Minerals Engineering 129 (2018) 41–46

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Understanding the flotation separation of Na and K feldspars in the presence of KCl through ion exchange and ion adsorption

Ilhan Gulgonul[a,*], Mehmet S. Çelik[b]

[a] Balikesir University, Mining Department, Balikesir, Turkey
[b] Istanbul Technical University, Mineral Processing Engineering Department, Maslak, Istanbul, Turkey

ARTICLE INFO

Keywords:
Feldspar
Albite
Microcline
Flotation
Potassium ion adsorption

ABSTRACT

Flotation is the only technique that enables the selective separation of Na and K feldspar minerals from each other. In this study, the flotation separation of Na-feldspar (albite) and K-feldspar (microcline) minerals were investigated in the presence of K^+ ion as counter ion. In order to identify the role of K^+ ions on the selective separation of feldspar minerals, solubility, adsorption, and desorption of K^+ ions from microcline and albite surfaces were independently measured using ion selective electrodes. Adsorption isotherms in feldspars/K ion system were constructed, and the regions representing the ion exchange and ion adsorption delineated. Furthermore, the effect of K^+ ions on selective separation of Na and K feldspars was confirmed through zeta potential, solubility, and micro-flotation studies along with adsorption/desorption studies. Our results revealed that K^+ ions depressed albite, though the K^+ ion acted as counter ion in this system, causing the flotation recovery of albite to sharply decrease compared to that of microcline. The mechanism of selective separation of albite and microcline in the presence of Na^+ and K^+ ions along with the implications of ion exchange/ion adsorption phenomenon to industrial operations is elaborated in the light of experimental and theoretical data.

1. Introduction

Feldspars are the most abundant mineral groups on earth. Granite, syenite, pegmatite, and aplits rocks contain considerable amounts of feldspar minerals, Na-feldspar (albite) and K-feldspar (orthoclase/microcline). Albite, orthoclase, and microcline have similar chemical structure and physicochemical properties which makes them difficult to individually separate. Approximately 90–95% of the feldspar production is utilized in the manufacture of glass or ceramics industries. While Na-feldspar is used in glass industry, K-feldspar is utilized in ceramics industry. In addition, feldspars are used industrially as raw materials for the production of dyes, plastics, and welding electrodes.

The quality of feldspar is typically judged on its Na/K ratio and the coloring impurities such as Fe and Ti. Typically K-feldspar concentrates must contain a minimum of 8% of K_2O and a maximum 4% of Na_2O to meet the requirements of the ceramics industry. As deposits containing high quality Na-feldspar or K-feldspar are becoming depleted, it is essential to understand how to selectively recover these minerals from mixed deposits.

Flotation method is used to selectively separate K-Feldspar from Na-Feldspar. A commercial interest goes back to sixties where three patents were issued (Yanis, 1968; Klyachin et al., 1969; Katayanagi, 1974). Filippov (2011) in a more recent patent claimed high recovery and selectivity from feldspar-derived rock in HF-free environment using a mixture of cationic/non-ionic surfactants. Studies in our laboratories have shed considerable light into the mechanism for this selective separation process (Demir et al., 2003a, 2003b, 2001; Karaguzel et al., 2006; Gulgonul et al., 2012, 2008, 2004). Our approach in summary involved depressing albite and allowing the microcline to float with sodium chloride in the presence of a primary amine either at natural pH or at low pH with hydrofluoric acid. Bulatovic (2015, 2001) determined that NaCl was more selective than KCl in the separation of Na-feldspar from K-feldspar at pH 3.2. However, the mechanism of how a simple salt, NaCl, improved the separation was perplexing and not well understood. In order to identify the mechanism of selective separation, it was necessary to determine how Na^+ and K^+ ions undergo adsorption/ion exchange on albite and microcline surfaces. The literature given below provides some insight into how these ions mainly those of Na, K, Ca, and Ba undergo ion exchange in aqueous solution with those in the feldspar matrix.

