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SEPARATION OF CHROMITE FROM OLIVINE BY ANIONIC COLLECTORS

Chromite is concentrated mostly with shaking tables and spirals. Flotation can be considered as a leading process to beneficiate the fine chromite which cannot be enriched by gravity separation. Because of the complex nature of chromite and olivine which is the most abundant adjoininig mineral, the type of collector is very important in this flotation. After examination of the effect of sodium oleate on chromite and olivine by adsorption studies and electrokinetic mobility measurements, sodium oleate and other anionic collectors were used in the chromite flotation. Flotation results showed that some special collectors such as modified fatty acid and alkyl phosphate are more effective on the separation of chromite from olivine.

INTRODUCTION

Separation of chromite from olivine by oleate flotation is poorly understood because of the variable compositions and physicochemical properties of both minerals. Chromite as a spinel mineral, consists of two and three valency metal oxides (XO, Y_2O_3). Although X^{2+} and Y^{3+} are generally iron (II) and chromium (III), magnesium is substituted to the ferrous ion while ferric and aluminium ions are substituted for chromium. Distribution of divalent and trivalent ions in crystal lattice also differs in normal and reverse spinels (Batley 1972). Olivine is an orthosilicate containing isolated silica tedrahedrons and divalent magnesium and ferrous ions in changeable proportion (Batley 1972).

The response of chromite to fatty acid flotation in a wide pH range has been discussed according to the various ionic species (Sobieraj and Laskowski 1973; Sagheer 1966) and metal hydroxy species (Palmer et al. 1975; Fuerstenau et al. 1986) on the mineral surface. As well as metal hydroxy cation adsorption metal soap precipitation at the mineral surface (Ananthpadmanabhan et al. 1985; Somasundaran et al. 1986) can be responsible for chromite flotation. Oleate chemistry is also very important to explain the adsorption phenomenon. At the high pH, the anionic form is predominant while at low pH the acidic form occurs as another phase due to its very low solubility ($2.5 \cdot 10^{-8}$ mol/l). In neutral medium, both species are active with

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ionomolecular complex which forms around pH 7–8, depending on the concentration of oleate ions (Ananthpadmanabhan et al. 1981). There are no available data for olivine–oleate system. But as a magnesium and ferrous silicate, similar behaviour can be expected for this primary gangue mineral of chromite. This mineral is susceptible to alteration producing serpentine, talc, limonite and chlorite. Alteration of olivine and the effect of some chemicals on it has been discussed in a previous work (Atak 1987) with the solubility studies and electrokinetic mobility measurements. This work stated that the solubility of olivine increased with the addition of sodium fluorsilicate and initial positive surface potential changed to negative. Recent works have shown that some collectors such as alkyl phosphates and modified fatty acids are more selective for chromite than fatty acids (Güney et al. 1993). Although the mechanism of collection is poorly understood, these reagents can be used in a laboratory and pilot scale.

In this paper adsorption experiments and electrokinetic measurements for chromite and olivine were evaluated and flotation tests were carried out to bring a better understanding of chromite flotation. Flotation tests were also done with selective collectors instead of sodium oleate to improve the flotation results.

EXPERIMENTAL MATERIALS AND METHODS

Chromite and olivine samples were purified by magnetic separation and panning, washed with triple distilled water, and ground under 200 mesh by an agat mortar. Surface areas of chromite and olivine were measured as 0.4 and 2.8 m^2/g, respectively.

For adsorption tests, 0.2 g of chromite and 0.1 g of olivine were aged in 20 ml water overnight. After adjusting the pH values, 10 ml of supernatant was pipetted to another vial, centrifuged and used for precipitation measurements. 10 ml of each oleate solution which was prepared with the mixture of radioactive and chemically pure oleic acid, neutralized by sodium hydroxide were added to both mineral suspension and supernatant solution. They were conditioned for 10 minutes by a magnetic stirrer, meanwhile readjusting the pH to the desired value. After 10 minutes, the mineral suspension and the supernatant solution were centrifuged, 1 ml of the aliquot was taken for the scintillometer measurement. Adsorption of oleate on mineral surface was calculated by subtracting the sum of precipitate and the residual oleate concentration from the initial oleate concentration.

Electrokinetic measurements were made with a zetameter by two different techniques. In the first one, finely ground dry samples were mixed with water in small vials for pH adjustments and, in the second, samples were mixed with water in a large container and set aside for equilibrium. Then the aliquots were taken to small vials for pH adjustments. Those two techniques had the same results for chromite, but for olivine the measurements were greatly different. After pH adjustment, samples of dilute suspensions were used in micro-electrophoresis cell with platinum anode and molybdenum cathode for measurement of electrokinetic mobility. On olivine, ageing effects were investigated with measurements at the time intervals.

