

FLOTATION BEHAVIOR OF SUDANESE CHROMITE ORES

Seifelnassr, A. A .S* and Tamam, T. A. K**

**Professor in Suez Canal University, Faculty of Petroleum and Mining Engineering*

***Lecturer in Omdurman Islamic University, Faculty of Eng. Sciences, Dept. Mining Engineering*

(Received March 20, 2011 Accepted April 8, 2011)

This study is concerned with the processing of low grade chromite ores, Ingassena Hills, Sudan, 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 180 μ m.

Froth flotation was used to upgrade this chromite ore. Oleic acid was used as collector. Several operating parameters influencing the floatability of the Sudanese chromite ores were investigated. These include the collector and depressant dosages, 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 , pH 9 , 2 min conditioning time, and 20% pulp density.

1. INTRODUCTION

Chromium is one of the most versatile and widely used elements. Its main uses in the metallurgical, chemical, and refractory industries are well known. It 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, impact strengths, and hardenability.

In Sudan, Chromite ore deposits occur in the Ingassana hills in the Blue Nile region. Other occurrences had been reported at Hamissana-sol Hamed in the northern Red Sea Hills, the Nuba Mountains in southern Kordofan, Jabal Rahib northwest Sudan and Jabal El Tawil in central Butana in southern Sudan. However, the Ingassana chromite ore is considered as one of largest chromite ore deposits in Sudan [Adli, 1998].

Low-grade deposits and the fines resulting in the mining operations can not be economically used. Therefore, beneficiation of low grade and finely disseminated ores is becoming 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 chromite from the fine size fractions below approximately 100 μ m.

Flotation offers an alternative concentration process for the separation of the fine materials and the reduction of chromium losses. However, earlier results of

flotation of lower-grade chromite ores were inferior to those obtained by tabling [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 (1946). The selectivity of the process is enhanced by adding a soluble fluoride 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 [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 depressant for silicate gangue minerals. Typically during processing, three pounds of sodium silicate, 1.0 to 3.0 pounds of tall oil, and 0.25 to 0.50 pounds of carboxymethylcellulose per ton of ore are added to the flotation cell.

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, Pryor, (1965) reported studies on a Turkish chromite ore containing 30% Cr_2O_3 , associated with oxides 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 (more than pH10) was used, with sodium oleate and oleic acid to float the serpentine. The pulp was then rendered acidic (pH3) and chromite was floated with 0.75lb/ton of fatty acid-amine collector. Olivine, which only floats in a neutral solution under these conditions, remained in the final tailing, the obtained concentrate grade was 45% Cr_2O_3 .

Preconditioning with fuel oil permitted flotation of the chromite from the flocculated siliceous-gangue slimes. Recoveries of up to 91 percent were realized with products containing up to 45 percent Cr_2O_3 [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 high grade chromite sample and a high grade serpentine using sodium oleate as the collector showed [Sagheer, 1966] that the chromite can be floated at collector dosages 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 sample (10Kg) and a similar high grade serpentine sample were selectively collected to investigate their flotation characteristics. Lumpy Samples, about 10 kg of low grade chromite ore were taken from Chickay and Romallic mines. Thin and polish sections were made for mineralogical analysis from the lumpy samples.

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 smaller samples of 1kg each for the mineralogical and wet chemical analysis. The mineralogical properties of the ore sample were examined by ore microscopy, while chemical analysis was conducted by wet chemical assaying methods, AAS, and XRF.

Low grade Sample was prepared for flotation tests by stage crushing and grinding down to a reasonable liberation size (0.180mm particle size). The ground sample was subjected to sieve analysis as shown in Table 1

Table 1: Particle size distribution of low chromite ore as feed for flotation tests

Particle size(mm)	Weight%	Cum.U.size %
-0.180+ 0.076	41.42	100
-0.076 + 0.038	13.7	58.58
-0.038	44.9	44.9

2.2.2 Flotation Tests

For each test, a certain weight of ore sample (chromite / serpentine / chromite ore) was transferred to a 2-liter flotation cell. 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, then the pulp was conditioned for 2 minutes. The collector (oleic acid) dosage was then added and conditioned for 2min., after which the frother was added and conditioned for 1 minute. Finally the air is opened and the froth was collected until the froth is barren. Both froth and sediment were filtered, dried, weighted and analyzed.

