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CONCENTRATION OF CHROMITE BY MEANS OF MAGNETIC CARRIER USING SODIUM OLEATE AND OTHER REAGENTS

Yasar UCBAS, Volkan BOZKURT, Kemal BILIR, Halil IPEK

Eskisehir Osmangazi University, Faculty of Engineering and Architecture, Department of Mining Engineering, 26480, Eskisehir, Turkey; corresponding author: vbozkurt@ogu.edu.tr

Abstract: Chromite recovery was studied using a magnetic carrier technology. Heavy media grade magnetite was used as the magnetic carrier. The effect of various reagents such as sodium oleate (NaOl) as a collector and carboxymethyl cellulose (CMC) as well as quebracho tannin as depressants on chromite removal was investigated. The effects of pH and reagent dosages were also determined. First, the zeta potential measurements were performed for different minerals in the absence and presence of NaOl, and then magnetic carrier tests were carried out under conditions based on zeta potential measurements. The magnetic carrier tests performed in the case of individual minerals (i.e. single minerals) showed that chromite (recovery of 95.1%) could be separated from serpentine (recovery of 3.2%) whereas it could not be separated from olivine. The best chromite concentrates containing 42.1% Cr₂O₃ were obtained with a 76% recovery from a synthetic mixtures of chromite and serpentine under optimum test conditions, that is at pH 10.5, 5.10⁻⁵ M NaOl, 20 g/Mg CMC, 0.5 g magnetite and 500 g/Mg kerosene (the feed contained 27% Cr₂O₃). Slime tailings of Turkish Maadin Company, Kavak Chrome Concentrating Plant in Eskisehir, which contain fine chromite, serpentine and olivine, were also investigated. It was found that chromite could not be satisfactorily recovered from the original slime sample in the presence and absence of NaOl by using the magnetic carrier technology. Additional FTIR studies performed with the investigated minerals showed that NaOl adsorption on chromite was greater than that on serpentine and magnetite minerals. It was also found that NaOl adsorption on serpentine is significantly reduced in the presence of magnetite while it increases only slightly on chromite.

Keywords: *chromite, serpentine, magnetite, magnetic carrier, sodium oleate, zeta potential, FTIR*

Introduction

The production of fine and ultrafine particles during the size reduction processes is unavoidable in mineral processing systems. The processing of these particles by conventional mineral separation methods is not satisfactory due to the problems associated with particle size. Studies aimed at finding new methods of upgrading of

fine and ultrafine materials began three decades ago (Fuerstenau et al., 1979). Most of these methods are based on the combination of aggregation and flotation processes. Separation of fine particles by magnetic carrier methods have been described in many papers (De Lafour, 1976; Nott, 1978; Schubert, 1980; Cook, 1981; Nott and Price, 1981; Parsonage, 1984, 1988). Selective separation of non-magnetic minerals such as chalcocite, sphalerite and coal from their associated gangue minerals has been described by Schubert (1980). Magnetic coating of iron and titanium bearing gang minerals by fine-sized magnetite particles before magnetic separation has also been applied in kaolinite concentration (Nott, 1978; Cook, 1981; Nott and Price, 1981). Magnetic carrier methods have also found application in water treatment process (De Lafour, 1976). The principle of the method is selective coating of the target mineral surfaces by magnetite particles in an agitated pulp followed by removal of the coated mineral from the pulp using magnetic separation. The factors that affect the coating of the magnetite are zeta potential of minerals and magnetite as well as the presence of adsorbed surfactant layer on the mineral and magnetite surfaces. Separation of many minerals such as apatite, barite, scheelite, magnesite, chromite and iron minerals from calcite, dolomite, serpentine, quartz and corundum minerals has been carried out on laboratory and pilot scales by controlling these parameters (Parsonage, 1984, 1988; Anastassakis, 1999, 2002; Prakash et al., 1999, 2001; Ucbas et al., 2014).

Chromite is primarily used as a refractory material. For this purpose, the Cr_2O_3 content of chromite should be more than 45%. Hence, concentration of chromite is often required. It is usually performed by gravity methods based on differences between the densities of chromite and gangue minerals, especially serpentine and olivine. The fine fraction below 100 μm is usually discarded as gangue due to the process and equipment inefficiencies. Therefore, substantial amount of chromite fines report to the tailings stockpiles in gravity separation plants. This results in resource loss considering the fact that the Cr_2O_3 content of these stocks reaches up to 20%. Since Turkey is one of the leading chromite ore producers in the world, it is obvious that the amount of chromite fines in tailings could be quite large throughout Turkey (Ucbas et al., 2014). Therefore, the utilization of these tailings could contribute to the economy while partially reducing the environmental problems.

Several studies have been attempted to recover chromite from slime stocks using column flotation, high intensity wet magnetic separation (WHIMS), WHIMS/column flotation (Guney et al., 1999; 2001) and multi gravity separation (Ozdogan et al., 1994; Cicek and Cocen, 2002) with a limited success. Magnetic carrier technology would well be an alternative method to recover chromite from such stocks (Ucbas et al., 2014).

Approximately 0.3 teragrams of tailings containing 17.36% Cr_2O_3 have been accumulated over the years in stockpiles of Turkish Maadin Company, Kavak Chrome Concentrating Plant located near the city of Eskisehir, Turkey. The aim of this study is to investigate possible concentration of chromite fines from these slime tailings using the magnetic carrier technology.

Materials and methods

Materials

Chromite, serpentine and olivine samples were obtained from the gravity concentration circuit while slime samples were obtained from the tailings stockpiles of Turkish Maadin Company, Kavak Chrome Concentrating Plant. Fine-sized heavy media grade magnetite was supplied by the ELI Manisa Coal Preparation Plant. All samples were, if needed, first crushed, then further ground using ceramic fast mill (Gabielli Fast Mill 2B) for 60 minutes.

