A COMPARATIVE STUDY ON INTERACTIONS OF IONIC COLLECTORS WITH ORTHOCLASE

Savas OZUN[*], Mustafa Umit ATALAY[**]

[*] Department of Mining Engineering, Suleyman Demirel University, Isparta, 32260, Turkey, savasozun@gmail.com

[**] Department of Mining Engineering, Middle East Technical University, Ankara, 06531, Turkey

Abstract: Flotation and adsorption characteristics of the most commonly used cationic and anionic collectors with high grade orthoclase were investigated through the electrokinetic potential measurement, microflotation, Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) studies. According to the obtained results, orthoclase had high flotation recovery with amine and oleic acid based (OAB) collector at certain pH ranges no flotation response was observed with petroleum sulfonate at different pHs. In contrast to the flotation recovery differences, the electrokinetic potential measurements, FTIR and AFM analyses presented similar adsorption characteristics for all collectors. The results of electrokinetic potential tests showed that amine had a strong influence on the zeta potential of orthoclase. While amine turned the zeta potentials of orthoclase from negative to positive, sulfonate and OAB collector provided slightly more negative zeta potentials at certain pHs. In the case of FTIR and AFM analyses, each collector-treated orthoclase (CTO) sample displayed similar characteristic FTIR bands of CH_2 group and micro topographical collector coated patches with different intensities. However, the interactions of each collector with orthoclase surfaces were altered by rinsing with acetone indicating that the interactions were mostly through the electrostatic forces and/or hydrogen bonding.

Keywords: collector interactions, zeta potential, microflotation, FTIR, AFM, orthoclase

Introduction

Feldspars are the most common rock-forming mineral group in nature. They are generally found together with other minerals like mica minerals, quartz, iron and titanium oxides. These associated minerals have to be removed in order to obtain a high quality feldspar concentrate. Upgrading of feldspar ores can be achieved by a number of conventional separation techniques such as gravitational, magnetic, flotation or by combination of either two or more of them and so on. Among them, flotation is the most widely used beneficiation method (Orhan and Bayraktar, 2005; Hacifazlioglu et al., 2012).

Beneficiation of feldspar by flotation is conventionally established in two stages under highly acidic conditions. Up to now, upgrading through flotation operations has been investigated by some researchers using different types of collectors. In the first stage, mica minerals were floated by using amine type collectors at pH 2.5–3.5 (Bayraktar et al., 1997). The iron-titanium oxide minerals were floated either by oleate at pH 5–5.5 or by sulfonates at pH 3–3.5 in the second stage. Succinamates, various vegetable oil soaps, sarcosine and collectors of hydroxamate type were used for removal of iron-titanium oxide minerals (Bayraktar et al., 1997; Celik et al., 2001). In the last decades, oleic acid based (OAB) flotation collectors, such as Aero 704, have been developed for removal of mica and iron-titanium bearing minerals together from feldspars under alkaline pH conditions by a single stage flotation operation (Ozun et al., 2009).

The surfactant/mineral interaction in an aqueous medium has a crucial importance in accomplishing the desired beneficiation. It has been studied mostly by indirect methods such as contact angle measurements, electrokinetic potential measurement, surface forces and recovery responses (Fuerstenau and Raghavan, 1980; Novich and Ring, 1985; Laskowski, 1989; Smith and Scott, 1990). A Fourier transform infrared spectroscopy (FTIR) analysis is another technique which is used to determine adsorption mechanisms of surfactants on mineral surfaces (Giesekke, 1983; Marabini et al., 1993; Vidyadhar and Rao, 2007). With development in analysis techniques, a few research studies have been done by using atomic force microscopy (AFM) as a direct method in order to visualize the collector/mineral interaction (Chennakesavulu et al., 2009; Paiva et al., 2011). However, this technique is still in its early stages.

The aim of the present study is two-fold. As a well-known fact, the relationship between the floatability and changes in the electrokinetic potential forms the basis for determination the collector/mineral interaction. First, the effects of the three commonly used ionic collectors on pure orthoclase will be investigated comparatively in terms of flotation recovery responses and zeta potential values as a function of collector concentration and pH. In the analysis, it is presumed that pH dependent solution chemistry of Aero 3000C (amine type), Aero 704 (OAB type) and Aero 825 (sulfonate type) would be similar to those of dodecylamine, oleic acid and sodium dodecyl sulfonate respectively (Somasundaran and Wang, 2006). Next, the aim is to determine the adsorption characteristics of each collector sample on orthoclase through FTIR and AFM analyses. Therefore, AFM micro topography studies will be also conducted on original and collector-treated orthoclase surfaces. Finally, all the results will be correlated with each other, presented in graphical illustrations and discussed comparatively with FTIR results.