3. RESULTS AND DISCUSSION

3.1 Chemical and mineralogical compositions

3.1.1 Characterization of high grade minerals

Both the chromite and serpentine samples were cleaned by hand sorting, magnetic separation and panning, and washed with triple distilled water. After drying, the sample was ground in agate mortar to pass 250 μ m sieve. The measured density of chromite and serpentine were determined to be 4.6 and 2.6 g/cm³ respectively. It should be noted that the true density of chromite mineral and serpentine rock is 4.5 – 4.8 g/cm³ and 2.5 – 2.6 g/cm³, respectively. The chemical compositions of the samples determined by wet chemical analysis are given in Table 2. Mineralogical composition of high grade chromite is chromite, magnetite, hematite and olivine, and also for serpentine are serpentine, chlorite, smectite, hematite and calcite.

Table 2: Chemical analysis of high grade chromite, high grade serpentine and low grade chromite samples

Property	Chromite	Serpentine	Low-grade ore
Cr ₂ O ₃ , %	57.6	1.2	24.9
Fe ₂ O ₃ , %	19	12	8.6
SiO ₂ , %	3	47	24.2
MgO, %	8.5	29	13.1
CaO, %	0.2	2.5	0.02
Cr/Fe	3.1	0.1	2.9

3.1.2 Characteristics of low grade chromite

The examination of thin and polished sections revealed that the main minerals were chromite [(Fe,Mg)O.(Al,Fe,Cr)₂O₃], serpentine[(Mg,Fe)₃Si₂O₅(OH)₄] with excess magnesium[Read,1956], talc[Mg₃ Si₄ O₁₀ (OH)₂], and chlorite[(Mg,Fe)₅Al(AlSi₃)O₁₀(OH)₈]. Intercrystalline euhedral and subhedral chromite crystals are filled with unehdrall and frequently fractured serpentine crystals (Fig.1). Traces of olivine can be detected as fine grains within the serpentinite matrix as well as trace quantities of iron oxides, antigorite (Mg,Fe)₃Si₂O₅(OH)₄, asbestos and talc-carbonate. These micrographs show also the relative grain size of the these components.

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

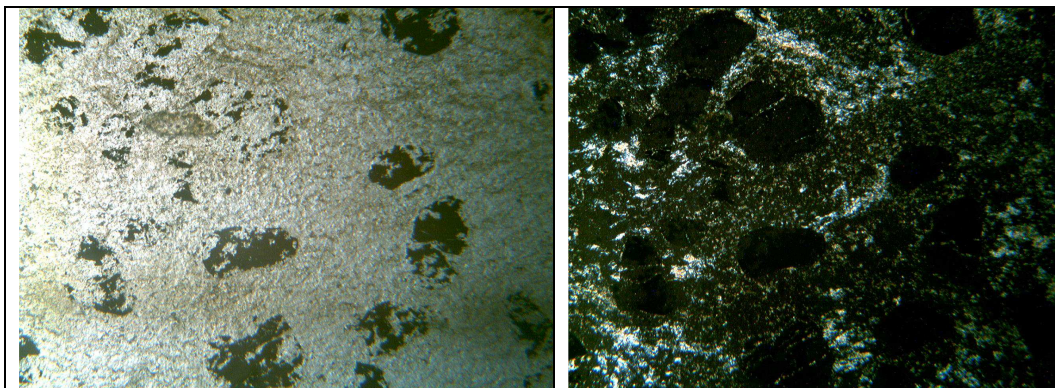


Fig.1: Highly disseminated and refractory chromite. The chromite crystals were subjected to restoration and dislocation in a serpentine ground mass thin section (XN, 4x10)

3.2 Flotation characteristics of high grade chromite

Figure 2 shows the chromite flotation recoveries as a function of various dosages of oleic acid at different pH values. The flotation results revealed that increasing the oleic acid dosage up to 3kg/t increases the recovery. Because the pH of the medium is an important factor in flotation, its effect was investigated. The higher flotation recoveries were attained at pH11, and this may be due the fact that ions Al^{3+} and $RCOO^-$ were predominant in the solution [Sobieraj, and Laskowski, , 1973; Shibata and Fuerstenau, 2003].

