SELECTIVE SEPARATION OF Na- AND K-FELDSPAR FROM WEATHERED GRANITES BY FLOTATION IN HF MEDIUM

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Granite and granodiorite deposits are widely scattered throughout in Eastern Black Sea region of Turkey. These granitic bodies also contain considerable amounts of quartz, Na-feldspar, K-feldspar, mica and other color-imparting ferruginous impurities. Average chemical composition of these rocks are SiO_2 = 65.00 ±5.60; K_2O = 3.05 ±1.35; Na_2O = 3.50 ±1.47 %. Modally, these rocks contain 21.5 ±5.2 quartz; 19.3 ±4.8 K-feldspar and 48.3 ±10.2 % plagioclase. Although the chemical composition of these run-of-mine granite masses cannot meet the specifications required for the glass and ceramic industry, application of some mineral processing methods may recover quartz, Na-feldspar and K-feldspar as separate products. This study deals with the selective separation of sodium feldspar from potassium feldspar from weathered granite using cationic flotation technique (HF + amine) in the presence of NaCl. The most striking result in this experimental study is the depressive effect of NaCl on Na-feldspar. NaCl addition controls amine adsorption on sodium feldspar through adsorption of Na^+ ions onto mineral surfaces. The use of NaCl in flotation was found to increase the K-feldspar grade in the concentrate. This study clearly demonstrates that an effective separation of sodium feldspar from potassium feldspar from a weathered granite can be achieved by cationic flotation in HF medium using NaCl as a depressant.

INTRODUCTION

Feldspar minerals are major commodities used in the production of glass and ceramics. K-feldspars are predominately orthoclase or microcline, whereas sodium feldspars are mostly albite. K-feldspar is generally used in the manufacture of high-strength electrical porcelain, vitreous china and hard glasses such as borosilicate glass. Na-feldspar is generally used in the manufacture of container glass, and fiber glass as well as pottery, plumbing fixtures, floor and wall tile, semi-vitreous dinnerware, and art ware. Its principal purpose is to lower the melting temperature of the mixture of materials to which it is added [1]. The essence of the role of alumina in glass can be understood by examining the position of the aluminum ion in a simplified two-dimensional diagram of the aluminosilicates glass structure. In glasses, the tetrahedral role for aluminum is much more common because it is generally more difficult to crystallize the rigid, strongly bonded covalent tetrahedral oxygen-based network than it is a loosely bonded, largely ionic octahedral network that can rearrange itself without expending much energy. Because a single positive charge is required to maintain electrical neutrality each time a $(AlO_4)^{5-}$ tetrahedron replaces a $(SiO_4)^{4-}$ tetrahedron, binary Al_2O_3–SiO_2 glasses have a very narrow range of stability [2]. Stable binary glasses can contain only about 7 wt % Al_2O_3. Above this amount, a liquid phase rich in Al_2O_3 results in its separation from a continuous high-silica glass matrix [3].

A major proportion of feldspar rocks such as granites, pegmatites and nepheline syenites embody both Na-feldspar (albite) and K-feldspar (microcline or orthoclase) in the matrix usually in quantities of about 3-5 % Na_2O and K_2O. The ultimate goal for a practical application is to raise one of the values of Na_2O or K_2O above 8 % while keeping the other below 3 %. Despite identical crystal structures and physicochemical properties of Na-and K-feldspars, flotation appears to be a plausible method of separating these minerals. In our past studies, amine flotation together with zeta potential, solubility, surface tension, and adsorption measurements were studied in the presence of mono and multivalent salts in order to understand the mechanism of selective separation between Na-and K-feldspars. However, all these studies were conducted with relatively pure minerals. In this study, sodium and potassium containing actual ores and rocks were tested in HF medium with NaCl. The results taken from pegmatites reveal that at particular salt concentrations of monovalent and multivalent salts, a required selectivity in flotation is achieved [1]. Sodium ions depress Na-feldspar during the flotation of alkali feldspar at natural pH and in HF medium in the presence of an amine type collector, Genamin-TAP [4,5]. The authors have also indicated that some bivalent salts can be used to induce this differential separation [6].