Materials and methods

A high grade orthoclase ($KAlSi_3O_8$) test sample was obtained from India. It was ground in an agate mortar, wet-sieved to obtain -212+38µm size range and divided

into a number of representative samples prior to experimental analyses. Characterization of the samples was done by X-ray diffraction (XRD) and X-ray fluorescence (XRF). According to the results obtained by the XRF analysis, the sample had oxides content of 1.80% Na_2O, 12.71% K_2O, 17.02% Al_2O_3, 68.56% SiO_2, < 0.008% TiO_2 and 0.063% Fe_2O_3. The elemental composition and all peaks in the XRD pattern of orthoclase (Fig. 1) were in consistence with the literature data (31-966) (ICDD, International Center for Diffraction Data 1986; Vidyadhar 2007).
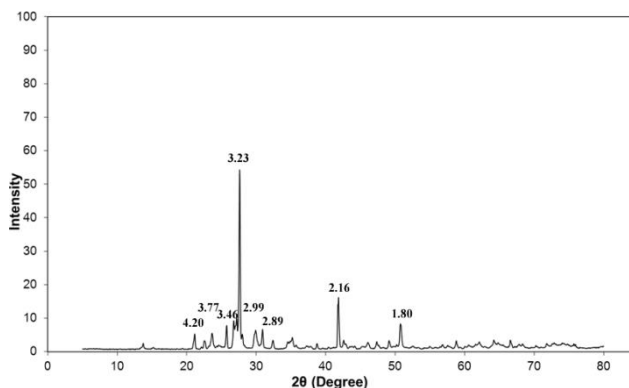

Fig. 1. X-Ray diffraction trace of orthoclase

Collectors, which are commercially named Aero 3000C, Aero 825 and Aero 704, were obtained from Cytec Industries Inc., USA (Thomas 2010). In the experiments, a certain volume of Aero 704 was mixed with the same volume of ethyl alcohol. Then, the mixture was treated with a calculated amount of NaOH solution to convert Aero 704 from the acidic to oleate form. For the analyses, the stock collector solutions (30 g/dm^3) were diluted freshly with distilled water to the desired collector concentration before use.

Microflotation test

Microflotation recovery responses of orthoclase (sized in -212+38 µm) were determined at an ambient temperature using EMDEE microflot agitator. An instrument consists of a timer/counter and agitator assembly. The agitator assembly produces a linear motion by means of a rodless pneumatic cylinder, which generates high accelerative field to subject the test-tube contents to high intensity agitation.

In the analysis, the pulp, constituted from 0.5 g mineral sample, chemical compounds and distilled water had a total volume of 65 cm^3. It was conditioned at the desired pH values for a pre-determined time (5 min), and then placed into the microflot agitator. The test tube was agitated for 30 cycles with an air pressure of 250 kPa. The flotation recovery under various flotation conditions was calculated by weighing the filtered and dried concentrate and tailing.

Electrokinetic potential measurement

The zeta-potentials (ζ) of the mineral particles were measured at ambient temperature with a Malvern Zetasizer Nano-Z meter. The instrument uses a laser doppler velocimeter (LDV) for measuring the zeta potential of particles. It takes a series of measurements (here 3 measurements) in the size range of 5 nm–10 µm and gives an average potential value.

The electrokinetic potential measurements were performed at ambient temperature. For the electrokinetic potential measurements, 10 mg of orthoclase was ground to -10 µm by the agate mortar, put into a 100 cm^3 of distilled water and agitated for 5 min before analyses. The same procedure was applied for the electrokinetic potential measurements in the presence of each collector samples.

Atomic force microscopy

The AFM samples were imaged at ambient temperature with a tapping mode in the air using a Pico SPM 300 (molecular imaging) device controlled with a Nano Scope E controller (digital instruments). The cantilever had a resonance frequency of 140–160 kHz. Images were collected using Phosphorus (n) doped silicon cantilever Probe at a constant scan rate of 2 Hz and 256 lines per sample. The images were flattened with Nano Scope E version 4.23 (Digital Instruments) and further analyzed by WSxM version 5.0 Develop 3.1 (Horcas et al., 2007).

The sample preparation for the AFM analysis included several steps. Pure orthoclase crystals were cut into 10 mm in diameter by crusher and then polished with 25 µm-8 µm sandpapers for 20 minutes each. The samples were then polished finely to get the smoothest surface by applying 1 µm, 0.50 µm, 0.25 µm and 0.05 µm grit size using diamond suspension (Metadi supreme diamond suspension, Buehler) and velvet cloths, respectively. Between each polishing stage, the mineral samples were rinsed with Millipore water (Milli-Q UV plus, Millipore Inc., 18.2 MΩcm), and sonicated for 10 minutes to remove the residue of the previous polishing stage. The AFM analyses were performed on orthoclase and collector-treated (CT) orthoclase samples. After the conditioning step, the samples were dried for 24 hours in an oven at 40±5ºC.

FTIR Analysis

The FTIR spectra of each sample were measured at 4 cm^{-1} resolution with an average of 200 scans by the Bruker 66 vs^{-1} instrument in ambient temperature as a KBr disc technique. The results were further analysed using Opus Version 5.0 software.

The FTIR analyses of orthoclase and CT orthoclase samples were performed. An approximately 0.01 g of orthoclase sample powder was mixed with 0.1 g of dry potassium bromide (KBr) powder and pelleted. When performing the FTIR measurements, the background was measured with a KBr only pellet containing no mineral sample.

Results and discussion

Microflotation Tests

Although the main purpose in this study was to outline the adsorption characteristics of different ionic collectors on orthoclase, the flotation responses of orthoclase in the presence of different collector concentrations were also examined individually as a function of pH. The results are presented in Figs. 2-4 for amine, sulfonate and OAB type collectors, respectively.