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

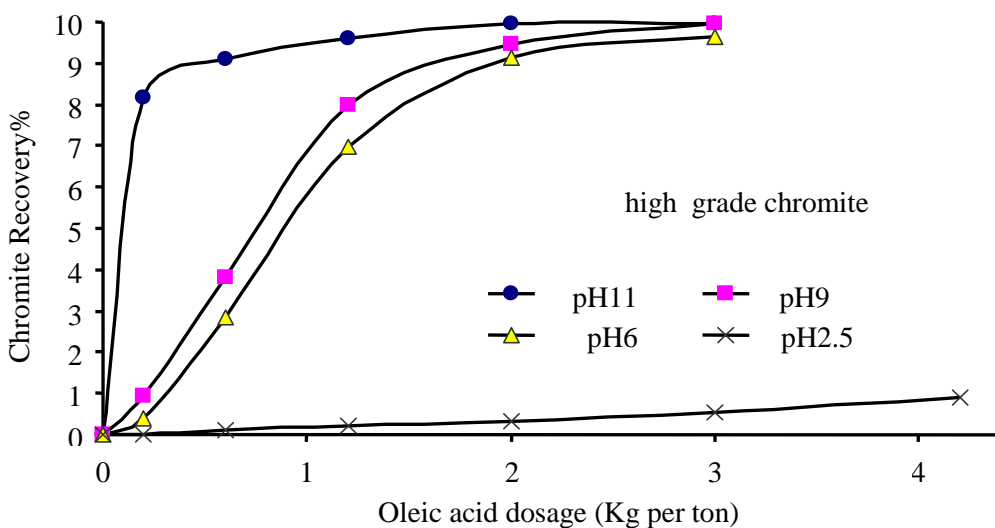


Fig.2: Flotation recoveries of chromite as a function of various dosages of oleic acid at pH 11; 9; 6 and 2.5

3.3 Flotation of serpentine

Figure 3 shows the serpentine flotation recoveries as a function of various dosages of oleic acid at pH 2.5; 6; 9 and 11. The flotation results revealed that increasing the oleic acid dosage increases the floatability of serpentine. The maximum flotation recovery using oleic acid was 94.6 %, which obtained at pH 11 when Al^{3+} (may be from chlorite) and $RCOO^-$ is predominant in the solution. Flotation results show that the recovery increased with increasing collector dosage. From the above results it is clear that, both chromite and serpentine minerals have similar flotation characteristics, but the response of chromite to changes in pH and collector dosage is more sensitive than that of serpentine.

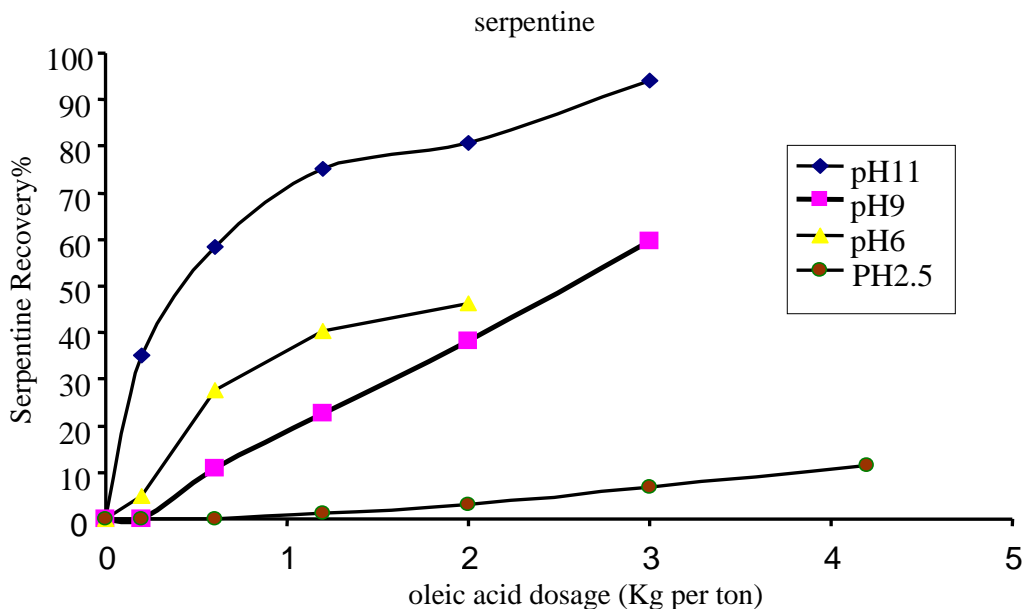


Fig.3: Flotation recoveries of serpentine as a function of various dosages of oleic acid at pH 11; 9; 6 and 2.5.