Sodium oleate (NaOl) was used as a collector (>99% Sigma-Aldrich). Quebracho tannin and carboxymethylcellulose (CMC) were used as depressants (Chevron Phillips Chemical Company LP Mining Chemical) and analytical grade HCl and NaOH were used to adjust pH. Deionized water was used in all experiments.

Methods

Sample characterization

The particle size of the samples was measured wet in a Malvern Model 2000 particle size analyzer. Chemical analyses of the samples were performed using X-ray fluorescence spectroscopy (XRF, Spectro X-Lab). Mineralogical analyses of the samples were carried out using X-ray diffraction spectroscopy (XRD, Rigaku Miniflex, 1.54056-CuK α 1).

Zeta potential measurements

For determining zeta potentials, electrophoretic mobility measurements of chromite, magnetite, serpentine and olivine were conducted using Zeta-Meter System 3.0+ equipped with a camera system in the absence and presence of NaOl ($2 \cdot 10^{-5}$ M). One gram of samples in 100 cm³ of solution was conditioned for 10 min after obtaining the preset pH. The slurry was kept unstirred for additional 5 min to let larger particles to settle. The pH was adjusted with diluted HCl or NaOH. Thirty particles were followed through camera at each pH value. The instrument gave the average electrophoretic mobility from which the zeta potential was calculated using the Smoluchowski equation (Eq. 1)

$$\zeta = \frac{4\pi\eta U}{\varepsilon} \quad (1)$$

where ζ is the zeta potential (mV), η is the viscosity of the medium (poise), U is the electrophoretic mobility ($\mu\text{m/s}$ per V/cm), ε is the dielectric constant.

Magnetic carrier tests

The tests were performed in a 100 cm³ beaker. A stirrer with a plastic impeller was used to keep the particles in the suspension. The pH was regulated with diluted HCl or NaOH. Initial tests were carried out individually for each mineral (i.e. single

minerals). One gram of the mineral, 0.5 g of magnetite and 500 g/Mg kerosene were conditioned for 10 min at the prefixed pH in the absence and presence of NaOH. After conditioning period, stirrer was stopped. The magnetite and magnetite coated particles were removed by using highly magnetic metal rod. Uncoated particles (i.e. material remained) in the beaker were weighted after filtering and drying them in an oven. The net weight, the weight of uncoated particles subtracted from initial weight, was determined. This value was presented as per cent recovery for the results of magnetic carrier tests. The magnetite coating on the mineral surfaces was removed by ethanol washing for mass balancing purpose. The effects of pH, collector and depressant dosages were studied.

In the case of synthetic mineral mixtures (chromite, serpentine and olivine), equal weight (1 g) of each mineral was used while the procedure was the same as described previously.

FTIR studies

All samples (chromite, magnetite, serpentine, and slime) were prepared according to the zeta potential measurement data and magnetic carrier test procedures described previously. The infrared spectra of the samples were registered after their air drying. The spectra of chromite and serpentine were also registered in the presence of magnetite (sharing the same solution but isolated) for imitating magnetic carrier tests. The FTIR spectra were recorded using a Perkin Elmer 2000 spectrometer equipped with its own Diffuse Reflectance Infrared Fourier Transform (DRIFT). Typical spectrum was an average of 200 scans in the 4000-400 cm^{-1} spectral range with a resolution of 4 cm^{-1} using a deuterated triglycine sulfate (DTGS) detector. At the concentration of collector used, the intensity of the bands with respect to adsorbed layers was low, and the samples were not mixed with KBr since dilution further reduces the sensitivity. Thus, the untreated samples were used as a reference.

Results and discussions

Characterization of samples

The particle sizes of the samples are given in Table 1. It can be seen that magnetite is the finest while olivine is the coarsest mineral in terms of 90% pass. Chemical compositions of the samples are shown in Table 2. The results confirm the purity of the minerals, especially in terms of Cr_2O_3 content for chromite, and SiO_2 as well as MgO contents for serpentine and olivine while Fe_2O_3 and FeO contents for magnetite.

Figure 1 and Table 3 show the XRD analysis of the samples and the values of 2θ characteristic peaks of the pure minerals obtained from X-ray diffraction database, respectively for comparison. The results of this analysis suggested that the 2θ characteristic peak values of the pure minerals were quite consistent with the mineral samples studied, validating the purity of the samples. A comparison of the X-Ray

diffraction of slime and the minerals (Fig. 1) reveals that the slime sample contains all the minerals to a certain extent.

Table 1. Particle size of investigated minerals (Ucbas et al., 2014), olivine and chromite slime

Pass (%)	Magnetite (µm)	Chromite (µm)	Serpentine (µm)	Olivine (µm)	Slime (µm)
%10	2.83	0.26	2.73	2.94	3.91
%50	8.95	6.67	22.84	20.83	42.19
%90	26.29	34.11	173.17	180.67	166.51
%97	42.00	86.25	243.19	263.63	254.61

Table 2. Chemical analysis of investigated minerals (Ucbas et al., 2014), olivine and chromite slime

Oxides (%)	Magnetite	Chromite	Serpentine	Olivine	Slime
Cr ₂ O ₃	0.08	54.00	0.51	0.97	17.36
Fe ₂ O ₃	67.16	16.79	8.23	7.09	8.91
FeO	31.21	-	-	-	-
Al ₂ O ₃	0.44	12.50	0.02	0.01	1.50
SiO ₂	0.11	0.02	46.00	33.00	24.09
MgO	0.02	14.95	31.00	42.00	32.21
CaO	0.38	0.14	0.09	0.20	0.34
LOI	-	1.14	13.65	16.31	15.09