The effects of amine concentration and pH on orthoclase flotation are given in Fig. 2. The maximum flotation recoveries are over 85% in the presence of 16, 24 and 32 mg/dm^3 of amine. For all amine concentrations tested, the flotation recovery plots are similar and bell shaped. The flotation starts at highly acidic pH values and rises rapidly to the maximum level at near neutral pH values.
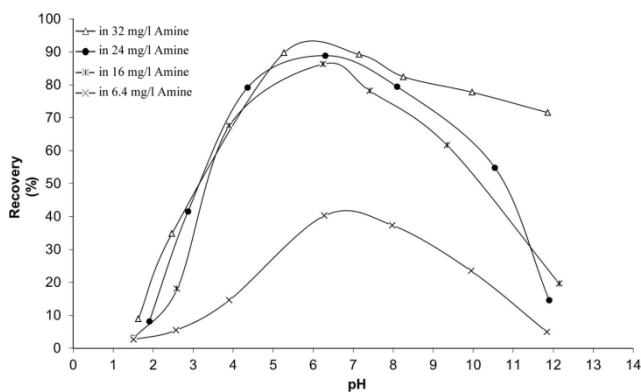

Fig. 2. Flotation recovery of orthoclase with amine as a function of pH

Figure 3 shows the effect of sulfonate on orthoclase flotation as a function of collector concentration and pH. According to the results, the flotation recovery response of orthoclase is independent on both sulfonate concentration and pH. For all sulfonate concentrations, the flotation response of orthoclase follows almost the same path and reaches to the maximum level between the pH range of 3.5 and 6.5. The recovery is less than 15% even in the presence of the highest sulfonate concentration (320 mg/dm^3) tested. Above and below the given pH range, the flotation recovery is almost zero.

In the presence of OAB collector, the flotation recovery plots (Figure 4) are bell-shaped for the certain collector concentrations and are similar to those of obtained with amine. However, flotation with OAB is more pH sensitive than amine, and it is obtainable between a narrow alkaline pH range of 8.5 and 11.5. Flotation starts at pH 8, rises rapidly and reaches the maximum level, over 75% with 88, 112 and 160 mg/dm^3 of Aero 704, between the pH range of 9 and 10. Above pH 10, the flotation recovery drops rapidly. The pH range, where the maximum flotation recoveries of

orthoclase are obtained in this study, is similar to that of a number of different minerals including rutile, hematite, ilmenite, zircon, garnet, etc. reported in the literature (Polkin and Najfonow, 1964; Ananthapadmanabhan and Somasundaran, 1979; Somasundaran and Wang, 2006).
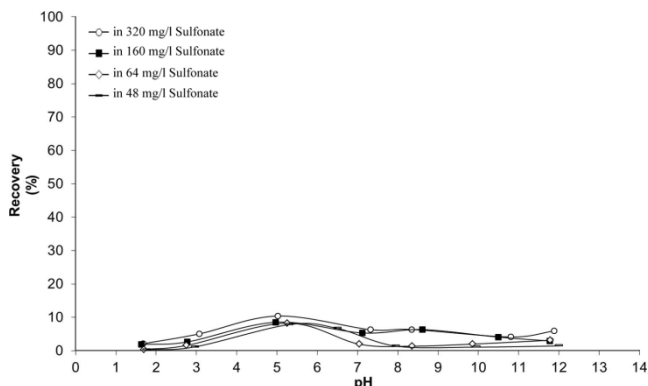

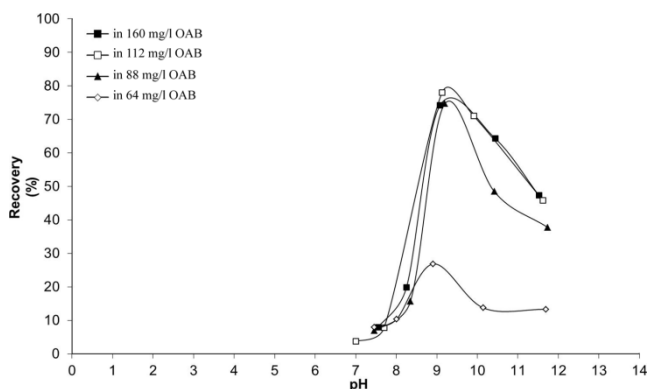Fig. 3. Flotation recovery of orthoclase with sulfonate as a function of pH

Fig. 4. Flotation recovery of orthoclase with OAB collector as a function of pH

Electrokinetic potential measurement tests

The zeta potential values of orthoclase in distilled water and in the presence of collectors at different pH values are presented in Figures 5-7. According to the results obtained in distilled water, the isoelectric point (iep) can be found by extrapolating the curve below pH 1.5 with no significant pH value. The results obtained in distilled water are similar to those of the experimental results obtained by Vidyadhar and Rao (2007).

The efficiency and effectiveness of surfactant adsorption on the mineral surfaces are strongly influenced by some factors such as the nature of the structural groups on mineral surface, homogeneity of mineral, molecular structure, chain length of

surfactant and pH. In addition to these factors, the interaction of surfactants with the mineral surfaces is strongly associated with their chemistry in solution (Parfitt and Rochester, 1983; Somasundaran, 2006). The surfactants in solution have different forms having also a variant of activities. Dodecylamine for example dominates as positively charged amine species, ionic (RNH_3^+), dimer ($(RNH_3)_2^{2+}$) in acidic pH range. The concentration of ion-molecular complexes ($RNH_2 \cdot RNH_3^+$) increases with increasing pH and the neutral molecules (RNH_2) precipitate at highly alkaline pH values. On the other hand alkyl sulfonates (R^-) are strong electrolytes. They exist and dominate in the ionized form in the entire pH range. Oleic acid/oleate is pH sensitive. It dissociates forming ions ($RCOO^-$) at high pH values, neutral molecules ($RCOOH$) at low pH values, ion-molecule complexes ($(RCOO)_2H^-$) in the intermediate pH region and dimer ($RCOO_2^{2-}$) in premicellar solutions (Somasundaran and Wang, 2006).