Slime of Üçköprü-Fethiye chromite plant (containing 20% Cr_2O_3) was used in the flotation tests. Anionic collectors which were consumed in these experiments were chosen as sodium oleate, modified fatty acid (OMC-377, Henkel Co.) and alkyl phosphate (Flotinor SM-15, Hoechst Co.). According to the selected collectors and pH values of flotation, sodium fluosilicate (in acid media) and sodium silicate (in basic media) were used as modifiers. Flotation tests were conducted in Denver flotation machine using 1 litre cell with 200 g slime samples.

EXPERIMENTAL RESULTS

Adsorption experiments which were conducted to find out adsorption isoterms (Fig. 1) show denser adsorption at pH = 4 than at pH = 10 on both minerals. This is not surprising, since by pH = 4, the oleate is in acid form showing another phase at all concentration levels examined and can simply coat surfaces as well as adsorb.

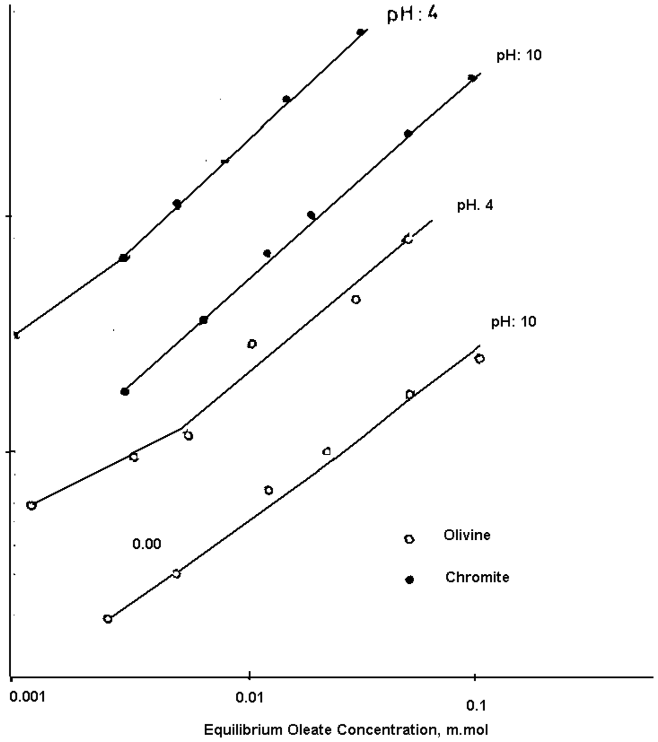

Fig. 1. Adsorption isoterms of oleate at pH 4 and 10

Effects of the pH values on the oleate adsorption are shown in Fig. 2. While adsorption on olivine shows little pH dependence, adsorption on chromite is affected but only above pH = 8 where it decreases. As shown in Fig. 2, adsorption density of oleate on chromite surface is about 0.43 mmol/m^2 until pH = 8 and, above this value it decreases gradually to 0.2 mmol/m^2. In the case of olivine, the magnitute of the adsorption density is much lower than that of chromite.

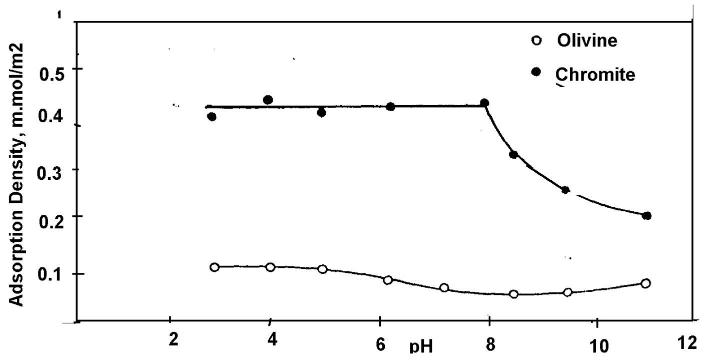

Fig. 2. Effect of pH values on the oleate adsorption

To determine the relationship between oleate adsorption and surface potential, electrokinetic measurements were conducted for chromite and olivine. Electrokinetic mobilities of olivine suspensions change continuously when they are prepared with dry samples. A series of experiments were conducted to determine the effect of ageing on zeta potential of olivine. Beginning with dry samples, zeta potentials were measured at constant pH values and different time intervals. The results are gathered in Fig. 3. Initially, the surface charge of olivine is positive in a wide pH range between 3 and 11.5, with higher magnitude in the acid media. After one hour, an isoelectric point is obtained at about pH = 7. After three hours, the surface charge of olivine is negative in all measured pH values. Zeta potential at intermediate times are shown by the broken lines.