3.4 Influence of pH

As shown in Fig.4, chromite floats in the presence of 200g/t oleic acid at pH region greater than 10. However, it is shown that chromite floats better at pH greater than pH 9.5 in presence of 600 g/t oleic acid [Palmer, et al, 1975.]. The lack of flotation recovery in the acidic pH range was attributed to adsorption of less surface active oleic acid ($RCOO^-$) [Somasundaran and Wang, 2006]. Among the various ions that can be present in the pulp, Al^{3+} ions which exert the most influence on the flotation behavior 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 is no difference in the floatability between chromite and serpentine. The results depicted in Fig.4, is in agreement with those reported by Havens (1946).

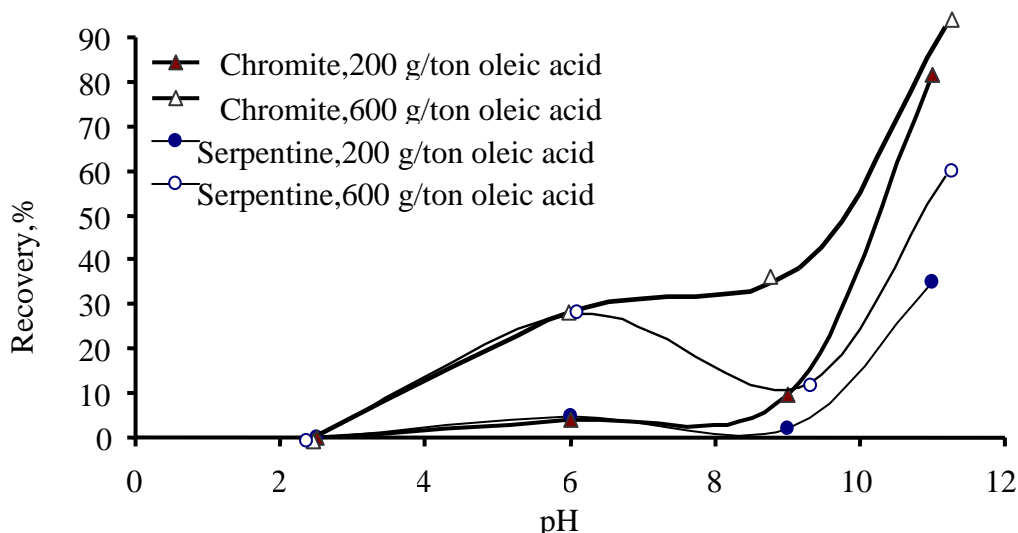


Fig.4: effect of pH on Recoveries of high grade chromite and serpentine at various oleic acid dosages.

3.5 Effect of depressant dosage

Figure 5 revealed that the addition of sodium silicate has significant depressing effect on chromite flotation at different pH. As silicate dosage increases the flotation recovery of chromite decreases at pH 9 and 11, which indicates the increase of adsorption of silicate on chromite surface in this pH range. Studies of the distribution of various silicate species as a function of pH have shown that silicic acid, $\text{Si}(\text{OH})_4$, and the monosilicate ions $\text{SiO}(\text{OH})_3^-$, predominate in the pH range 9 to 10 [Lagerstrom, 1959; Klassen and Krokhin, 1963].

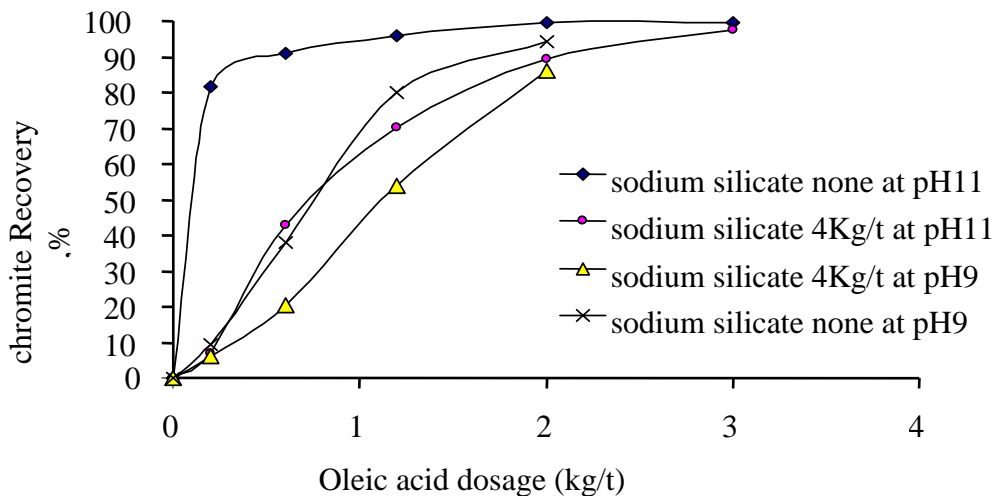


Fig.5: Flotation recoveries of chromite as a function of various dosages of oleic acid in sodium silicate conc. none kg/t; 4kg/t at pH 9, 11.