Orthoclase will have unsaturated active points caused by a large amount of broken Si-O and Al-O bonds when mineral crystals are crushed forcedly (by crushing and grinding). When mineral particles are brought into contact with aqueous solutions, ions on the mineral surfaces chemically bond to water molecules as a consequence of surface complexation. By either protonation or deprotonation, the hydroxyl groups of surface sites form charged surface species depending on pH values of the medium (Churchill et al., 2004). Ionization of hydroxylated surface groups on orthoclase is pH dependent. The surface charge of orthoclase becomes more negative towards the more alkaline region with an increasing number of both $\sim SiO^-$ and/or $\sim AlO^-$ ionized groups (Kumar and Raju, 2002).

In the presence of amine, the results presented in Fig. 5 show that the zeta potential plots of orthoclase follow almost the same pattern for all amine concentrations tested. The maximum zeta potential values are obtained between acidic and moderately alkaline pHs. At this pH range the ionic and ion-molecular complex species become dominant in the solution (Somasundaran and Wang, 2006). Orthoclase has positive zeta potential values up to pH 11.0. The major factor which causes the positive zeta potential value below pH 11 is by the Coulombic interaction, the interaction of the negatively charged orthoclase surface with the positively charged amine species. In addition to this, as reported before, the interaction is also by the hydrogen bonding formed between alkylamine group (RNH_2) and surface hydroxyl group of orthoclase. The hydrogen-bonding formation of amine can be given by the following reaction for silanol group on the surface as an example (Vidyadhar et al., 2002)

$$\sim SiOH + H_2N\text{-}R \leftrightarrow \sim SiO^- + H_3^+N\text{-}R. \tag{1}$$
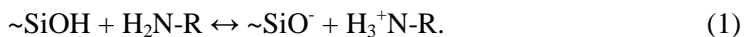
Considering the microflotation response of orthoclase under alkaline conditions, it is worth to mention that the flotation recovery values at alkaline pH range decrease with both/either decreasing concentration of charged amine species and/or increasing concentration of amine precipitate (Somasundaran and Wang, 2006).
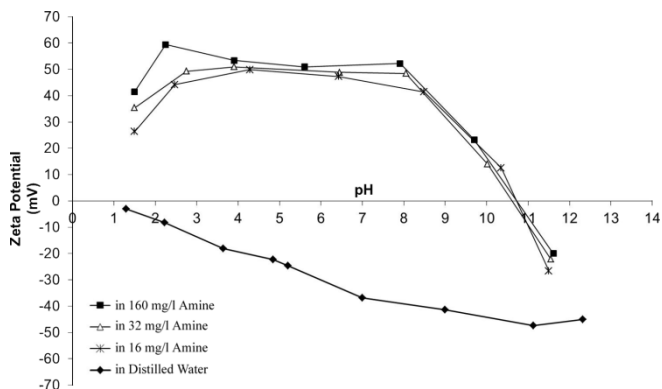
Fig. 5. Zeta potential values of orthoclase with amine as a function of pH

The effects of anionic sulfonate and OAB collectors on the zeta potential values of orthoclase are presented in Figure 6 and Figure 7 respectively. It is well-known that sulfonates exist in predominantly in anionic forms such as R^-, R_2H^-, R_2^{2-} in entire pH range of flotation (Somasundaran and Wang, 2006). Even so, orthoclase displays more negative zeta potentials with sulfonate and the magnitude of zeta potentials increases with increasing concentration (Figure 6). This could be mostly by the interaction of possible pH based adsorption sites formed on the orthoclase surfaces with sulfonate, which leads limited flotation recoveries. In addition, the low flotation recovery, even with higher sulfonate concentration, may come from the interaction of the ionic dimer (R_2^{2-}) form of sulfonate with the orthoclase surface. By this way, the low flotation response occurs as the orthoclase surface is not sufficiently hydrophobic.
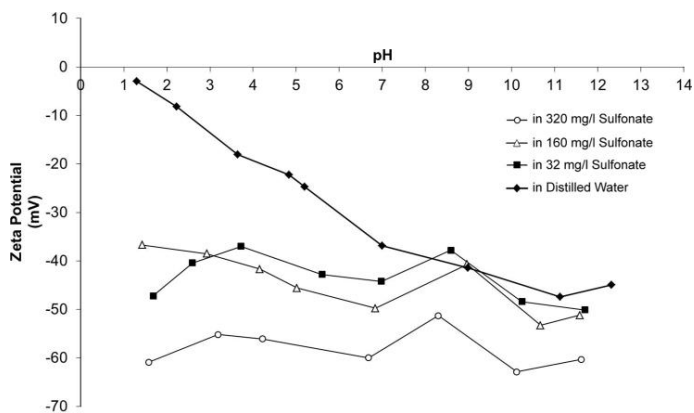