The possibility of recovering mica, feldspar and quartz from granite quarry operations in Missouri, Minnesota and Wisconsin showed that recovery of feldspar and quartz concentrates is possible [7]. The recovery of feldspar and glass sand from South Carolina waste granite fines using HF-amine method showed the possibility of recovering high-grade feldspar and quartz products from South Carolina waste granite fines when the froth flotation was supplemented by magnetic separation [8]. The suitability of weathered granitic rocks for the raw material of feldspar and silica sand indicated that granite is more useful than granodiorite as a raw material, because the former is rich in quartz and potash feldspar. Good results of feldspar flotation was obtained for granite compared to granodiorite. They also explained that a coarser grain is more difficult to float than a finer one, and K-feldspar is easier to float than plagioclase [9].

In this study, cationic flotation has been studied as a function of NaCl concentration in HF medium to obtain individual feldspar minerals, i.e. Na-feldspar and K-feldspar as separate products from weathered granitic rocks.

EXPERIMENTAL

Materials

The granitic sample used in these experiments was obtained from the Rize-İkizdere region of Turkey. The chemical and microscopic analysis of the samples shown in Table 1, coupled with XRD determinations (Figure 1), reveal that the ore contains quartz, albite and orthoclase with minor amounts of hornblend, biotite, apatite, and small quantities of weathered clay minerals. The sample has K_2O and Na_2O contents of 4.19 and 3.83 wt.% respectively.

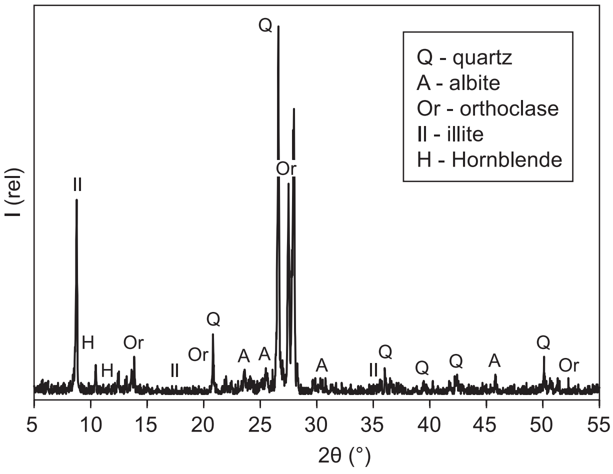

Figure 1. XRD pattern of the investigated granitic sample

The ore sample received from İkizdere Province, Turkey was reduced to -1 mm in size by a combination of jaw, cone and roll crushers. All the samples of the ore were wet ground in a ceramic mill to produce a sample below 250 mm, and then sieved through 325 mesh size. The particles of approximately 37 mm were separated as slimes, which amounted to about 20 % by weight. Particles in the size range of –250 + 37 mm were subjected to Permroll magnetic separator to remove magnetic impurities.

Table 1. Whole-rock composition of the granite sample used.

Item	(wt.%)	Item	ppm
SiO_2	69.85	Ba	1140
Al_2O_3	15.21	Ni	< 20
Fe_2O_3	2.76	Sr	251
MgO	0.75	Zr	137
CaO	2.44	Y	20
Na_2O	3.83	Nb	< 10
K_2O	4.19	Sc	5
TiO_2	0.25		
P_2O_5	0.04		
MnO	0.08		
Cr_2O_3	< 0.001		
LOI	% 0.3		
C/Total	% 0.02		
S/Total	% 0.01		
Total	% 99.98		

Methods

Flotation tests were conducted in a self-aerated Denver machine equipped with a 1.5 liter cell. Initially, 300 g mineral sample was conditioned at the desired pH and salt concentration for 5 minutes followed by 5 minutes of conditioning with Genamine-TAP and then floated for 3 minutes. The pH was adjusted by H_2SO_4 and HF. Pine oil of 20 g/t was used as a frother. The float and unfloat fractions were analyzed for Na_2O and K_2O by an X-Ray flourescence spectrometer (XRF). The electrokinetic measurements were performed by a Zeta Meter 3.0 equipped with a microprocessor unit to directly calculate the zeta potential. A sample of 0.4 g albite and orthoclase in 100 ml of solution was conditioned for 10 minutes. The suspension was kept still for 5 additional minutes to let larger particles settle. All measurements were made at ambient temperature and converted to 22 ±1°C at which flotation tests were performed.

