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SELECTIVE FLOCCULATION BEHAVIOR OF CHROMITE AND SERPENTINE

Application of selective flocculation using starch to separate chromite from serpentine has been investigated. It was determined that starch has a specific affinity towards chromite which can be exploited in selective flocculation. However, it was found that this could only be achieved when the amount of serpentine in the chromite-serpentine mixture is below 30% by weight and in the presence of a dispersant such as sodium silicate or ultrasonic treatment of the pulp.

Key words: selective flocculation, chromite, serpentine, starch

INTRODUCTİON

Concentration separation of finely ground minerals has been a common industrial practice for a long period. Slimes, defined as -20 μm particles, are an unseparable part of such operations and may contain significant amounts of valuable minerals. Conventional techniques, such as gravity concentration, magnetic separation and flotation, are generally ineffective in treating slimes. Thus, slimes are usually discarded prior to concentration. Discarded slimes are not only an economical loss but their disposal may be an environmental concern and costly to manage as well.   Many techniques have been developed to treat slimes. Among them are shear flocculation, selective flocculation, carrier flotation, high gravity separators, etc.

Selective flocculation is one of the techniques applicable to the enrichment of slime fraction. The technique is based on the preferential adsorption of an organic flocculant on the mineral particles to be flocculated, leaving the rest of the minerals suspended. Separation is brought about by the different settling rates of mineral particles controlled by the effective diameter which can be altered by flocculation or dispersion of a particular mineral. For a successful selective flocculation process, the pulp must

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be fully dispersed prior to the addition of the flocculant. Considerable success has been achieved in applying this technique for the separation of finely disseminated valuable minerals from ores on experimental as well as commercial scale (Yarar and Kitchener, 1970; Read, 1971; Attia, 1977; Lien and Morrow, 1978; Drzymala and Fuerstenau, 1981; Pradip and Moudgil, 1991; Moudgil and Mathur, 1994; Weissenborn et al., 1994; Sworska et al., 2000).

Chromite ores are usually concentrated by gravity concentration methods based on differences between specific gravities of chromite and gangue minerals, i.e., olivine and serpentine. Considerable amount of fine chromite is lost in the conventional gravity separation plants as a result of the process and/or equipment inefficiency in the fine particle size range. As much as $3x10^6$ Mt of fine chromite tailings having upto 20% Cr_2O_3 have been accumulated in several disposal sites in Turkey (Anon.; Güney and Önal, 2000). Several researchers, employing gravity separation, flotation and magnetic separation have attempted to recover the chromite values from these sites with limited success (Doğan et al., 1996; Çiçek et al., 1998; Güney and Önal, 2000).

The mineral chromite is the main valuable mineral in chromite ores. It belongs to the spinel group and has the chemical formula of $FeCr_2O_4$. The gangue mineral, serpentine, is a magnesium hyroxysilicate mineral with a chemical formula of $Mg_3Si_2O_5(OH)_4$. Replacement of the cations in both minerals is a common occurrence in natural deposits.

Starch is a natural polymer and known to have a specific affinity towards iron bearing minerals (Iwasaki, et al., 1969; Balajee and Iwasaki, 1969; Dogu and Arol, 2004). This affinity has been related to a complex formation and hydrogen bonding between metal ions on the mineral surfaces and starch molecules (Khosla, et al., 1984; Laskowski, et al., 1991; Ravishankar, et al., 1995 and Weissenborn, et al., 1995). Because of this property, starch and its derivatives have been used in the commercial application of flotation and selective flocculation to iron ores (Lien and Morrow, 1978; Balajee and Iwasaki, 1969; Iwasaki et al., 1969).

The facts that chromite has iron oxide in its structure and that starch has a specific affinity towards iron oxide were exploited in the present study. Possibility of applying selective flocculation to chromite-serpentine mixture using starch, in a similar fashion to the selective flocculation of iron oxide-silica system, was explored.

MATERİALS AND METHODS

Both the chromite and serpentine samples were obtained from the Kavak Chromite Mine, Eskişehir, Turkey. The final size of both samples were reduced to –45μm by stage crushing and grinding. The grinding was carried out on –150μm roller crusher product wet in a porcelain mill. The -45μm material was washed with distilled water 5 times to remove the dissolved species from the mineral surfaces, drained and dried at 105°C, and kept in plastic bags to be used in the experiments. The size and specific surface areas, analyzed by Sympatec Helos Laser Sizer (H1305), chemical and

mineralogical compositions of the samples, determined by XRF and XRD methods, are given in Table 1.