Various studies on the solubility of feldspar minerals (Aagard and Helgeson, 1982, Helgeson et al., 1984, Chou and Wollast, 1985) have reported that Na^+, K^+, and Ca^{2+} in the feldspar structure undergo ion exchange with H^+ and H_3O^+ protons in the acidic conditions, and Si-O

---

[*] Corresponding author.
E-mail addresses: gulgonul@balikesir.edu.tr (I. Gulgonul), mcelik@itu.edu.tr (M.S. Çelik).

https://doi.org/10.1016/j.mineng.2018.08.038
Received 8 May 2018; Received in revised form 9 August 2018; Accepted 29 August 2018
0892-6875/

and Al-O bonds on the surface of the feldspar go through hydrolysis. The feldspar solubility is strongly dependent on pH but independent at neutral pH or near-neutral pH (pH = 5.7–7.5), and likely to occur by two distinctly different mechanisms under acidic or basic conditions (Chou and Wollast, 1985; Knauss and Wolery, 1986; Murphy and Helgeson, 1987; Amrchein and Suarez, 1992). Wild et al. (2016) stated that the dissolution rate of labradorite was pH dependent, and the dissolution rate at pH 1.5 remained constant over time. Their studies also showed that the formation of surface layers can affect the dissolution kinetics of labradorite indicating that the dissolution mechanism of feldspar minerals is still not well understood. Crundwell (2014) proposed a dissolution mechanism of silicates based on two steps in acidic solutions: (i) the metal atoms react with water to form solvated cations, and (ii) silicate groups are attacked by H^+ to form hydrated anions.

Others have shown dissolved cations to strongly affect the dissolution kinetics of feldspar and quartz in the solution (Dove and Crear, 1990; Nesbitt et al., 1991; Burch et al., 1993; Stillings and Brantley, 1995). The solubility rate of feldspar generally decreases in the presence of dissolved alkali ions such as Na^+ and K^+. These ions compete with non-active protons at the surface which lowers the solubility rate of albite (Chou and Wollast, 1985), K-feldspar (Stillings and Brantley, 1995), and labrador (Nesbitt et al., 1991). Other cations such as Na^+, K^+, Ca^{2+}, and Al^{3+} are also known to decrease feldspar solubility when added to solutions containing inorganic acid solutions. Demir et al. (2001) also found that depending on the concentration of KCl, the released Na ion concentration from albite exhibited higher levels than that released from microcline.

To understand the uptake mechanism of K^+ ion (Demir et al., 2001), knowledge of adsorption and ion exchange of K ions onto microcline and albite is required. In this study, solubility measurements in the presence of Na and K ions on albite and microcline were carried out using Na and K ion selective electrodes. The concentration of free Na^+ ions released and adsorbed onto feldspars against KCl concentration was measured and the adsorption isotherms were constructed based on the regions of ion exchange and ion adsorption. The contribution of these ions to ion exchange and ion adsorption together with zeta potential and micro-flotation measurements was used to discuss the mechanism of selective separation of K-feldspar from Na-feldspar.

2. Materials and methods

2.1. Materials

The feldspar samples of high purity albite and microcline used for the experiments were obtained from the Aydin-Cine region of Turkey. The albite and microcline samples were in the form of crystals and their bulk chemical analyses were performed using ICP (Inductively Coupled Plasma) and is reported elsewhere (Gulgonul et al., 2012). The samples were crushed by a hammer and ground in an agate mortar −150 µm followed by wet screening to produce a sample 150 × 53 µm in size for the microflotation studies. The fine fraction (−53 µm) was used for the zeta potential, solubility, and adsorption studies. The salt of potassium (KCl) used in this study was obtained from Merck with 99.5% purity. Cationic collectors are well known for their effective use in silicate flotation (Sekulić et al., 2004; Fuerstenau and Pradip, 2005; Filippov et al., 2012). For this purpose, a commercial reagent, Genamin-TAP, manufactured by Clariant was used for the flotation experiments. Genamin-TAP (R-NH-CH2-CH2-CH2-NH2 R = tallow) was in the solid form and prepared at pH 3 as recommended by the manufacturer. The pH of the suspension was adjusted by H_2SO_4 and HF.