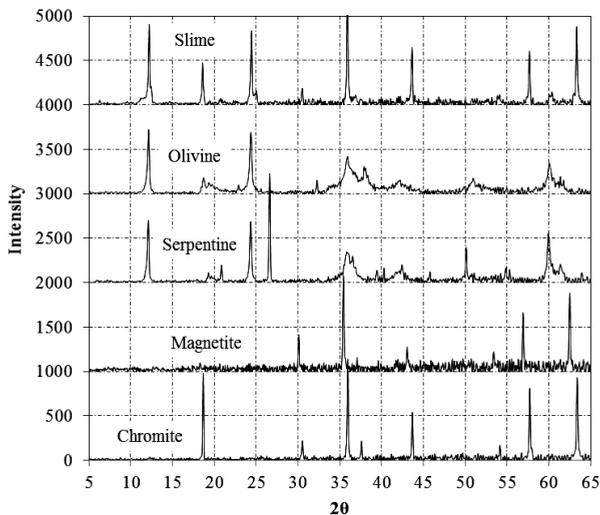


Fig. 1. XRD analysis of investigated minerals (Ucbas et al., 2014), olivine and chromite slime

Table 3. 2θ characteristic peaks of the investigated minerals (Ucbas et al., 2014) and olivine

Minerals	2θ	2θ	2θ
Chromite	35.6(100)	63.7(90)	57.6(90)
Magnetite	35.5(100)	62.7(85)	57.2(85)
Serpentine	12.1(100)	24.4(70)	19.4(50)
Olivine	24.3(100)	35.9(80)	60.8(70)

Zeta potential measurements in the absence of NaOI

The measured zeta potentials of magnetite, chromite, serpentine and olivine at different pH's are shown in Fig. 2. It can be observed that the zero point of charge (zpc) of chromite, magnetite, and serpentine are 7.2, 5.0, and 3.1, respectively (Ucbas et al., 2014). Olivine is positively charged at all pH values studied. Similar zpc values were reported in the literature (Iwasaki et al., 1962; Laskowski and Sobieraj, 1969; Sobieraj and Laskowski, 1973; Smith and Allard, 1983; Atak, 1987; Guney and Atak, 1997; Allesse et al., 1997; Anastassakis, 1999, 2002; Prakash et al., 1999).

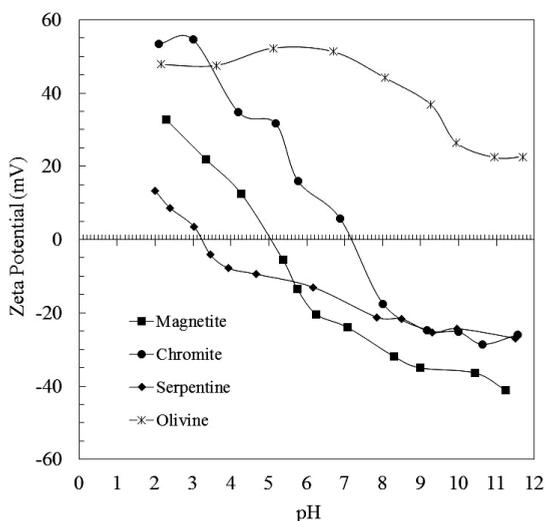


Fig. 2. Zeta potential of magnetite, chromite, serpentine (Ucbas et al., 2014) and olivine

Zeta potential measurements in the presence of NaOI

The measured zeta potentials of magnetite, chromite, serpentine and olivine at different pH in the presence of $2 \cdot 10^{-5}$ M NaOI are shown in Fig. 3. It can be seen that the zeta potential of all minerals decreases towards the negative direction beginning from pH value around 2 and charge reversal takes place at pH values between 2 and 4 for all minerals. The pzc of all minerals shifts to lower pH values as well. This could be explained by binding of oleate anions on cationic surface sites and reducing the net charge of the surfaces through physical adsorption. Above the pzc, where the surface

net charge was negative, zeta potential values of chromite, magnetite and serpentine kept decreasing until reducing its magnitude towards the higher alkaline region. This could be attributed to chemisorption (i.e. complexation of oleate anions with metal hydroxyl species) (Iwasaki et al., 1962; Laskowski and Sobieraj, 1969; Sobieraj and Laskowski, 1973; Smith and Allard, 1983; Atak, 1987; Guney and Atak, 1997; Allesse et al., 1997; Anastassakis, 1999, 2002; Prakash et al., 1999; Fuerstenau and Palmer, 1976; Ananthpadmanabhan and Somasundaran, 1979). However, in the case of olivine, charge reversal takes place at pH around 4 and olivine has net negative surface charge above this pH value. This could be interpreted as the presence of physical adsorption of NaOl onto olivine surfaces.