The commercial corn starch of Cargill, Turkey, was used as the flocculant. Reagent grade NaOH and HCl were used for pH adjustments. Distilled water was used in all experiments.

Table 1. Chemical, physical and mineralogical properties of chromite and serpentine

Property	Chromite	Serpentine
%80 passing size, μm	25	18
Specific surface area, cm^2/g	1.63	2.91
Specific gravity	4.71	2.70
Cr_2O_3, %	57.6	0.8
Fe_2O_3, %	19.0	12.5
Al_2O_3, %	8.0	2.5
SiO_2, %	3.0	47
MgO, %	8.5	29.0
CaO, %	0.2	2.5
Mineralogical composition	Chromite, γ-hematite, magnetite, olivine	Serpentine, chlorite, smectite, hematite, calcite, amorphous silicate

Starch was dissolved by cooking in distilled water for 30 min. in an autoclave at 140°C and 207 kPa. The cooked starch was homogenized in a Waring Blender and stored in 1mg/mL concentration. The starch solution was freshly prepared daily to avoid degradation (Iwasaki et al., 1969).

Starch adsorption of minerals was determined by mixing 2.5 g of minerals with a starch solution of known concentration for 10 minutes. The mixture was centrifuged to separate the solids. Starch remaining in solution was analyzed by sulfuric acid-phenol method (Dubios et al., 1956).

Flocculation and single stage selective flocculation tests were performed in a 250 ml graduated glass cylinder of 35 mm in diameter. In multiple stage selective flocculation experiments, tests were carried out in 1000 ml graduated cylinder of 6,5 cm diameter. All flocculation experiments were performed at a pulp density of 5% solids by weight. After adjusting the pH, starch was added in three equal increments and the cylinder was inverted 3 times after each addition and 5 times after the last addition. The pulp was allowed to settle for 60 seconds and the supernatant of the upper 80 % part of the cylinder was siphoned off, dried and weighed to determine the suspended solid and Cr_2O_3 content. For the multiple stage selective flocculation tests, the same procedure was followed up to the first stage flocculation. The subsequent flocculation tests were carried out by adding a make-up water to the settled portion of the previous stage. This allows the cleaning of the flocs. All the suspended and settled products were collected, weighed and analyzed for Cr_2O_3. Complete details of the tests are given else where (Beklioğlu, 2002).

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RESULTS AND DISCUSSION

It is well known that selective flocculation can be applied to ores which are fully dispersed prior to polymer addition, and one of the minerals selectively adsorbs the polymer and flocculates after polymer addition. Flocculation-dispersion behavior as well as polymer adsorption characteristics of chromite and serpentine were investigated to determine under which conditions these prerequisites are achieved. As known coagulation-dispersion behavior of minerals in the absence of salts and polymers is dependent on the pulp pH governing the surface charge of the minerals. Dispersion behaviors of chromite and feldspar as a function of pH, expressed in terms of percentage of solids settled, are given in Figure 1. As seen from the amount of settled solids in the figure (also visually observed during the tests), neither chromite nor serpentine fully settled at any pH as a result of coagulation. Normally, a coagulated suspension would lead to around 90-100 % settling.   Relatively higher amounts of settled fraction for chromite is a result of higher density as well as coarser size distribution of that mineral than serpentine.
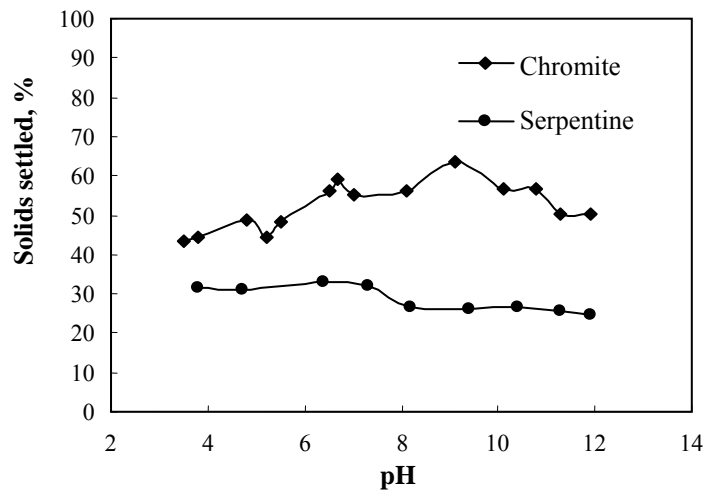

