentine increase with increase conditioning time, but chromite remained relatively constant for all conditioning times tested.

Figure (10): Effect of Conditioning Time on the Flotation Performance of Chromite and serpentine.

3.7 Flotation of Low Grade Chromite Ore

The optimum conditions attained from the flotation study concerned with the pure minerals were applied on the flotation of the low grade chromite ore sample.

Low grade chromite ore (containing 20.27% Cr_2O_3 , %100-177 μm) was used in the flotation tests. Flotation tests were conducted in Cominor flotation cell machine with 2-liter capacity.

Flotation test conditions were: Feed size ,100% -177 μm , Pulp density ,20% solids for conditioning and flotation; Wetting time 5minutes; neutral pH 9 ;Addition of collector (300g/t of Oleic acid);Condition time of collector 2 min; Flotation time 3min. The results are show in table (4).

Table (4): Result of Rougher Flotation of Ore Sample %100 -177 μm

Fraction	weight	weight%	Cr ₂ O ₃ %	Recovery%
Floats	133	33.25	3.33	5.46
Pulp product(sediment)	267	66.75	28.71	94.54
Feed	400	100.00	20.27	100.00

The results shown in Table 4 could attributed to the following: metal ions such as Mg^{2+} , Ca^{2+} , and Fe^{3+} depress chromite and do not influence serpentine, but the depression of chromite by Mg^{2+} depends on the anions in the solution. Moreover, the sample contain very fine particle (44.9% - 38 μm), this cause depression of chromite. It is expected, that a high grade concentrate could be obtained by applying several cleaning stages.

4. Conclusions

- Ingassana hills area consists of different chromite deposits assaying 23% Cr₂O₃, which classified as low grade ore. The ore minerals from these deposits were similar in their mineralogical characteristics.
- The major minerals are chromite and serpentine .Olivine, iron oxides and talc have been identified as minor minerals.
- The degree of liberation of chromite minerals from their gangue could be obtained by size reduction to -0.177 mm.
- Flotation recoveries of chromite and serpentine increased with increasing collector concentration.
- Floation in alkaline media showed somewhat different floatability characteristics of both chromite and serpentine minerals.

- Using sodium silicate as depressant indicated a somewhat similar effect on flotation behavior of both minerals.
- The optimum conditioning time of oleic acid was found to be 2 minutes.
- A concentrate of 28.71% Cr_2O_3 with recovery of 94.54% from a feed assay 20.27% Cr_2O_3 was obtained. . It is expected, that a high grade concentrate could be obtained by applying several cleaning stages.

5. References

- [1] Havens, R., 1946, Froth flotation of chromite with fluoride. U.S.Patent :2,412,217. pp. 7 (<http://www.freepatentsonline.com/4311584.html>)
- [2] Hunter, W. L., and Sullivan. V., 1960, Utilization studies on chromite from Seiad Creek, Calif. U.S. Bureau of Mines, Report of Investigations 5576, pp. 37
- [3] Koster, J., 1936, Studies on the treatment of domestic chrome ores. U.S. Bureau of Mines, *Report of Investigations* 3322, pp. 37.
- [4] Palmer B. R., Fuerstenau M.C., Aplan F.F., 1975, Mechanism involved in the flotation of oxides and silicates with anionic collectors. Part 2. Trans. AIME, 258, p.261.
- [5] Poyor E. J., 1965, Mineral processing, third edition , Amsterdam, London-New York.
- [6] Ralph H. Nafziger, 1982, A review of the deposits and beneficiation of lower-grade chromite, Journal of the South African Institute of Mining and Metallurgy, pp. 205-226.
- [7] Sagheer, M. 1966. Flotation characteristics of chromite and serpentine. *Trans. AIME*, vol. 235, no. 1. pp. 60 - 67.

- [8] Shibata J., and Fuerstenau, D.W., 2003, "flocculation and flotation characteristics of fine hematite with sodium oleate", International Journal of Mineral Processing, 72, pp.30
- [9] Sobieraj, S. and Laskowski, J. , 1973, Flotation of chromite Trans. Instn Min. Metall. Section C, vol. 82, no. 805. pp. C207 - C213. (<http://www.freepatentsonline.com/4311584.html>). 30/11/2007.
- [10] Somasudaran,P., and Wang, Dianzuo ,2006, ^١ solution chemistry :minerals and reagents^١ ,Elsevier publisher, Development in mineral processing 17,pp.18-22
- [11] U.S. Pat. No. 3,473,6(<http://www.freepatentsonline.com/4311584.html>) Chem. Absts., 78, 1973, 128755C.