Figure 6 reveals that the floatability of serpentine decreased as a result of the addition of sodium silicate. It is stated by Lagerstrom, 1959; Klassen and Krokhin, 1963, 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. 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.

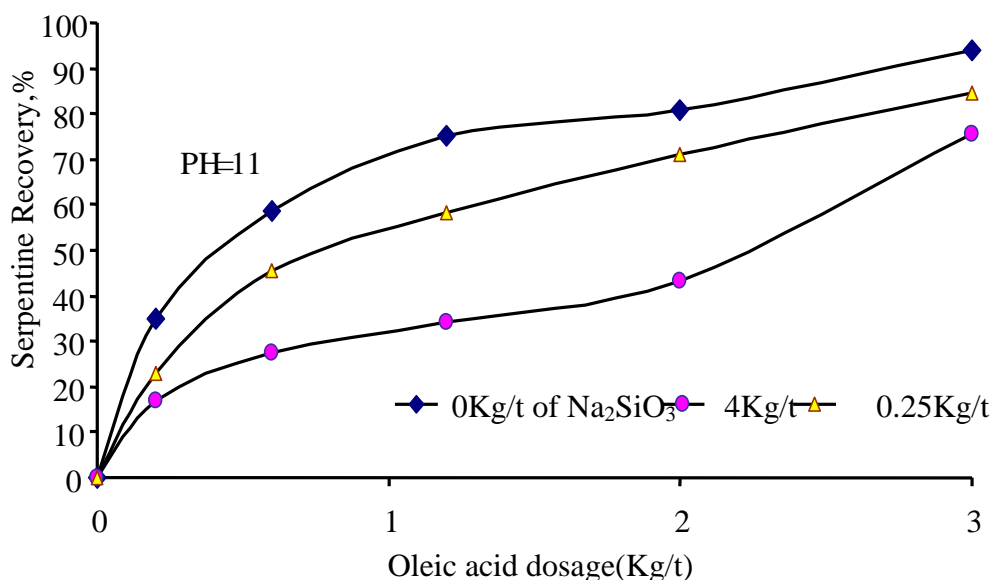


Fig.6: Flotation recoveries of serpentine as a function of various dosages of oleic acid in sodium silicate dosage of 0 Kg/t ;0.25Kg/t ; 4Kg/t at pH 11.

Using of sodium silicate (4kg/t) as a 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 the difference in their floatability markedly (Fig.7).

3.6 Effect of conditioning time

Studies to date have revealed that conditioning time plays an 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 be seen from Fig.8, that the rate of increase of the flotation recovery of serpentine as a function of collector dosage increases with the increase in conditioning time at a rate higher than that of all conditioning times tested.