Fig. 1**.** Flocculation-dispersion behavior of chromite and serpentine as a function of pH

Adsorption of starch as a function of pH is another factor in selective flocculation. It is known that to have a successful selective flocculation process, starch must be adsorbed on one of the minerals while the other mineral adsorbs little or no starch. Starch adsorption as fuction of pH was determined at a costant starch addition of 150 mg/mL at all pH values. As seen in Figure 2, in acidic and neutral pH values both chromite and serpentine adsorbed substantial amount of starch. In fact, in acidic pH range, serpentine adsorbed more starch than chromite. However, above pH 9, while chromite did still adsorb starch, adsorption by serpentine sharply decreased. It has been reported that pzc values of chromite and serpentine is around pH 5.5 and 8.7,

respectively (Sobieraj and Laskowski, 1973; Akdemir, 1995). Thus, adsorption by the respective minerals below these pH values can be partly attributable to the electrostatic attraction between the positively charged minerals and the negatively charged starch molecules (Iwasaki et al., 1969; Drzymala and Fuerstenau, 1987). Adsorption of starch by chromite above the pzc value of pH 5.5 may be explained by a specific affinity of chromite which contains iron in its crystal lattice towards starch in a similar fashion to iron minerals reported by many investigators (Iwasaki et al., 1969; Hanumantha, et al., 1985; Hanumantha and Narasimhan, 1985; Bagster and McIlveny, 1985; Weissenborn et al., 1994 & 1995; Ravishankar, et al., 1995 and Doğu, 2002).
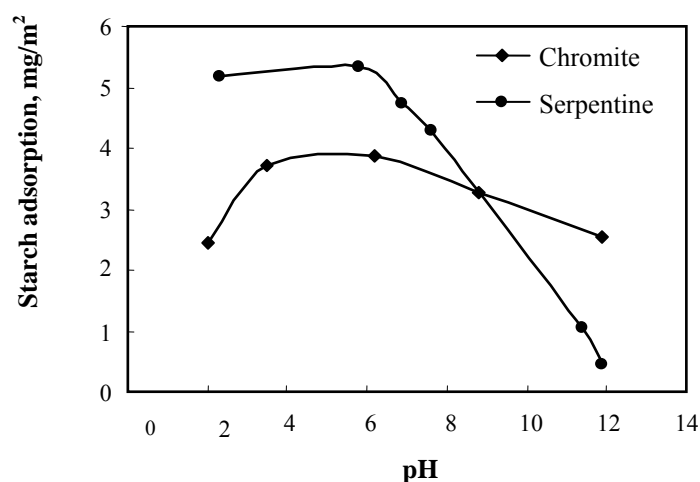

Fig. 2. Adsorption of starch by chromite and serpentine as a function of pH (initial starch concentration of solution: 150 mg/L)

Starch adsorption behavior of serpentine and chromite as a function of starch concentration were conducted at pH 5.5 and 11.9 in order to understand the nature of adsorption. The results are given in Figure 3. It was found that starch adsorption by serpentine was strongly pH dependent. At pH 5.5, serpentine completely adsorbed starch from solution at low concentration level and reached surface saturation with regard to starch above around 4 mg/m^2 adsorption density. However, at pH 11.9, very littled starch was adsorbed at all starch concentartion levels tested. Chromite, on the other hand, exhibited a different behavior. Its starch adsorption behavior was pH independent. At low starch concentration levels, the amounts of adsorption for both pH values were virtually the same. Starch adsorption at higher starch concentration levels at pH 11.9 was slightly lower than those at pH 5.5. From these results, it can be concluded that starch has a specific affinity towards chromite but not towards serpentine and selectivity can be achieved at around pH 11-12.
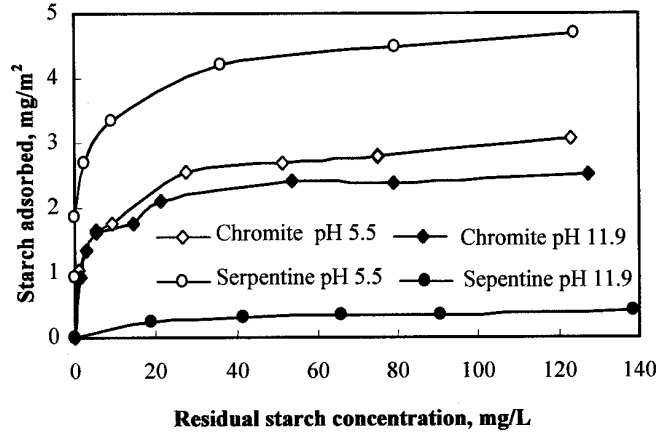
Fig. 3. Starch adsorption characateristics of chromite and serpentine as a function of starch concentration at pH 5.5 and 11.9
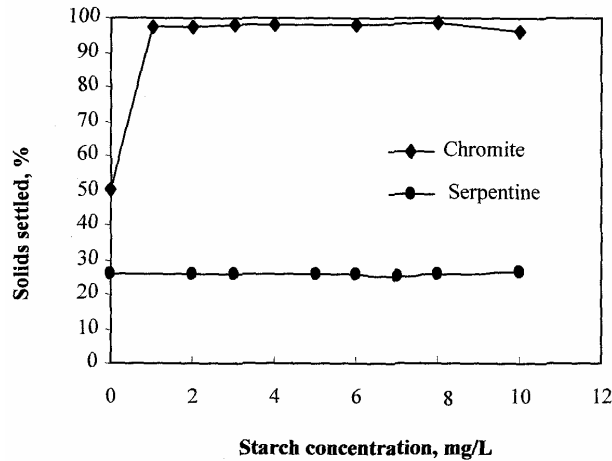