Fig. 6. Zeta potential values of orthoclase with sulfonate as a function of pH

The zeta potential values of orthoclase in the presence of OAB collector become more negative with increasing the collector concentration (Figure 7). The effect of OAB on the zeta potential values of orthoclase is low below neutral conditions due to

the limitation in solubility. Above the neutral conditions, especially at moderately alkaline pHs, orthoclase displays more negative zeta potentials. As reported in the literature, the most active oleate solutions that can be expected are the conditions where acid soap (ion-molecule) complexes are present in the maximum amounts (Ananthapadmanabhan and Somasundaran, 1988; Somasundaran and Wang, 2006). They possess higher surface activity and provide higher flotation recovery for many minerals compared to their corresponding ionic complexes (Kumar and Raju, 2002). Similarly in this study, the maximum orthoclase recoveries were obtained at moderately alkaline pHs. The results are similar to those of obtained by Polkin and Najfonow (1964), Ananthapadmanabhan and Somasundaran (1979) and Somasundaran and Wang (2006), for a number of minerals.
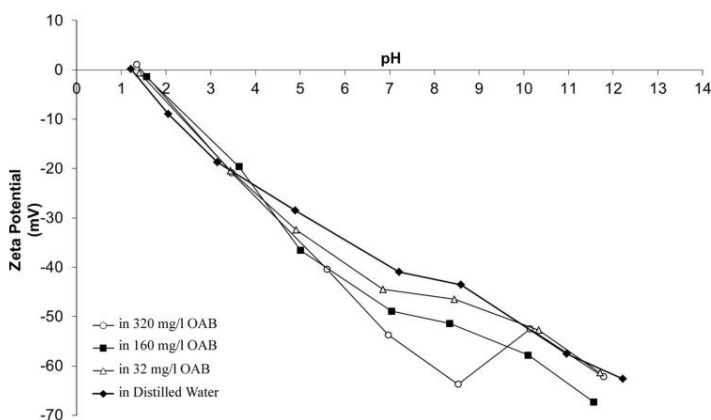

Fig. 7. Zeta potential values of orthoclase with oab collector as a function of pH

To explain the effect of the OAB collector species on the flotation recovery response of orthoclase at moderately alkaline region, two mechanisms can be suggested: either oxygens of carboxylate (O=C-O-) group or neutral molecules of OAB collector are hydrogen bonded to surface hydroxyl groups (~AlOH) of orthoclase. The protons of OAB collector are expected to polarize easily toward the surface hydroxyl groups and form water molecule by neutralizing the surface –OH groups (~AlOH) of orthoclase (chemical bonding). Thus, the hydrophobicity can be facilitated by the adsorption of either ionic or neutral species of OAB collector on the surface hydroxyl group of orthoclase and co-adsorption of OAB collector species due to the hydrophobic attraction or the combination of two mechanisms.

AFM studies

The interaction of different ionic collectors with orthoclase was followed by analysing the micro topography of orthoclase surfaces using AFM. The analyses were conducted on both original and collector-treated (CT) orthoclase samples in order to make comparison. The term CT is used for the orthoclase samples which were rinsed with

distilled water after conditioning with the collectors. For the analysis, the appropriate collector concentration and pH were determined considering the values where high flotation recoveries were obtained. that is 16 mg/dm^3 of amine at pH 6.0, 64 mg/dm^3 of sulfonate at pH 5.0 and 88 mg/dm^3 of OAB collector at pH 9.5.

In the contact mode AFM imaging, the force of tip can easily remove collector species adsorbed on the substrate. Besides, the collector species are less stable under collector solution (Paria and Khilar, 2004). In order to eliminate the difficulties of AFM imaging in contact mode use, the tapping mode imaging was developed. In the tapping mode AFM imaging, the tip of cantilever contacts the surface for a very short time allowing the visualization of the adsorption process on the surfaces without modifying the surface (Binnig et al., 1986). Thus, the AFM images in this study were recorded by the tapping mode in air at ambient temperature. The tapping mode AFM 3D (three dimensional) micro topographies of orthoclase (O) (Figure 8) and CT samples are given in 100x100 nm and 1 x1 μm scanning size ranges in Figures 8-11.

The resulting values of the roughness analyses are given in Table 1. According to the results, the roughness values, average height values of the collector-treated orthoclase (CTO) samples increase both for 100 nm and 1 μm scanning size ranges when compared to those of original orthoclase. In order to describe the adsorption characteristics of each collector on orthoclase surface, it is worth to mention that the length of hexadecyleamine, petroleum sulfonate and oleate is theoretically calculated as 2.12 nm, 1.75 nm and 2.60 nm respectively (O'Dwyer et al., 2006; Wang et al., 2001 and Chennakesavulu et al., 2009). When these values are taken into account, the maximum peak and average height value differences between original orthoclase and CTO samples coincide with mono and bi-layer collector adsorption on the orthoclase. It is clearly seen from the micro topographical images in Figs. 9, 10 and 11 that all collectors adsorb on orthoclase forming patches with different intensities. Amine, for example, forms quite flat patches spreading on the orthoclase surface. The complete spreading of the collector adsorbed on the orthoclase surface is due to the affinity of the collector species with the orthoclase surfaces. Adsorption of the collector species on the surface is very flat and contributes to more interaction sites and in compact form which attributes an aggregation of the collector species at the surface of orthoclase by lateral interaction of the hydrocarbon chains, leading the high flotation recovery. In the case of sulfonate, the height values of the collector-coated patches are much higher. This suggests that the chain-chain interaction of sulfonate species with each other is disoriented, far apart from each other, leading no or low flotation recovery. On the other hand, in the presence of OAB collector, many small patches with lower height values appear which indicates that OAB collector adsorbs on the orthoclase surface with a quite high density. The OAB collector-coated patches formed on the orthoclase surface also indicates that the hydrocarbon chains of the collectors form bonding with each other before the orthoclase surface is completely covered with the collector monolayer.