RESULTS AND DISCUSSIONS

Literature results discussed earlier for the selective separation of sodium feldspar from potassium feldspar seems to employ only HF medium. The first mechanism on fluoride activation of feldspar at low pH has been given by Buckenham and Rogers [10]. They proposed that fluoride gives rise to sites of charged aluminum/fluoride complexes at the mineral surface on which cationic collectors adsorbs. Second explanation was given by Smith [11] who investigated the activation of beryl and feldspar with fluoride in cationic collector systems; He proposed that fluoride attacks the surface silicic acid on the mineral resulting from the adsorption of the fluorosilicate ions onto surface aluminum sites, gives rise to negatively charged sites onto which cationic collectors could adsorb. The authors also proposed an alternative mechanism involving the formation of $RNH_3SiF_6^-$ complexes in solution, which then adsorb by replacing the surface hydroxyls.

The formation of negatively charged alumina-fluoride complexes at mineral surfaces is one of the reasons for fluoride activation. Sodium and potassium feldspars possess the same crystal-chemical properties. Subtle differences are respectively amplified by the presence of Na^+ ions in their crystal lattices. The magnitude and sign of the surface potential, which determines the extent of adsorption and in turn flotation, are dependent upon the concentration of Na^+ and K^+ cations (Me^+), and pH of solution have been calculated elsewhere [1]. According to the calculations microcline is only 9 mV more negative than albite. This confirms the identical flotation data obtained in Figures 2 and 3 illustrating changes in the recoveries and grades in the presence of amine (G-TAP) and HF; the cationic collector alone provided no selectivity over a wide concentration range tested.

Figure 4 illustrates the flotation recovery (the percentage of the recovered metal versus the total metal content of the ore) and grade or assay (percent of metal or mineral in the ore) of the weathered granites as a function of added NaCl concentration. Evidently, while the flotation recovery decreases, the K_2O content of the concentrate increases with increasing the added salt concentration. A set of flotation experiments were investigated at constant HF (1 kg/t) and NaCl (15 g/l)

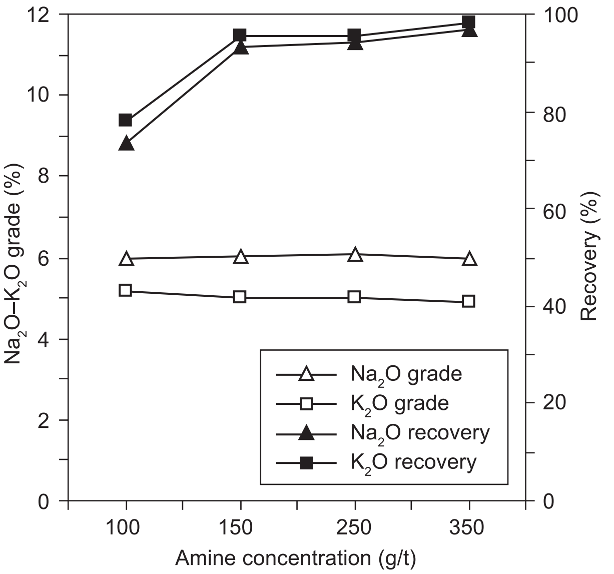

Figure 3. Flotability of weathered granites as a function of amine concentration at constant concentration of 1000g/t HF without salt.

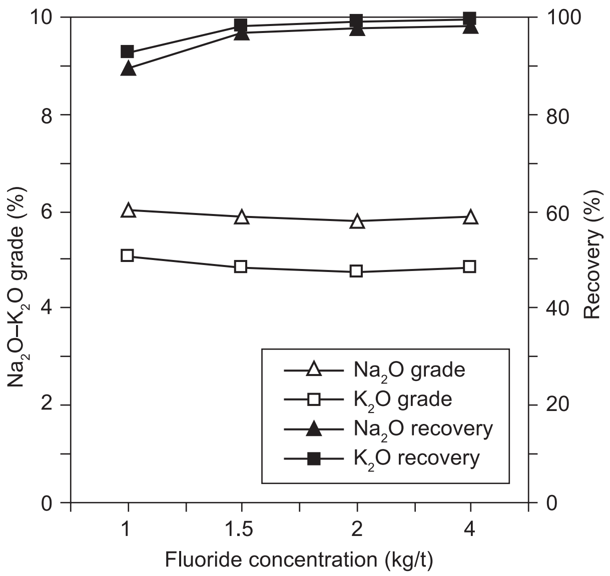

Figure 2. Flotability of weathered granites as a function of fluoride concentration at constant amine concentration of 150 g/t without salt.