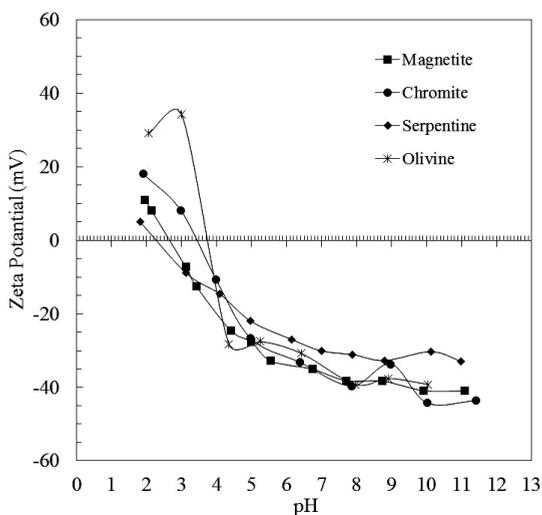


Fig. 3. Zeta potential of minerals in $2 \cdot 10^{-5}$ M NaOl solution

Magnetic carrier tests for single minerals

Magnetic carrier tests in the absence of NaOl

From the results of zeta potential measurements of minerals in the absence of NaOl (Fig. 2), it can be seen that magnetite and serpentine are negatively charged while chromite and olivine are positively charged at the pH range between 5 and 7. This could suggest that chromite and olivine minerals could be coated with magnetite due to the electrostatic attraction. Magnetic carrier tests conducted under these conditions revealed that minerals (chromite, serpentine and olivine) could well be coated with magnetite as predicted but magnetite attachment to minerals were so loose that even a gentle stirring of resulted in the detachment of the magnetite. This demonstrates that electrostatic attraction itself is not enough for effective magnetite coating. Similar results were obtained in the literature (Anastassakis, 1999, 2002; Prakash et al., 1999, 2001; Ucbas et al., 2014). This was attributed to the presence of a thin film of water

between the hydrophilic surfaces of magnetite and minerals. Thin film of water could not be ruptured even though magnetite and mineral particles are very close to each other as a result the particles are easily detached under even gentle stirring conditions (Anastassakis, 1999, 2002).

Magnetic carrier tests in the presence of NaOH

From the zeta potential measurements of minerals in the presence of NaOH (Fig. 3), it is observed that chromite and olivine are positively charged while magnetite and serpentine are negatively charged at pH 3. This could suggest the possible magnetite coating of chromite and olivine through electrostatic attraction, as a result, their separation from serpentine. Magnetic carrier tests were carried out with chromite, olivine and serpentine separately in the presence of $1 \cdot 10^{-4}$ M NaOH at pH 3. Chromite recovery was 95.5% while serpentine recovery was 53%. Olivine recovery was similar (90% <) to chromite recovery suggesting difficulty in separation of chromite from olivine using magnetic carrier. Therefore, further magnetic carrier tests were mainly focused on separation of chromite from serpentine. In order to increase the chromite recovery to target values (> 98%), new tests were performed at increased NaOH dosage ($2 \cdot 10^{-4}$ M). Recovery of chromite was increased up to 99.2% while recovery of serpentine remained similar (54.1%). Obtained recovery values clearly indicated that chromite could not be separated from serpentine selectively under the conditions based on the zeta potential measurements alone. Similar results were observed in previous studies performed by the present authors (Bozkurt et al., 2006; Ucbas et al., 2014). This is attributed to the fact that hydrophobicity of mineral surfaces is more important than the surface charge differences of minerals (i.e. hydrophobic interaction forces dominate the magnetite coating rather than electrostatic interaction forces). The strength of hydrophobic interaction forces was investigated in a study by measuring surface forces between two hydrophobic surfaces (Israelachvili, 1992). It was found that hydrophobic interaction forces are extremely strong due to the rearrangements of hydrogen bond configurations in the overlapping solvation zones as two hydrophobic species come together.

Further magnetic carrier tests were carried out within the pH range of 2-12 in the presence of $5 \cdot 10^{-5}$ M NaOH (Fig. 4, 0.5 g magnetite, 500 g/Mg kerosene). Recovery of chromite increases with an increasing pH while serpentine recovery is decreasing. At pH 10.5, recovery of chromite and serpentine are 94.4 and 14.5% (difference of 74.8%), respectively. In order to improve the difference in chromite and serpentine recoveries, the effect of NaOH dosage on recoveries were investigated further at pH 10.5. However, as seen in Fig. 5 (pH 10.5, 0.5 g magnetite, 500 g/Mg kerosene) the difference in chromite and serpentine recoveries cannot be increased by altering NaOH dosage. Higher chromite recoveries obtained with increasing pH in magnetic carrier tests coincides with the literature knowledge where high chromite and magnetite flotation recoveries were obtained at relatively high concentrations of NaOH solutions at highly alkaline pH values (Iwasaki et al., 1962; Atak, 1987; Guney and Atak, 1997;

Fuerstenau and Palmer, 1976; Ananthpadmanabhan and Somasundaran, 1979). This could be explained by the aggregation of chromite and magnetite (recovery of 94.4%). The lower recoveries obtained with serpentine could be attributed to the less magnetite and serpentine aggregation (recovery of 21.6%) due to the lower adsorption levels of NaOl on serpentine compare to chromite as further confirmed by FTIR studies.