Fig. 4. Flocculation behavior of chromite and serpentine alone as a function of starch addition at pH 11.9

Based upon the above findings, flocculation tests were conducted for chromite and feldspar alone at pH 11.9 as a function of starch addition. As seen from the results presented in Figure 4, chromite starts to flocculate at a relativly low starch concentration with almost complete settling of chromite particles which are suspended with no starch addition. However, serpentine remained dispersed regardless of the starch addition level. Such behavior of the individual minerals is a prerequisite for a successful selective flocculation process.

The flocculation tests indicated that selective flocculation can be applied to an ore consisting of chromite and serpentine using starch as flocculant at pH 11.9. Thus, selective flocculation tests for artificial mixtures of chromite and serpentine were run

to observe the behavior of such mixtures. Two different chromite:serpentine ratios, namely 50%:50% by weight (the first value refers to chromite and the second to serpentine throughout this paper) and 70%:30% by weight, were tested. The results are given in Figures 5 and 6 as grade vs recovery curves. In such plots, a line extending along the full dispersion line shows dispersion; a line to the right of the full dispersion line indicates some degree of selectivity (the farther to the right, the more selective is the separation) in flocculation and all data points at around the feed means indiscriminate flocculation.
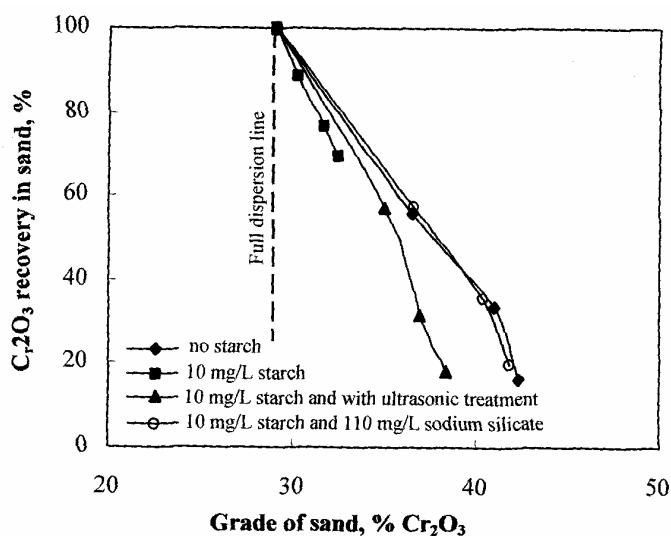

Fig. 5. Selective flocculation of chromite-serpentine mixture (50%:50% wt), pH 11.9