Table 1. The roughness analysis results of the collector-treated orthoclase

Scanned area	Roughness analysis	Orthoclase	Amine-treated orthoclase	Sulfonate-treated orthoclase	OAB-treated orthoclase
100 nm x 100 nm	Roughness (nm)	0.2001	0.5131	0.2687	0.4264
	Average height (nm)	0.8434	1.6793	1.0676	1.2551
1 µm x 1 µm	Roughness (nm)	0.8953	1.4677	2.1019	1.1422
	Average height (nm)	3.2007	4.3441	10.2350	3.7867
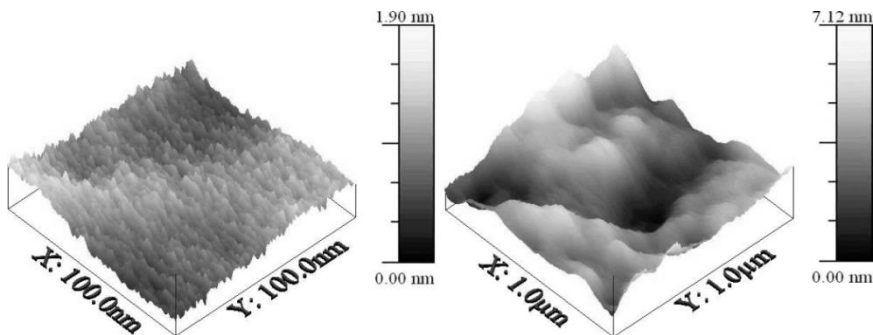
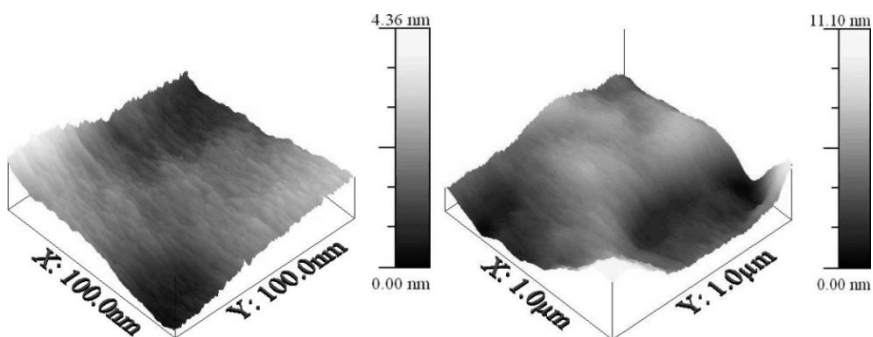Fig. 8. 3D micro topographies of orthoclase (natural pH)

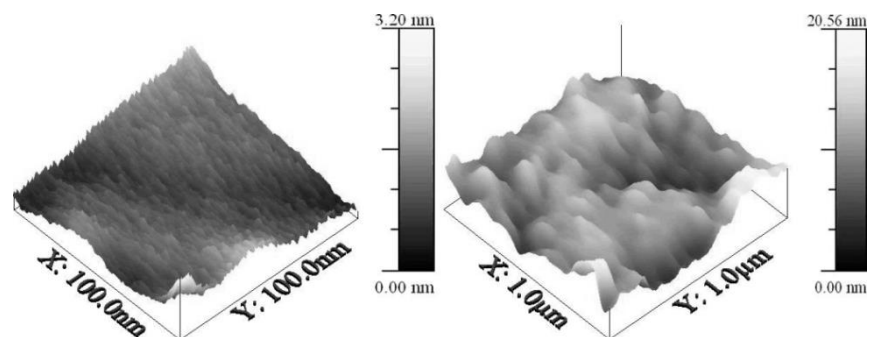Fig. 9. 3D micro topographies of amine-treated orthoclase (pH = 6)

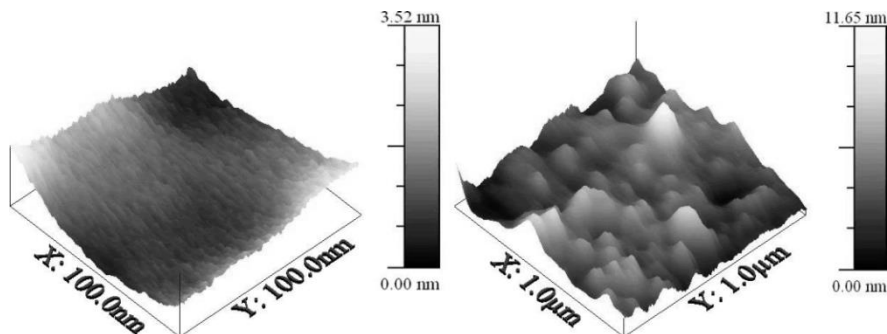Fig. 10. 3D micro topographies of sulfonate-treated orthoclase (pH = 5)

Fig. 11. 3D micro-topographies of OAB-treated orthoclase (pH = 9.5)

Concerning that AFM imaging is a useful tool to determine collector adsorption on the mineral surfaces (Chennakesavulu et al., 2009; Paiva et al., 2011), the roughness analyses results of the orthoclase samples in the absence/presence of three different ionic collectors are discussed. It should be underlined that although the orthoclase used in the analyses is freshly cleaved with excellent cleavage and no visible inclusions, AFM imaging can reveal the imperfect sites, tips and mounds on the flat mineral cleavage surfaces which can be the effects of mineral weathering, crystal defects and domain boundaries resulting in internal dissolution. Analysing the micro topography of atomically flat mineral surfaces can also reveal mounds which are ultrafine particles held to the mineral surface electrostatically.