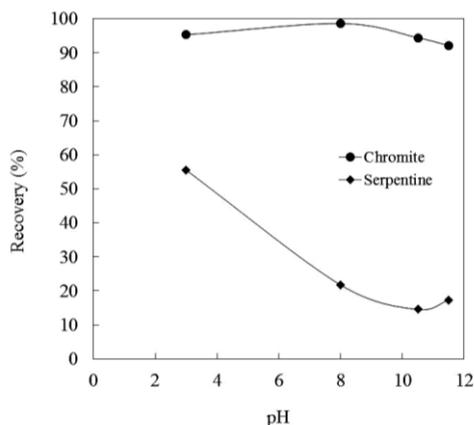


Fig. 4. The effect of pH on recovery

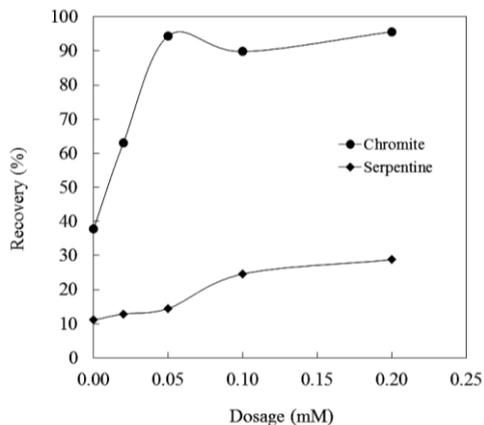


Fig. 5. The effect of NaOl dosage on recovery

The effects of depressants such as quebracho and carboxymethyl cellulose (CMC) were also investigated for the same aim (Last and Cook, 1952; Bulatovic, 1999). Results of these tests are given in Figs. 6 (pH 10.5, $5 \cdot 10^{-5}$ M NaOl, 0.5 g magnetite, 500 g/Mg kerosene) and 7 (pH 10.5, $5 \cdot 10^{-5}$ M NaOl, 0.5 g magnetite, 500 g/Mg kerosene), respectively. As can be seen from Fig. 6, the difference in recoveries moderately increases at 20 g/Mg quebracho dosage (difference of 83.3%) compare to recoveries obtained in the absence of depressant (difference of 74.8%). Even though the difference is increased, it is not found satisfactory for the selective separation of these minerals.

In the case of tests performed with CMC, the highest difference in chromite and serpentine recoveries is obtained at dosage of 20 g/Mg (Fig. 7). The recovery of chromite is 95.1% while serpentine 3.2% (difference of 91.9%). The difference in recoveries significantly increases, when compared to recoveries obtained in the absence of depressant (Atak, 1987), suggesting the possible separation of these minerals in the presence of CMC. This could be attributed to the depressant effect (blinding agent) of CMC influencing collector adsorption on the minerals (creating negative surfaces on minerals) and inducing particle dispersion (Atak, 1987; Guney and Atak, 1997; Shortridge et al., 2000; Dalvie et al., 2000; Gallios et al., 2007; Laskowski et al., 2007). It can be seen from Figs 6 and 7 that a careful control of depressant dosage is essential since recovery of chromite decreases significantly over certain dosages.

Tests performed with chromite-magnetite and serpentine-magnetite were carried out also with olivine. It was found that the recoveries of olivine were similar to those of chromite obtained in the absence and presence of depressants. This suggested that chromite could not be separated from olivine selectively.

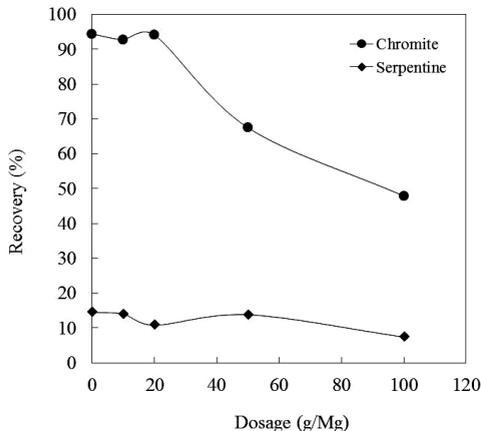


Fig. 6. The effect of quebracho dosage on recovery

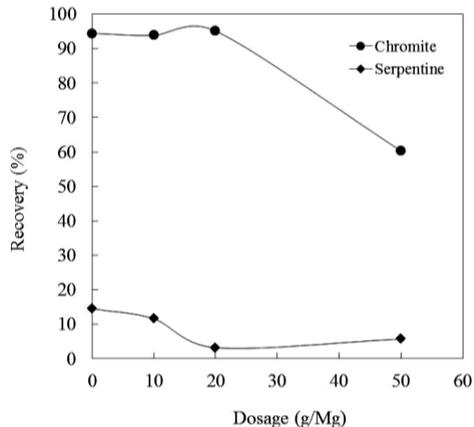


Fig. 7. The effect of CMC dosage on recovery

Magnetic carrier tests for mixed minerals and slime tailings

The tests performed with synthetic mixture of chromite and serpentine (1 g each) at pH 10.5, $5 \cdot 10^{-5}$ M NaOI, 0.5 g magnetite, 500 g/Mg kerosene, 20 g/Mg CMC provided chromite concentrates containing 42.1% Cr_2O_3 with 76% recovery. The feed grade was 27.0% Cr_2O_3 . The same conditions applied for the slime sample provided chromite concentrate containing 22.8% Cr_2O_3 with 60.9% recovery. The feed grade of the slime sample was 17.36% Cr_2O_3 . This result shows that upgrading is poor and could not be obtained with the industrial chromite slime sample. This could be due to the high olivine content in the slime sample.

The chemistry of NaOI interaction with investigated minerals

FTIR studies in the absence of NaOI

The reference DRIFT spectra of chromite, serpentine, slime and magnetite mineral samples are depicted in Fig. 8. The bands between 3500 and 3750 cm^{-1} are due to the stretching vibrations of the O-H groups. The strong bands between 900 and 1150 cm^{-1} are attributed to the Si-O stretches and Si-O-Si stretching vibration modes (Ucbas et al., 2014). The bands between 500 and 1000 cm^{-1} are assigned to bond between groups II-III transition metal cations in spinel oxides and oxygen anion (Povnnennykh, 1978; Moroz et al., 2001). Strong band observed with magnetite at 570 cm^{-1} is assigned to Fe-O bending vibration (Liese, 1978; Kim et al., 2007).