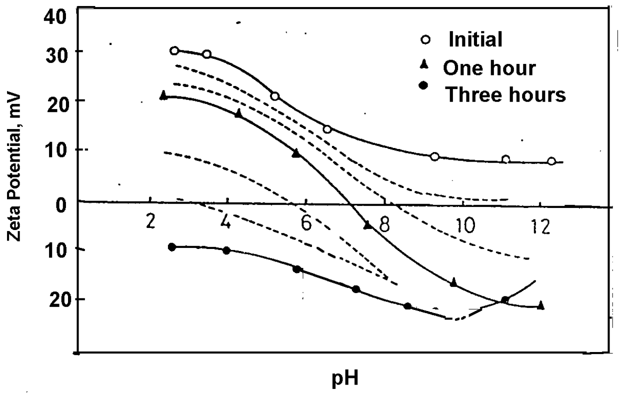

Fig. 3. Effect of ageing on zeta potantial of olivine

Figure 4 shows electrokinetic potentials of chromite as a function of pH. The isoelectric point of the chromite tested is at pH = 6.8 and ageing makes no difference on it. Sodium oleate (Fig. 5), with $5 \cdot 10^{-5}$ mol/l concentration changes to surface charge of chromite significantly by magnitude and sign below pH 8. Above pH 8.5 the curve is almost similar to that range of Fig. 4. In olivine, negative surface charge of mineral increases to some extent with oleate.

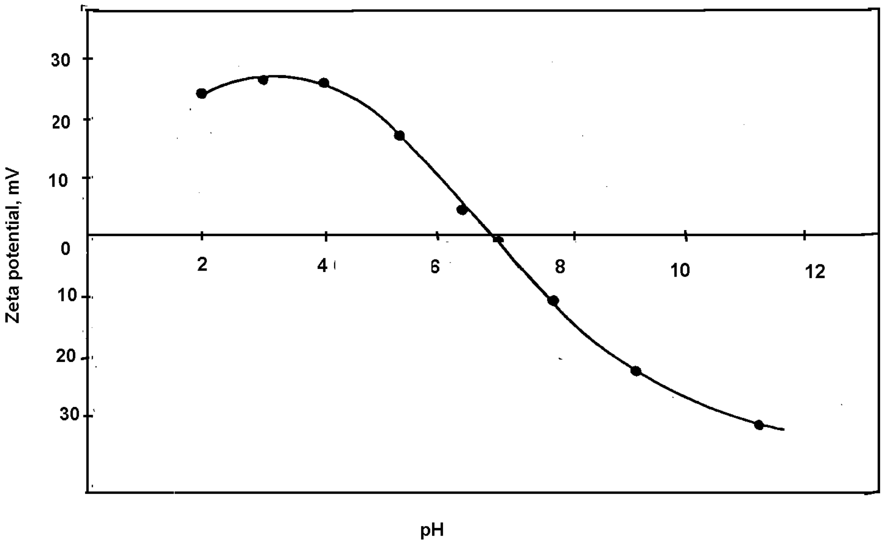

Fig. 4. Zeta potentials of chromite as a function of pH value

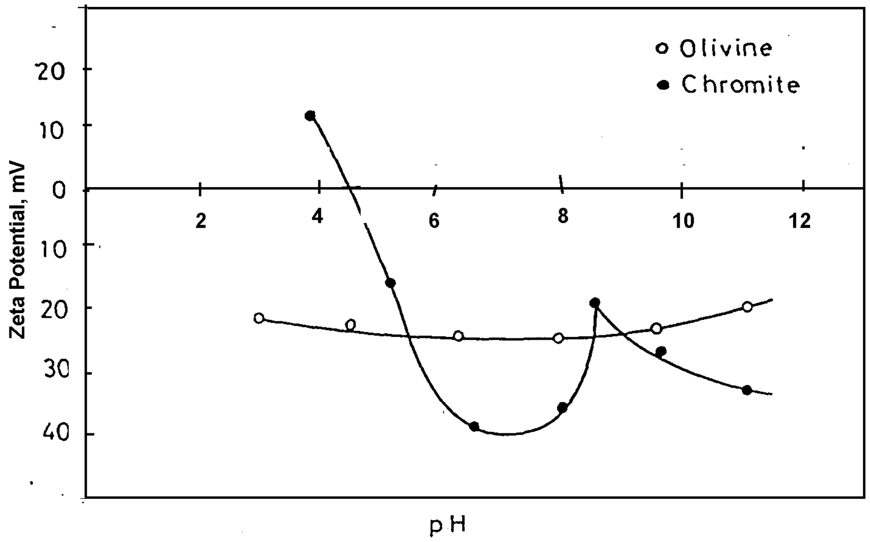

Fig. 5. Zeta potential of chromite and olivine in the presence of sodium oleate ($5 \cdot 10^{-5}$ mol/l) as a function of pH

FLOTATION TESTS

Anionic collectors which were characterized in the experimental section were used in the flotation tests. The tests results are given in Tables 1– 4.