FTIR studies

The FTIR spectra of the orthoclase, each collector and CT orthoclase samples are compared with each other to determine the existence of possible additional bands qualitatively due to the interaction of the collectors with the orthoclase surface. As reported by Hendrik et al. (2003) and Moon and Fuerstenau (2003), acetone is a solvent to be used to determine the strength of the interaction layer of adsorbate on various types of adsorbents. If the adsorbate is not removed by acetone rinsing, it is assumed that the interaction is strong. Thus, determination of the interaction strengths of each collector with the orthoclase surface was also aimed by conducting the FTIR analysis after rinsing the collector-treated orthoclase (CTO) samples with acetone.

For the analysis, the appropriate collector concentration and pH for conditioning of orthoclase were determined considering the same criteria as given in AFM studies. Although the samples were analysed in collector based on four major zones between 4000-400 cm^{-1}, the major zones, except for the wavelengths between 3250-2750 cm^{-1} for amine-treated orthoclase, 3750-2750 cm^{-1} for sulfonate-treated orthoclase and 3500-2750 cm^{-1} for OAB-treated orthoclase do not display any additional bands indicating the collector-orthoclase interaction. Thus, in this part of the study, the FTIR spectra of CTOs are given according to the pre-determined major zones.

The FTIR spectra of orthoclase and each collector sample are given as the reference spectra in Figs. 12-14 for amine, sulfonate and OAB type collectors, respectively. According to the results, orthoclase has vibration peaks only in the finger print region below 1500 cm^{-1}. The reference spectra of the collectors over the finger print region are as follows: amine displays N-H stretching vibration peak at 3269 cm^{-1}, C-H stretching vibration peaks of alkyl chains at 2957 cm^{-1}, 2922 cm^{-1}, 2853 cm^{-1} and N-H bending vibration peaks at 2183 cm^{-1}, 1639 cm^{-1}, 1570 cm^{-1} and 1513 cm^{-1}, the reference spectra of sulfonate display a broad OH stretching vibration peak at 3456 cm^{-1}, OH bending vibration peaks at 1632 cm^{-1} and 1605 cm^{-1} and C-H stretching vibration peaks of alkyl chains at 2957 cm^{-1}, 2922 cm^{-1}, 2853 cm^{-1} and the reference spectra of OAB collector display a weak OH stretching vibration peak at 3009 cm^{-1}, CH_2 stretching vibration peaks of alkyl chains at 2961 cm^{-1}, 2926 cm^{-1} and 2854 cm^{-1} and a H-OH bending vibration peak at 1711 cm^{-1}.

The FTIR spectra of amine-treated orthoclase (Figure 12) have three additional bands compared to the spectra of orthoclase. The characteristic additional alkyl chain bands result from the asymmetrical stretching vibrations of CH_2 group at 2957 cm^{-1} and 2922 cm^{-1} and symmetrical stretching vibration of CH_2 group at 2853 cm^{-1} (Suarez et al., 1998; Kumar et al., 2002; Kuznetsov et al., 2003; Labidi and Iddou, 2007). Since orthoclase has the negative zeta potential at pH 6 and amine dominates as positively charged species, RNH_3^+, $(RNH_3)_2^{2+}$, the positively charged amine species adsorb on the orthoclase surface through the electrostatic interactions leading to high flotation recovery. In addition to the electrostatic interactions formed between the amine species and the orthoclase surface, the alkylamine group may also form the hydrogen bond with the surface hydroxyl group of orthoclase (Vidyadhar et al., 2002) (see reaction I).
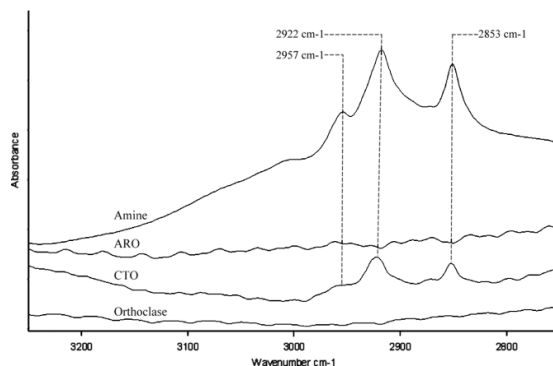

Fig. 12. FTIR spectra of orthoclase with amine (pH = 6)

In Figure 13, the FTIR spectra of sulfonate-treated orthoclase show three additional weak bands of asymmetrical and symmetrical stretching vibrations of CH_2 group at 2951 cm^{-1}, 2924 cm^{-1} and 2854 cm^{-1} compared to those of orthoclase. Since orthoclase has the negative zeta potentials and sulfonates are negatively charged at pH 5, the

electrostatic repulsion can be expected instead of the electrostatic attraction. Even so, the zeta potential measurement results show that orthoclase has more negative zeta potentials when sulfonate concentration increases. Adsorption of negatively charged sulfonate species on the orthoclase surface having negative zeta potentials could be at least partly by the chemical interaction (Andersen et al., 1991) and/or by the precipitation of sulfonate species with the cationic aluminum species, $\sim AlOH_2^+$, on the orthoclase surfaces (Siracusa and Somasundaran, 1987). However, the flotation recovery of orthoclase with sulfonate is negligible at any pH and collector concentration. This can be explained as follows: the collector species interact with each other in a disoriented manner before the orthoclase surface is covered with monolayer adsorption, or basically dimer (R_2^{2-}) species adsorbs on orthoclase leading insufficient hydrophobic surfaces.