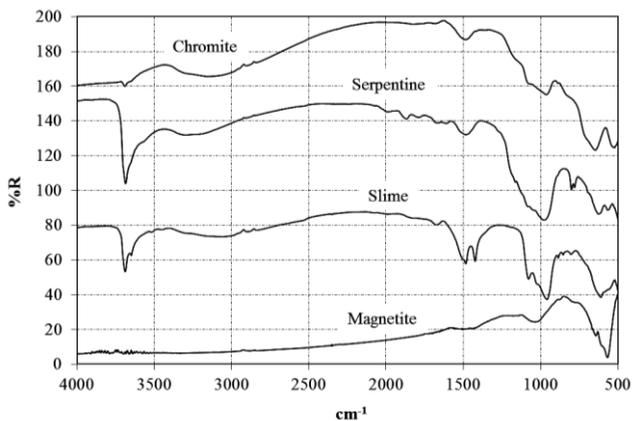


Fig. 8. Reference DRIFT spectra of minerals (Ucbas et al., 2014) and the slime sample

FTIR studies in the presence of NaOI

The reference infrared spectrum of NaOI is shown in Fig. 9. The characteristic alkyl chain bands at 2920 cm^{-1} and 2850 cm^{-1} are due to asymmetric and symmetric C-H stretching vibrations of CH_2 group, respectively. The weak band at 2945 cm^{-1} is due to an asymmetric C-H stretching vibration of CH_3 group. The bands at lower wavenumbers were assigned to asymmetric (1555 cm^{-1}) and symmetric ($1400\text{--}1500\text{ cm}^{-1}$) C=O (carbonyl) stretching vibrations of carboxylate ion (RCOO^-) (Peck et al., 1967; Wensel et al., 1995; Lu et al., 1998; Hamid and Forsberg, 2006).

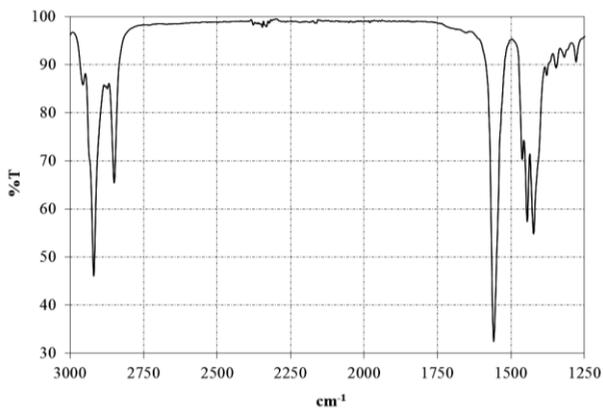


Fig. 9. Reference FTIR spectrum of NaOI

DRIFT spectra for chromite, serpentine and magnetite minerals were acquired at optimum conditions ($\text{pH } 10.5$, $5 \cdot 10^{-5}\text{ M NaOI}$) of magnetic carrier tests (Fig. 10). The bands in the presence of NaOI are quiet identical to bands observed at wavenumber of

2920 cm^{-1} and 2850 cm^{-1} with the reference spectrum of NaOl (Fig. 9) indicating adsorption of NaOl on minerals. Furthermore, the band shifts observed, especially more pronounced for chromite compare to serpentine and magnetite minerals due to higher level of collector adsorption, at wavenumbers between 1250 and 1600 cm^{-1} indicates the chemisorption of NaOl (Peck et al., 1967). Bearing in mind that intensities of adsorption bands are quiet reproducible due to the procedure used to acquire spectra of NaOl treated minerals, comparing spectra of minerals in terms of adsorbed band intensities (Fig. 10), it is apparent that NaOl adsorption on chromite is higher than on serpentine and magnetite minerals. However, the presence of some adsorption on serpentine effects separation of minerals negatively as observed in magnetic carrier tests performed under the same conditions.

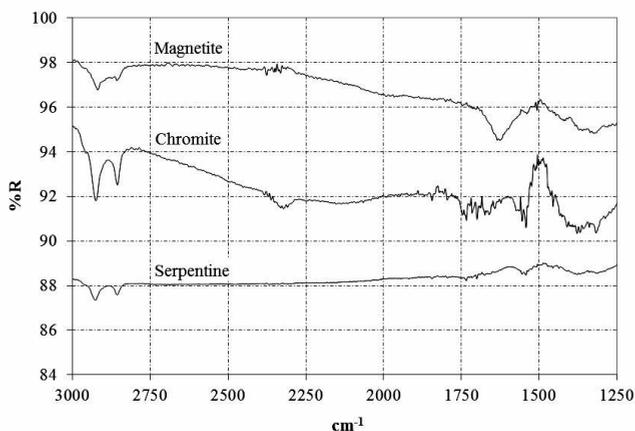


Fig. 10. DRIFT spectra of the minerals in $5 \cdot 10^{-5}$ M NaOl

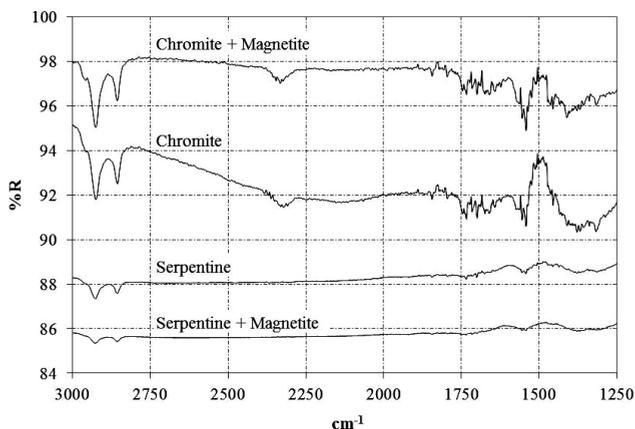


Fig. 11. DRIFT spectra of chromite and serpentine in the presence of magnetite

The spectra of chromite and serpentine were acquired in the presence of magnetite (sharing the same solution but isolated) as well since the magnetic carrier tests were performed in the presence of magnetite. The results are presented in Fig. 11. It can be seen that the amount of NaOl adsorption, indicated by band intensities, on chromite slightly increases when compared to chromite alone. In the case of serpentine, the situation is reversed because the amount of NaOl adsorption is reduced in comparison to serpentine alone. Without strong evidence this could be attributed either to competitive adsorption of NaOl on minerals or the activation of chromite by ions possibly dissolving from magnetite. These results are consistent with magnetic carrier tests performed under the same experimental conditions (Fig. 5).