Table 1. Flotation test results carried out with sodium oleate

Products	Yield [%]	Content of Cr_2O_3 [%]	Recovery of Cr_2O_3 [%]
Concentrate	10.7	23.49	12.9
Middlings	46.4	21.65	51.15
Tailings	42.9	16.16	35.6
Total	100.0	19.49	100.0

Table 2. Flotation test results carried out with modified fatty acids

Products	Yield [%]	Content of Cr_2O_3 [%]	Recovery of Cr_2O_3 [%]
Concentrate	12.0	29.12	17.4
Middlings	55.5	22.14	61.3
Tailings	32.5	13.09	21.3
Total	100.0	20.04	100.0

Table 3. Flotation test results carried out with alkyl phosphate

Products	Yield [%]	Content Cr_2O_3 [%]	RecoveryCr_2O_3 [%]
Concentrate	3.7	35.89	6.4
Middlings	63.1	22.97	69.6
Tailings	33.2	15.09	24.0
Total	100.0	20.83	100.0

Table 4. Flotation test results carried out with mixture of modified fatty acid and alkyl phosphates

Products	Yield	Content of Cr_2O_3	Recovery of Cr_2O_3

	[%]	[%]	[%]
Concentrate	19.3	41.88	38.8
Middlings	60.4	18.80	54.5
Tailings	20.3	6.66	6.7
Total	100.0	20.83	100.0

DISCUSSION OF RESULTS

Previous works have shown different surface properties such as isoelectric points, solubilities and flotation responses in tested several chromites. Surface properties of minerals are strongly dependent on its chemical composition and physical structure. In normal spinel, the tetraedral sites are occupied by divalent ions (Mg^{2+}, Fe^{2+}). There are ferric ions in spinels; the tedrahedral sites contain the half of the trivalent ions and the octahedral sites are filled by the rest of the trivalent ions and the divalent ions; they are named inverse spinels. These characteristics of spinels which are very important in their magnetic properties, may be important also in their solubilities and surface properties.

Olivine is an island silicate which contains isolated silica tedrahedrons and divalent metal ions such as Mg^{2+} and Fe^{2+}. It is very susceptible to alteration producing serpentine, talc, limonite, carbonate and chlorite. Olivine is slowly soluble in water at the low pH values.

Adsorption experiments with chromite show higher adsorption density in the acidic media indicating to the physical adsorption of oleate. However, isoelectric point of chromite was found at pH = 6.8 and adsorption density of oleate remains at the highest level until pH = 8 suggesting the chemistry of oleate and acid soap formation is also responsible for oleate adsorption on the chromite surfaces.

In the case of olivine, number of interesting and puzzling phenomena were observed. First, the surface electricity and isoelectric point of mineral is changeable in water by ageing. Although the surface charge of mineral is initially positive over a wide pH range, it completely changes to negative values when the measurements are made after three hours, revealing different values and isoelectric points in these three hours periods. This phenomenon can be explained by slow solubility of mineral. Initially, magnesium ions are on the surface, creating positive surface charge in a wide pH range such as other magnesium bearing minerals. Loss of magnesium ions from olivine surface creates the negative net charge on the surfaces. Secondly, the adsorption density of oleate on olivine surface is much lower than that on chromite. Low adsorption density on olivine surface may suggest that it is a contamination rather than an adsorption.

Adsorption tests and electrokinetic measurements showed that sodium oleate is not a proper collector to separate chromite from olivine. As well as poor selectivity of this collector, the flotation results are not reproducible because of the ageing effets of olivine. Special collectors are essential to separate chromite from olivine depending on the mineralogical characterstics of both minerals.

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Wzbogacanie surowców zawierających chromity obywa się na stołach koncentracyjnych i za pomocą spiral. Jeżeli chromity nie dają się wzbogacać na drodze grawitacyjnej, najważniejszym procesem wzbogacania drobnych ziarn chromitu staje się flotacja. Z powodu kompleksowej natury chromitu i towarzyszącego mu oliwinu, dobór kolektora do flotacji staje się ważnym zagadnieniem. W wyniku analizy działania oleinianu sodu na chromit i oliwin, którą oparto o badania adsorpcyjne i elektrokinetyczne, do flotacji chromitu zastosowano oleinian sodu i inne anionowe kolektory chromitu. Wyniki badań wykazały, że modyfikowane kwasy tłuszczowe i fosforany alkilowe są najbardziej efektywnymi kolektorami do rozdziału chromitu i oliwinu na drodze flotacji.