2.2. Methods

Solubility measurements of feldspar were carried out at 5% solids concentration. The vials were shaken using an orbital shaker (Edmund Buhler KL-2) at 400 rpm for 1 h both in the absence and presence of salt followed by centrifugation for 10 min. Na ion measurements were made by Orion Ross brand Sodium Glass Electrode (Model 86-11), and K ion measurements were conducted by Orion Plus Potassium Membrane Electrode. The measurements were recorded in potential (mV) through which calibration curves were constructed to interpolate the unknown concentrations. Electrodes were used in conjunction with an Orion Digital pH/mV meter. All experimental studies were carried out at room temperature (23 ± 2 °C).

The adsorption density was calculated by Eq. (1) as:

$$\Gamma = (C_i - C_d) \cdot V/1000\,\mathrm{M} \tag{1}$$

where C_i and C_d represent the initial and residual concentrations in M, V is the volume of the solution in ml, M denotes the amount of solid in g, and Γ the adsorption density in mole/g. The parking area (*P.A.*) or cross sectional area of ions on feldspar surfaces was calculated using Eq. (2):

$$P.\,A. = 10^{20}\, S/\Gamma_{max} \cdot \mathrm{A} \tag{2}$$

P.A. is in units of $Å^2$/ion, S is the surface area in m^2/g, A is the Avogadro number ($6.02 \cdot 10^{23}$), and Γ_{max} is the maximum adsorption density in mole/g. Eq. (2) was then used to determine the degree of coverage of Na or K ions. The specific surface areas of albite and microcline (−53 µm size fraction) were respectively determined as 0.97 and 1.43 m^2/g by BET method using nitrogen gas.

The electrokinetic properties of feldspar minerals were determined by the Zeta meter 3.0 equipped with a microprocessor unit to automatically calculate the electrophoretic mobility of particles, and then convert it to zeta potential. A sample of 0.4 g feldspar mineral in 100 ml of solution (0.4% w/v solids) was conditioned for 10 min. The suspension was kept still for additional 5 min to allow the larger particles to settle down. The aliquot taken from the upper level of the suspension was used to measure the zeta potential of the particles. Typically, ten particles were taken to calculate the average zeta potential of particles.

The microflotation tests were carried out in a 150-ml column cell (25 × 220 mm) with a 15 µm frit and magnetic stirrer. The feldspar sample of 1 g was conditioned in 150 ml of solution containing the desired collector for 10 min, and then floated for 1 min with nitrogen gas at a flowrate of 50 cm^3/min. The float and unfloat fractions were dried and weighed to calculate the percent floated (Hancer and Celik, 1993).

3. Result and discussion

Sodium and potassium feldspars have the same crystal-chemical properties. Small differences are magnified when the surface of feldspar is substituted by mono and multivalent ions. If these ions are counter or common ions at the crystal lattice such as Na^+ and K^+ ions, solubility, pH, and reactions at the solid-liquid interface have a considerable role on the surface charge of feldspars (Demir et al., 2001). To explain the mechanism of selective separation of Na-K feldspars in the presence of K^+ ions, the amount of released Na^+ and K^+ ions from albite and microcline into solution as well as the adsorption of K^+ ions onto albite and microcline needed to be determined.

The solubility measurements in pure water at 5% solid concentration showed that albite yielded 1.68×10^{-4} M Na^+ and 2.88×10^{-6} M K^+; whereas microcline released 2.99×10^{-5} M Na^+ and 1.06×10^{-4} M K^+ (Gulgonul et al., 2012). At these solubility measurements, the amounts of released K^+ ions from microcline (K_2O: 13.24% and Na_2O: 1.23%) were close to those Na^+ ions released from albite (Na_2O: 10.51% and K_2O: 0.17%). On the other hand, the amount of released K^+ ions from albite was very low in quantity, and the amount of released Na^+ ions from microcline was substantially high. This is an important property of microcline which inherently withholds relatively large quantities of Na ions in its crystal structure. This feature constitutes a major property in the selective flotation of feldspar minerals as the surface charge is modified accordingly (Demir et al., 2001).