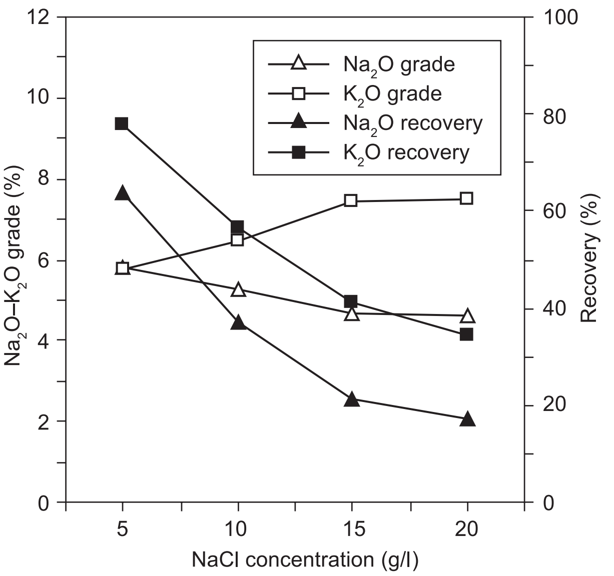

Figure 4. Effect of NaCl concentration on flotation separation of Na-feldspar from K-feldspar at constant amine (100 g/t) and HF (1 kg/t) additions.

concentration to determine the effect of amine on the selective separation of albite from orthoclase, seen in the Figure 5, the most efficient separation with high K_2O % grade is obtained in the range of 50-125 g/t amine concentration.

Preliminary studies have shown that the addition of common ion, i.e. Na^+ ion into albite (Na-feldspar) and K^+ ion into microcline (K-feldspar), reduces the negative charges on feldspar minerals. The reduction in zeta potential values of Na-feldspar/NaCl and K-feldspar/KCl systems is similar to adsorption of common ions in the electrical double layer as potential determining cations [1].

However, in Figure 6, it is shown that increasing the cation concentration of the common ion in solution leads to the displacement of the potential values for albite and microcline to more positive values and hence; this is indeed not favorable for the adsorption of a cationic collector onto feldspar minerals.

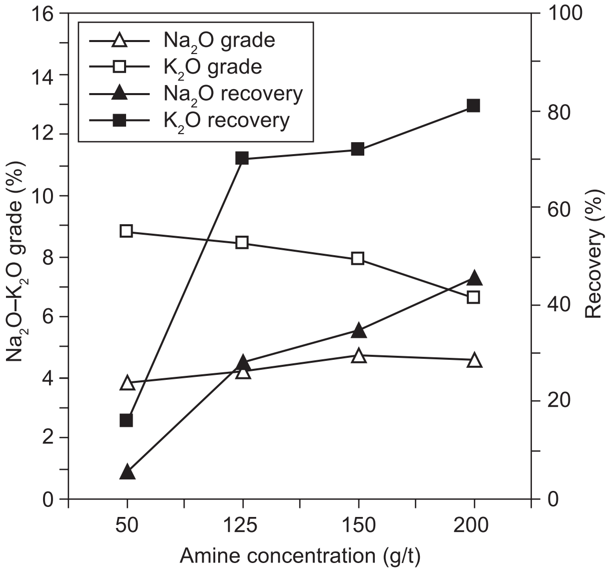

Figure 5. Effect of amine concentration on flotation separation of Na-feldspar from K-feldspar at constant HF (1 kg/t) and NaCl (15 g/l) dosages.

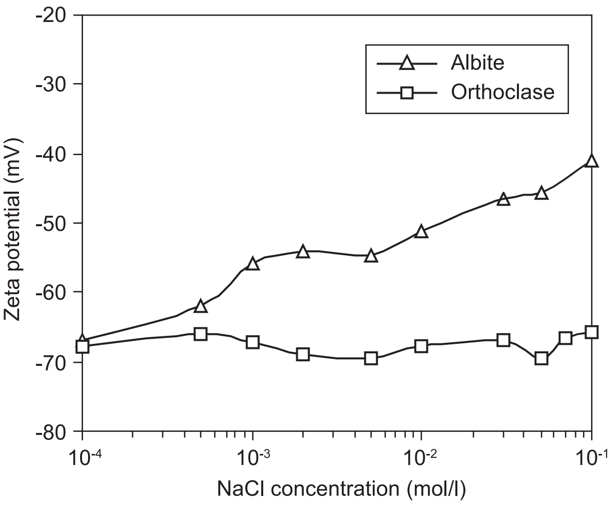

Figure 6. Zeta potential profiles of albite and orthoclase as a function of added salt concentration [1].