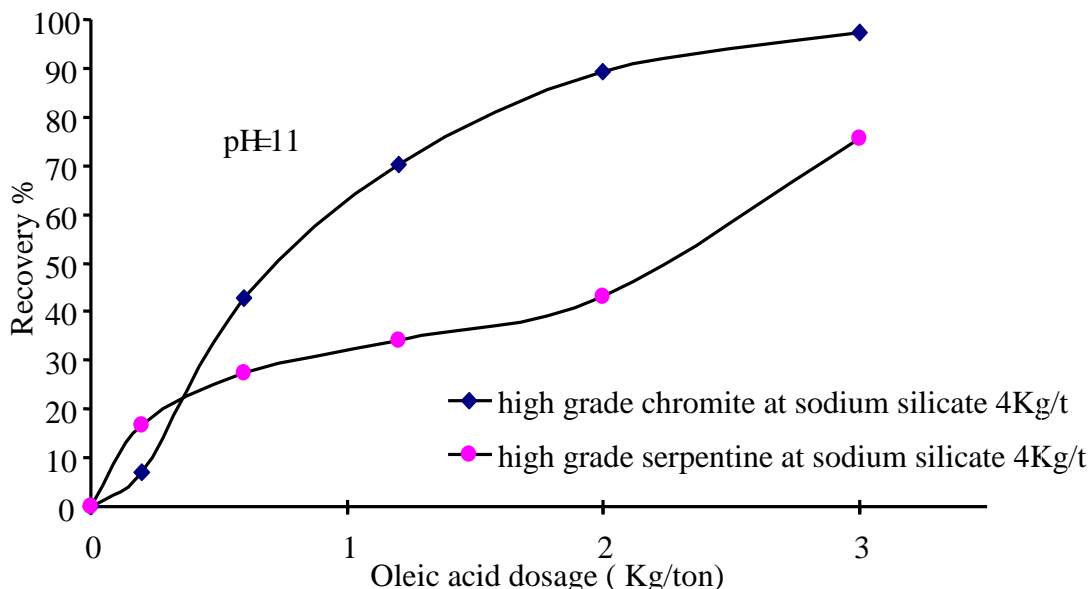


Fig.7: Flotation recoveries of serpentine and chromite as a function of various dosages of oleic acid in sodium silicate dosage of 4Kg/t at pH 11

3.7 Flotation of low grade chromite ore

The optimum conditions obtained from the flotation of high grade chromite and clean serpentine minerals were applied to the flotation of the low grade chromite ore sample.

Low grade chromite ore (containing 20.27% Cr₂O₃ and ground to pass %100-180µm) was used in the flotation tests using the 2-liter flotation machine.

Flotation test conditions were: Feed size -180 µm, pulp density of 20% solids for conditioning and flotation, wetting time of 5 minutes, pH 9, and addition of collector (300g /t of Oleic acid), condition time of collector for 2 min, and flotation time 3min. The results are shown in Table 3.

Table 3: result of rougher flotation of ore sample %100 -180 µm

Fraction	weight	Weight%	Cr ₂ O ₃ %	Recovery%
Froth product	133	33.25	3.33	5.46
Sink product	267	66.75	28.71	94.54
Feed	400	100.00	20.27	100.00

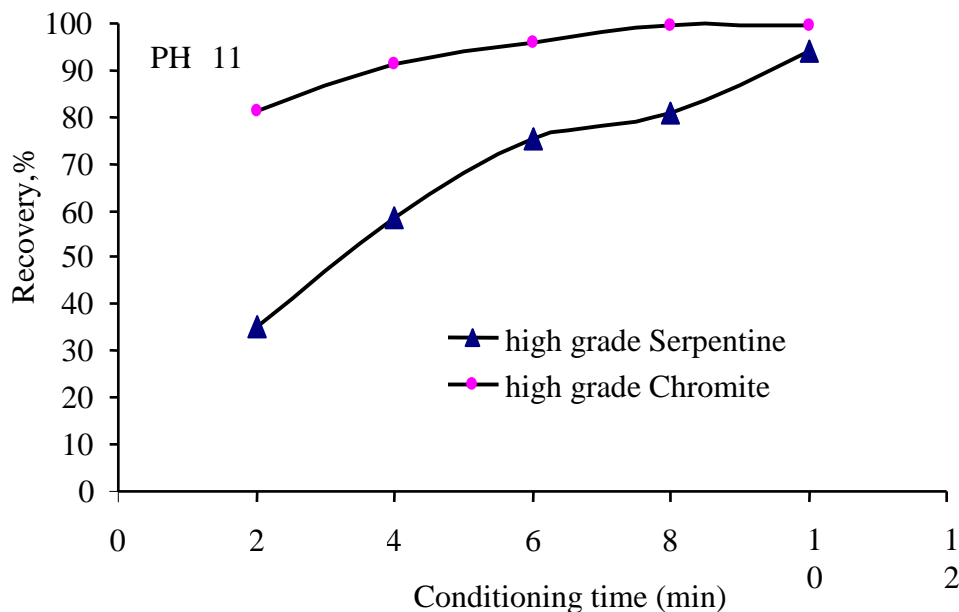


Fig.8: Effect of conditioning time on the flotation performance of chromite and serpentine.