The selective flocculation tests yielded rather unexpected results, Figure 5 and 6. Both mixtures had some selectivity of separation with no starch addition. This can be attributed to the different settling velocities of denser chromite particles and lighter serpentine particles, Table 1. However, upon 10 mg/L starch addition for 50%:50% mixture and 14 mg/L starch addition for 70%:30% mixture, the pulp indiscriminatly flocculated. Obviously, an interaction between chromite, serpentine and starch occured. Although the nature of this interaction was not investigated in this study, it can be postualted that chromite and serpentine heterocoagulated and as starch flocculates chromite, both chromite and serpentine flocculated. A similar occurence has been reported for the hematite-montmorillonite mixture (Arol and Iwasaki, 1986). The remedy for the adverse effect of a heterocoagulating solid is to remove it from the surface of the mineral to be flocculated. Use of a dispersant is a common practice and ultrasonic treatment of the pulp, albeit less common, can be applied (Heerema et al., 1982; Krishnan and Iwasaki, 1984; Arol and Iwasaki, 1987; Manukonda and Iwasaki, 1987).
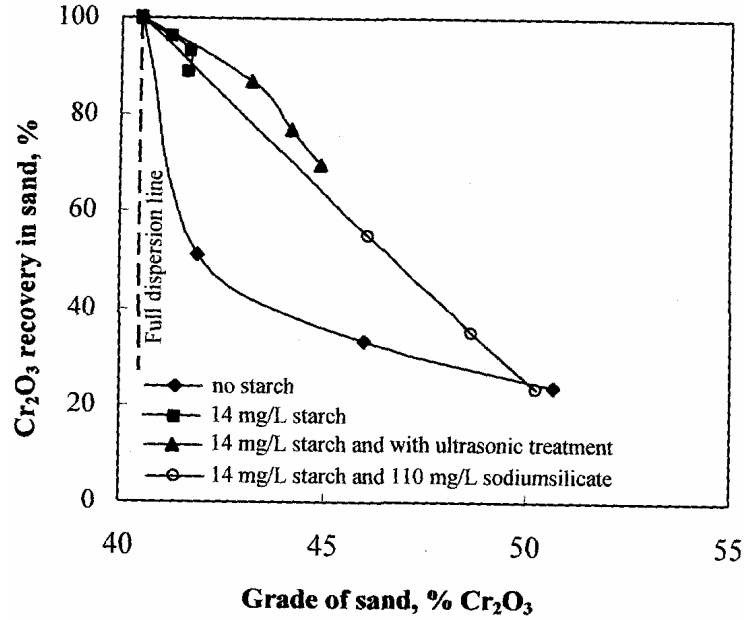
Fig. 6. Selective flocculation of chromite-serpentine mixture (70%:30% wt), pH 11.9

In this study, both methods were tried. As dispersant, 110 mg/L sodium silicate was added to the pulp prior to the starch addition. In another series of selective flocculation tests, the pulp was subjected to ultrasonic treatment for 60 seconds with a horn type sonication device after the starch addition. The results reported here were obtained under optimized conditions (Beklioglu, 2002) and are also included in Figures 5 and 6. As seen in Figure 5, both sodium silicate and ultrasonic treatment restored some selectivity lost by starch addition. However, there was no improvement over what was obtained with no starch addition. It is likely that both sodium silicate and ultrasonic treatment did prevent heterocoagulation but too many serpentine particles crowded the environment and hampered bridge formation between chromite particles by starch. When the amount of serpentine in the mixture was reduced to 30%, Figure 6, better selectivity was obtained with sodium silicate and ultrasonic treatment as the separation curves moved to the upper right direction. Improved selectivity can be attributed to the lessening of the crowding effect by serpentine particles. This behavior of chromite-serpentine mixture in the presence of sodium silicate and with ultrasonic treatment is also similar to the hematite-montmorillonite mixture (Arol and Iwasaki, 1987). Thus, it could be stated that selective flocculation of chromite from a chromite-serpentine mixture could only be possible at lower concentration of serpentine.

CONCLUSION

It was determined that starch has a specific affinity towards chromite but not serpentine. At above pH 11, chromite alone can be flocculated with starch while serpentine alone remains dispersed. When mixed, chromite and sepentine heterocoagulate which makes it difficult to separate the two minerals. Selective flocculation of chromite from a chromite-serpentine mixture is only possible in the presence of lower amounts of serpentine. A dispersant (sodium silicate) or ultrasonic treatment must be used to have a successful separation. Higher amounts of serpentine in the pulp leads to crowding which prevents any separation at all.

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Metoda selektywnej flokulacji z użyciem skrobi jako flokulanta, została użyta do oddzielenia chromitu od serpentynitu. Zostało ustalone, na podstawie badań, że skrobia wykazuje specyficzne powinowactwo do chromitu, który dzięki temu może ulec selektywnej flokulacji. Okazało się jednak, że selektywny rozdział jest możliwy do osiągnięcia w warunkach, gdy ilość serpentynitu w chromicie nie przekracza 30% wagowych. Proces separacji został zrealizowany w obecności dysperganta - krzemianu sodu, a zawiesina była traktowana ultradźwiękami.