Contact angles investigations of albite and orthoclase using thin-layer wicking technique yielded close values in the absence and presence of amine collector. The addition of NaCl on contact angles and surface free energy components at constant amine concentration indicate that albite is significantly affected by salt addition whereas orthoclase remains less affected; such affinity leads to differences in the flotability of respective minerals. This result cannot be attributed to only the structure making ability of Na^+ ions on albite because they mainly adsorb via ion adsorption but also on orthoclase surface which occurs through ion exchange [12].

In general, mica and iron minerals are removed prior to the separation of feldspar from quartz. But in other cases, mica is initially floated in acidic circuit with sulfuric acid using tallow amine acetate together with either fuel oil or kerosene as a collector. This is followed by anionic flotation in acidic circuit where iron minerals and residual mica are removed with petroleum sulfonate. This separation of feldspar from quartz is induced by activating feldspar with hydrofluoric acid (at a dosage of 1-2 kg/ton) and using cationic collector [13].

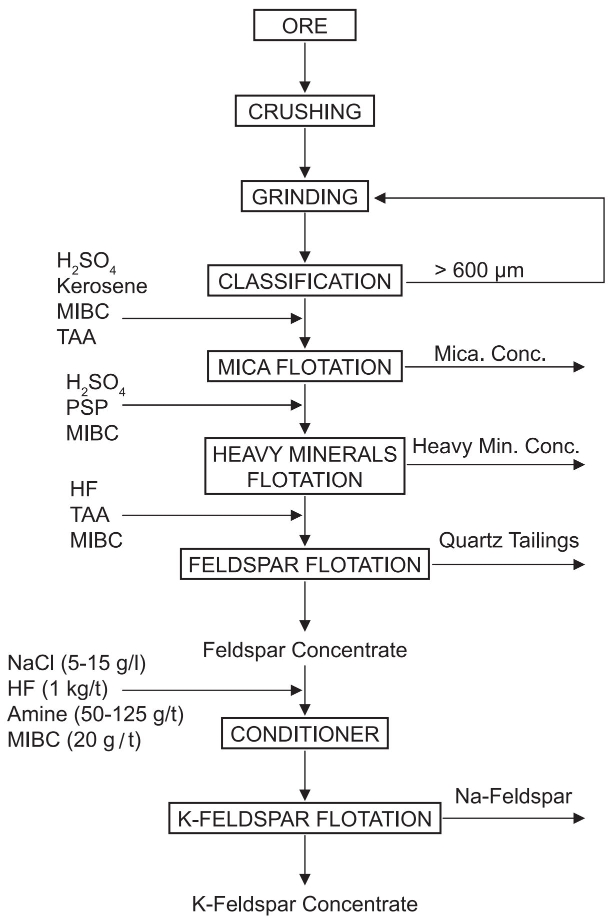

Figure 7. Flotation flowsheet for the continuous processing of weathered granite ore.

The concentrate taken from feldspar flotation circuit is composed of a mixture of albite and orthoclase and can be used in ceramics applications. However, K-feldspar is generally used in the manufacture of high-strength electrical porcelain, vitreous china and hard glasses such as borosilicate glass. Na-feldspar is generally used in the manufacture of container glass, and fiberglass as well as pottery, plumbing fixtures, floor and wall tile, semi-vitreous dinnerware, and art ware. Hence, selective separation of feldspar minerals process must be applied on this concentrate to meet the demand of the industry for high quality albite and orthoclase. Concentration of K-feldspar from a pegmatitic feldspar ore by flotation showed that selective separation is possible in the presence of Na ions in acidic medium using HF [14]. A flotation flowsheet can be proposed for producing individual feldspar concentrates seen in Figure 7.

CONCLUSIONS

Since sodium and potassium feldspars exhibit the same crystal-chemical properties, the selective flotation between Na and K feldspars is insufficient using amine at HF medium. However, the use of a simple salt NaCl enabled the selectivity between the feldspar minerals.

Flotation data indicate that separation of Na- and K-feldspars from weathered granites with 1 kg/t HF and 50-125 g/t amine concentration is possible using NaCl in the range of 5-15 g/l. Under these conditions, the most efficient separation of orthoclase from albite is achieved with assays of 8.43 % K_2O and 4.19 % Na_2O and recoveries of 70.18 % and 28.27 % respectively; this concentrate is suitable for both glass and ceramic industry. Research is in progress to identify the ability of this technique at natural pH or without the use of HF.

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