In the case of OAB collector-treated orthoclase, the similar additional bands with the peaks at 2961 cm^{-1} and 2926 cm^{-1} were identified when compared to the FTIR spectra of original orthoclase sample (Figure 14). The affinity of orthoclase having the negative zeta potentials with the negatively charged collector species of OAB collector at moderately alkaline pHs can be explained through the non-electrostatic interactions such as hydrogen bonding and/or hydrophobic attraction (see electrokinetic potential measurement test section).

The FTIR spectra of each acetone-rinsed orthoclase (ARO) samples (represented as grey solid line in each figure) show that the existence of additional bands representing the interaction of each collector with the orthoclase surface were altered by rinsing the CTO samples with acetone. The characteristic chain bands representing the asymmetrical and symmetrical stretching vibration of CH_2 disappeared indicating the interaction of each collector with orthoclase was weak. In order to identify the effect of acetone rinsing on the interaction of the collectors with the orthoclase surface and support the FTIR analysis results of ARO samples, the electrokinetic potential measurements and microflotation tests were conducted separately on the each ARO samples. According to the results, ARO samples gave no flotation recovery and displayed similar zeta potential values compared to those in distilled water.
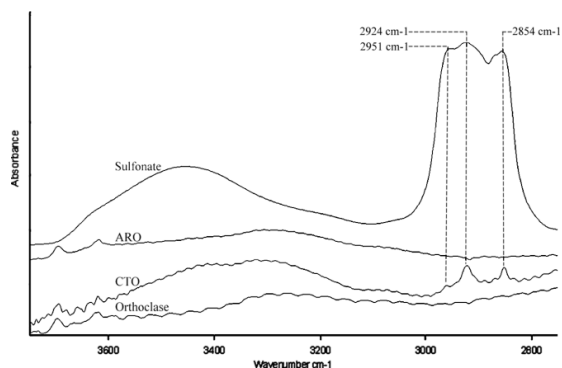

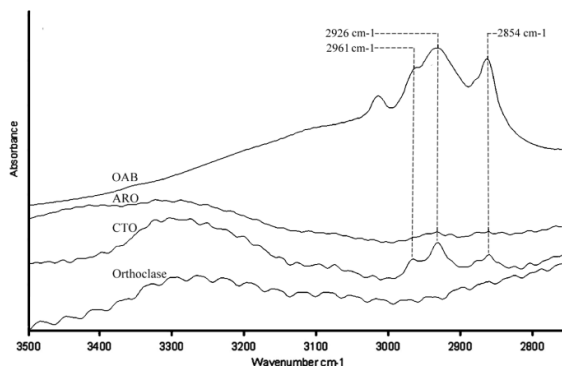Fig. 13. FTIR spectra of orthoclase with sulfonate (pH = 5)

Figure 14. FTIR spectra of orthoclase with OAB collector (pH = 9.5)

Conclusions

The isoelectric point (pH_{iep}) of orthoclase was found to be below pH 1.5 in distilled water, increased to highly alkaline pH values, at pH 11.0, with amine and no obvious pH_{iep} could be observed with petroleum sulfonate and OAB collector.

As both amine species and zeta potentials of orthoclase were oppositely charged above the orthoclase pH_{iep}, the interaction leading over 90% flotation recovery was mostly because of the electrostatic forces as well as hydrogen bonding of alkylamine group with surface hydroxyl groups of orthoclase. On the other hand, adsorption of similarly charged sulfonate species on the orthoclase surface with the negative zeta potentials under moderately acidic conditions could be at least partly by the chemical interaction and/or by precipitation of sulfonate species with the cationic aluminum species, ~$AlOH_2^+$, of orthoclase leading negligible amount of flotation recoveries. The other reason which caused more negative zeta potentials could be particle size differences used in microflotation and electrokinetic potential measurements. In the case of OAB collector, the interaction under moderately alkaline conditions could be explained by non-electrostatic interactions such as hydrogen bonding and/or hydrophobic attraction; between the cationic aluminum species, ~$AlOH_2^+$, of orthoclase and the oxygens of carboxylate (O=C-O-) group of OAB collector and/or hydrophobic attraction. Considering the fact that OAB type collectors are used for mica and Fe-Ti bearing minerals from feldspars, a certain percent of orthoclase could be taken as a froth product, lost, during beneficiation.

In the case of AFM imaging and roughness of orthoclase and CTO samples, the results confirmed that all collectors adsorbed on orthoclase forming patches with different intensities. The amine species at pH 6.0 spread on orthoclase forming more quite flat surfaces. In the case of sulfonate at pH 5.0, sulfonate adsorbed on orthoclase forming patches with higher height values which were mostly by the disoriented chain-chain interaction of sulfonate species before the surface of orthoclase covered with monolayer adsorption. In the presence of OAB collector at pH 9.5, many small

patches with lower height values appeared which indicated that OAB collector adsorbed on orthoclase with a quite high density.

FTIR test results showed that each CTO sample displayed the similar additional FTIR bands which represent the asymmetrical and symmetrical stretching vibrations of CH_2 group, even though each collector yielded different flotation recovery results for orthoclase with the same collector concentration. However, these qualitatively determined additional bands were altered by rinsing the CTO samples with acetone. These results were confirmed by the electrokinetic potential measurements and microflotation tests conducted for acetone-rinsed CTO samples.

Acknowledgements

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