Conclusions

X-Ray diffraction analysis of the minerals studied revealed that the slime sample contains chromite, serpentine and olivine minerals, to a certain extent. As a result of the magnetic carrier tests, chromite could be separated from serpentine in fine sizes using magnetic carrier technology as confirmed by the tests performed in the case of individual and mixed minerals under the optimal test conditions of $5 \cdot 10^{-5}$ M NaOl in the presence of 20 g/Mg carboxymethyl cellulose at pH 10.5. Chromite separation from serpentine could also be achieved in the presence of quebracho tannin with limited success. However, chromite could not be separated from olivine selectively as confirmed by tests performed in the case of individual and mixed minerals. In addition, it was also realized that separation of chromite from olivine was a challenging research subject. Chromite could not be recovered satisfactorily as well from the original slime sample, perhaps mostly due to the olivine content of it.

The zeta potential and FTIR studies confirmed the chemical nature of the NaOl adsorption on chromite, serpentine and magnetite minerals. The FTIR studies indicated that NaOl adsorption on chromite was higher than those of serpentine and magnetite. It was also found that NaOl adsorption on serpentine declined significantly while that on chromite increased slightly in the presence of magnetite. Thus, selective separation of chromite from serpentine was elaborated further.

Magnetic carrier tests carried out in the absence of NaOl suggested that electrostatic attraction itself was not enough for the successful magnetite coating of minerals. The adsorption of collector onto the mineral surfaces was essential.

It has been demonstrated that the magnetic carrier methods could be used for selective separation of minerals even in fine sizes when their surface could be adapted by proper reagents.

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References

- ALESSE V., BELARDI G., FREUND J., PIGA L., SHEHU N., 1997, *Acidic Medium Flotation Separation of Chromite from Olivine and Serpentine*, Transactions of American Society of Mining Engineers, 302, 26–35.
- ANANTHPADMANABHAN K., SOMASUNDARAN P., HEALY T.W., 1979, *Chemistry of Oleate and Amine Solutions in Relation to Flotation*, T. Am. I. Min. Met. Eng. 266, 1–7.
- ANASTASSAKIS G.N., 1999, *A Study on the Separation of Magnesite Fines by Magnetic Carrier Methods*, Colloids and Surfaces A: Physicochemical Engineering Aspects, 149, 585–593.
- ANASTASSAKIS G.N., 2002, *Separation of Fine Mineral Particles by Selective Magnetic Coating*, Journal of Colloid and Interface Science, 256, 114–120.
- ATAK S., 1987, *Adsorption of Oleate on Chromite and Olivine*, Aufbereitungs-Technik, 12, 727-733.
- BOZKURT V., UCBAS Y., SONMEZ E., IPEK H., KOCA S., 2006, *Separation of Feldspar Minerals from Quartz Using Magnetic Carrier Technology*. Proceedings of the XXIII IMC, Vol. 2., Onal G., Celik M.S., Arslan F., Atesok G., Guney A, Sirkeci A.E., Yuce A.E., Perek K.T. (eds), Istanbul, Turkey, 963–968.
- BULATOVIC S.M., 1999, *Use of Organic Polymers in the Flotation of Polymetallic Ores: A Review*, Minerals Engineering, 12, 4, 341–354.
- CICEK T., COCEN I., 2002, *Applicability of Mozley Multigravity Separator (MGS) to Fine Chromite Tailings of Turkish Chromite Concentrating Plants*, Minerals Engineering, 15, 1–2, 91–93.
- COOK J.A. 1981, *Magnetic Beneficiation of Clays Utilizing Magnetic Seeding and Flotation*, British Patent 2092026A.
- DALVIE M.A, HARRIS P.J., BRADSHAW D.J., 2000, *The Effect of Polymeric Depressants and Inorganic Dispersants on the Surface Characteristics of Talc*, in: Proceedings of XXI International Mineral Processing Congress, (P. Massacci, Ed.) Elsevier, Amsterdam, B8b-25–B8b-32.
- DE LAFOUR C., 1976, *Seeing Principles of High Gradient Magnetic Separation*, Journal of American Water Works Association, 68, 443–446.
- FUERSTENAU D.W., CHANDER S., ABOUZEID A.M., 1979, *The Recovery of Fine Particles by Physical Separation Methods*, in: *Beneficiation of Mineral Fines: Problems and Research*, P. Needs, Somasundaran, N. Arbitor (Eds.), AIMMPE Inc., New York, 3–59.
- FUERSTENAU M.C., PALMER B.R., 1976, *Anionic Flotation of Oxides and Silicates*, in: *Flotation - A. M. Gaudin Memorial Volume -*, Volume 1 Chapter 7 - *Fundamentals of Nonmetallic Flotation*, SME Publications, New York, 148–196.
- GALLIOS G.P., DELIYANNI E.A., PELEKA E.N., MATIS K.A., 2007, *Flotation of Chromite and Serpentine*, Separation and Purification Technology, 55, 232–237.
- GUNEY A., ATAK S., 1997, *Separation of Chromite from Olivine by Anionic Collectors*, Fizykochemiczne Problemy Mineralurgii, 31, 99–106.
- GUNEY A, ONAL G., CELIK M.S., 1999, *A New Flowsheet for Processing Chromite Fines by Column Flotation and the Collector Adsorption Mechanism*, Minerals Engineering, 12, 9, 1041–1049.
- GUNEY A, ONAL G., ATMACA T., 2001, *New Aspect of Chromite Gravity Tailings Re-Processing*, Minerals Engineering, 14, 11, 1527–1530.
- HAMID S.H., FORSBERG K.S.E., 2006, *XPS & FTIR Study of Adsorption Characteristics Using Cationic and Anionic Collectors on Smithsonite*, Journal of Minerals & Materials Characterization & Engineering, 5, 1, 21–45.
- ISRAELACHVILI J.N., 1992, *Intermolecular and Surface Forces*, 2nd Edition, Academic Press, London.
- IWASAKI I., COKE S.R.B., KIM Y.S., 1962, *Some Surface Properties of and Flotation Characteristics of Magnetite*, Transactions of American Society of Mining Engineers, 223, 113–120.