The results shown in Table 3 shows different flotation behavior from that obtained in flotation of pure chromite and serpentine minerals. This could be attributed to the following reasoning. The presence of chlorite mineral (rich in aluminum), as one of the gangue minerals in the low-grade chromite ore, may be the reason for this exceptional behavior (reverse behavior) in flotation between high-grade chromite and high-grade serpentine flotation systems and the low-grade flotation system. The chlorite releases excess amount of Al^{+3} ions in the system which preferably replaces the Mg^{+2} on the serpentine surface rendering the serpentine surface more positive than the chromite surface. In this case, the anionic species, $RCOO^-$, absorbs preferentially on the serpentine surface, rather than the chromite surface, causing the serpentine to float. Mean while, the depressant species silicic acid and/or the monosilicic ions are adsorbed on the chromite surface, and hence chromite is depressed. Figure 9 shows a schematic representation for a serpentine particle before and after the ionic exchange of Al^{+3} and Mg^{+2} on the serpentine surface.

4. CONCLUSIONS

- Ingassana hills area consists of different chromite deposits assaying 23% Cr_2O_3 , 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.
- A reasonable degree of liberation of chromite minerals from their gangue could be obtained by size reduction to -0.180 mm.

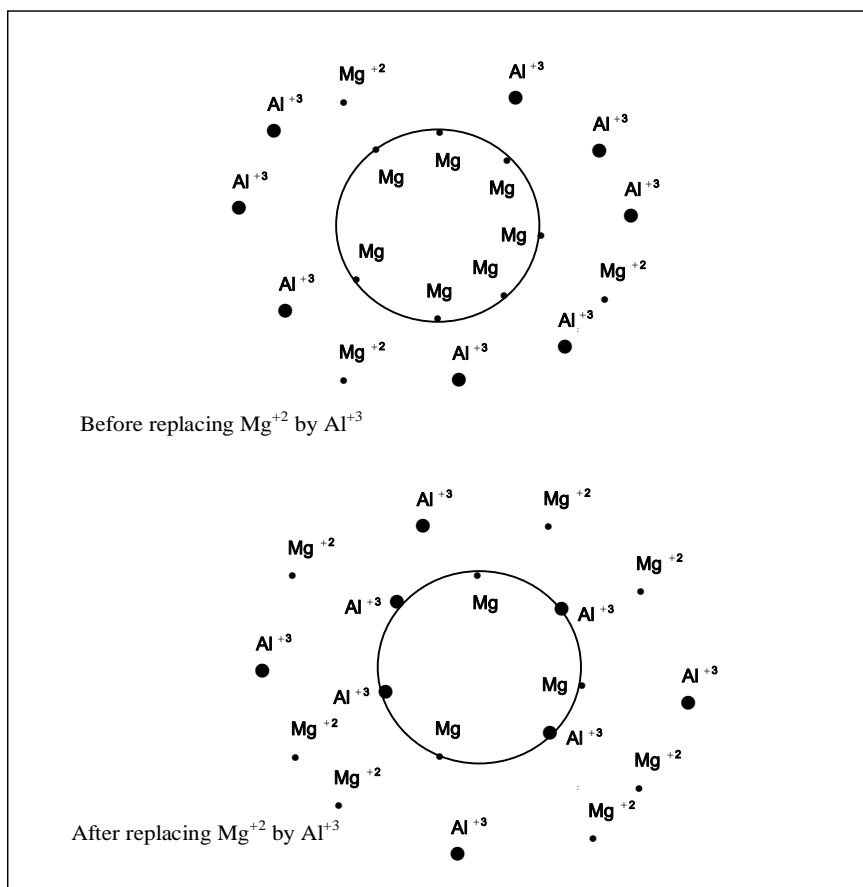


Fig. 9 A schematic representation of the ionic exchange of Al^{+3} and Mg^{+2} on the serpentine surface.

- Flotation recoveries of chromite and serpentine increased with increasing collector concentration.
- 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.

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سلوك خامات الكروميت السودانية عند التعويم

هذا البحث يهتم بمعالجة ، خامات الكروميت السودانية من جبال الانقسننا حيث تم الفحص المعدني وتحديد الخصائص المعدنية والفيزيائية قبل التركيز و دراسة امكانية معالجة خام الكرومايت بواسطة الفصل بالتعويم 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 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 التهية و درجة الاس الهيدروجيني علي عينات عالية الدرجة من الكرومايت والسيرينتين. وبتطبيق ظروف التشغيل المثلى التى تم الحصول عليها على خام كروميت منخفض الدرجة 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 التهية دقيقتان و درجة الاس الهيدروجيني الطبيعى(9 pH) و نسبة المادة الصلبة إلى الماء فى الخليط 20 %.