- KIM M.J., LIM B., JEONG Y.K., CHO Y.W., CHOA Y.H.B., 2007, *Surface Modification of Magnetite Nanoparticles for Immobilization with Lysozyme*, Journal of Ceramic Processing Research, 8, 4, 293–295.
- LASKOWSKI J.S., SOBIERAJ S., 1969, *Zero Points Of Charge of Spinel Minerals*, Transactions of the Institution of Mining and Metallurgy Section C, 78, C161–C162.
- LASKOWSKI J.S., QUI L., O'CONNOR C.T., 2007, *Current Understanding of the Mechanism of Polysaccharide Adsorption at the Mineral/Aqueous Solution Interface*, International Journal of Mineral Processing, 84, 59–8.
- LAST I., COOK P., 1952, *Collector Depressant Equilibria in Flotation: II. Depressant Action of Tannic Acid and Quebracho*, Journal of Physical Chemistry, 56, 643–648.
- LIESE H.C., 1967, *Mineralogical Notes an Infrared Absorption Analysis of Magnetite*, American Mineralogist, 52, July–August, 1198–205.
- LU Y., DRELICH J., MILLER J.D., 1998, *Oleate Adsorption at an Apatite Surface Studied by Ex-Situ FTIR Internal Reflection Spectroscopy*, Journal of Colloid and Interface Science, 202, 1998, 462–476.
- MOROZ T., RAZVOROTNEVA L., GRIGORIEVA T., MAZUROV M., ARKHIPENKO D., PRUGOV V., 2001, *Formation of Spinel from Hydrotalcite-Like Minerals and Destruction of Chromite Implanted by Inorganic Salts*, Applied Clay Science, 18, 29–36.
- NOTT A.J., 1978, *Magnetic Beneficiation of Clay Using Magnetic Particulate*, US Patent 4087004.
- NOTT A.J., PRICE W.M., 1981, *Magnetic Beneficiation of Clays using Magnetic Particulate*, US Patent 4125460.
- OZDAG H., UCBAS Y., KOCA S., 1994, *Recovery of Chromite from Slime and Table Tailings by Multi Gravity Separator*, in: Proceedings of Innovations in Mineral Processing, Sudbury, Canada, 267–78.
- PARSONAGE P., 1984, *Selective Magnetic Coating for Mineral Separation*, Transactions of the Institution of Mining and Metallurgy Section C, 93, C37–44.
- PARSONAGE P., 1988, *Principles of Mineral Separation by Selective Magnetic Coating*. International Journal of Mineral Processing, 24, 269–93.
- PECK A.S., RABY L.H., WADSWORTH M.E., 1967, *An Infrared Study of the Flotation of Hematite with Oleic Acid and Sodium Oleate*, Transactions of American Institute of Mining and Metallurgical Engineers, 238, 301–07.
- POVNNENNYKH A.S., 1978, *The Use of Infrared Spectra for the Determination of Minerals*, American Mineralogist, 63, 956–959.
- PRAKASH S., DAS B., MOHANTY J.K., VENUGOPAL R., 1999, *The Recovery of Fine Iron Minerals from Quartz and Corundum Mixtures Using Selective Magnetic Coating*, International Journal of Mineral Processing, 57, 87–03.
- PRAKASH S., MOHANTY J.K., DAS B., VENUGOPAL R., 2001, *Characterization and Removal of Iron from Fly Ash of Talcher Area, Orissa, India*, Minerals Engineering, 14, 1, 123–26.
- SHUBERT R.H., 1980, *Magnetic separation of particulate mixtures*, U.S. Patent RE 30.360.
- SHORTRIDGE P.G., HARRIS P.J., BRADSHAW D.J., KOOPAL L.K., 2000, *The Effect of Chemical Composition and Molecular Weight of Polysaccharide Depressants on the Flotation of Talc*, International Journal of Mineral Processing, 59, 215–224.
- SMITH R.W., ALLARD S.G., 1983, *Effects of Pretreatment and Aging on Chromite Flotation*, International Journal of Mineral Processing, 11, 163–74.
- SOBIERAJ S., LASKOWSKI J.S., 1973, *Flotation of Chromite: 1- Early Research and Recent Trends; 2- Flotation of Chromite and Surface Properties of Spinel Minerals*, Transactions of the Institution of Mining and Metallurgy Section C, 82, C207–213.

- UCBAS Y., BOZKURT V., BILIR K., IPEK H., 2014, *Separation of Chromite from Serpentine in Fine Sizes using Magnetic Carrier*, Separation Science and Technology, 49, 6, 1–11, DOI: 10.1080/01496395.2013.869602.
- WENSEL R.W., PENALOZA M., CROSS W.M., WINTER R.M., KELLAR J.J., 1995, *Adsorption Behavior of Oleate on Mg(OH)₂ as Revealed by FTIR Spectroscopy*, Langmuir, 11, 4593–595.