

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/288393855>

Differential separation of albite from microcline by monovalent salts in HF medium

Article in *Minerals and Metallurgical Processing* · August 2003

DOI: 10.1007/BF03403143

CITATIONS

15

READS

176

4 authors, including:



İlhan Gulgonul

Balikesir University

15 PUBLICATIONS 114 CITATIONS

[SEE PROFILE](#)



İsmail Bentli

Inonu University

33 PUBLICATIONS 148 CITATIONS

[SEE PROFILE](#)



Mehmet S Celik

Istanbul Technical University

249 PUBLICATIONS 4,246 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



German Academic Exchange Service (DAAD) [View project](#)



FineFuture „Innovative technologies and concepts for fine particle flotation: unlocking future fine-grained deposits and Critical Raw Materials resources for the EU”. [View project](#)

Differential separation of albite from microcline by monovalent salts in HF medium

C. Demir

—TITLE—, Karadeniz Technical University, Mining Engineering Department, Trabzon, Turkey

I. Gülgonul

—TITLE—, Balıkesir University, Balıkesir Meslek Yuksek Okulu, Cagis, Balıkesir-Turkey

I. Bentli

—TITLE—, Dumlupınar University, Mining Engineering Dept., Kutahya-Turkey

M.S. Çelik

Mining faculty, Istanbul Technical University, Coal and Minerals Processing Section, Istanbul, Turkey

Abstract

Na-feldspar (albite) and K-feldspar (microcline or orthoclase) are major feldspar minerals with identical crystal structures and physico-chemical properties. Flotation appears to be a unique method of separating these minerals. Fundamental studies on an amine/feldspar system in the presence of monovalent salts have shown that separation of these feldspar minerals by flotation is possible at certain a concentration of monovalent salts at natural pH. In this study, flotation separation in hydrofluoric acid (HF) medium in the presence of salt was found to occur at higher amine concentrations at natural pH. A general mechanism based on differences in the charge of albite and microcline is proposed to be responsible for creating a surface charge on albite and microcline onto which amine adsorbs.

Key words: Albite, Microcline, Feldspar, Flotation, Hydrofluoric acid, Amine

Introduction

Feldspars are used for their alumina and alkali contents in a variety of industries, including glasses, glazes, enamels, tile and porcelain. Albite and microcline are the most important commercial feldspars, but the marketed products usually contain varying proportions of the other members of the system (O'Meara et al., 1939). Granites, pegmatites, nepheline syenites, aplites and feldspathic sands constitute the feldspar reserves of the world. The major impurities in feldspars are mica, quartz and other color-imparting ferruginous impurities. Flotation is the most popular method for removing these impurities in the order of mica, colored impurities and quartz.

A hydrofluoric acid (HF) process has been the most efficient method found for separating feldspar from quartz. Hence, a number of studies have been devoted to this problem, despite the fact that the use of HF suffers from a growing awareness of environmental and health problems. A number of investigators have developed a mixture of cationic and anionic collector formulations in an acidic circuit (pH 2) for the separation of quartz from feldspar in the absence of fluoride ions (Katayanagi, 1974; Shimoizaka et al., 1976; Malghan, 1981). Other investigators using the same reagent scheme, but unexpectedly at natural pH, reported the possibility of separating feldspar from quartz (Tang et al., 1988;

Liu et al., 1993; Ardha and Atangsaputra, 1994; Cheng et al., 1995). Buckenham and Rogers (1954) emphasized that quartz and soda-potash feldspars show practically identical responses to solutions of dodecylamine hydrochloride between pH 4 and 12. Suliin and Smith (1966) made similar tests with concentrated HCl and HF pretreated microcline and showed that HF pretreatment resulted in activation, while HCl pretreatment depressed flotation. Rao and Forsberg (1993) investigated the fundamentals of quartz/feldspar separation by asserting that the success of flotation selectivity mainly depends on the flotation pH at which there is a variation in surface charges of feldspar and quartz, so that the amine cation adsorbs on feldspar but not on quartz.

The majority of feldspar ores, Na-Feldspar (albite, $\text{NaAlSi}_3\text{O}_8$) and K-feldspar (microcline or orthoclase, KAlSi_3O_8), are found in the same matrix, usually in quantities of about 3% to 5% Na_2O and K_2O . The objective is to separate feldspar into pure phases of Na and K, as the latter is more valuable to the industry. The aim for a practical application is often to raise one of the values of Na_2O or K_2O above 8% while keeping the other below 3%.

The separation of individual feldspars using various salts in HF medium, to the authors' knowledge, was carried out by Russian researchers in the late sixties and early seventies, and

Preprint number 02-172, presented at the SME Annual Meeting, Feb. 25-27, 2002, Phoenix, Arizona. Revised manuscript received and accepted for publication April 2003. Discussion of this peer-reviewed and approved paper is invited and must be submitted to SME Publications Dept. prior to Feb. 29, 2004. Copyright 2003, Society for Mining, Metallurgy, and Exploration, Inc.

Table 1 — Complete chemical analysis of the albite and microcline.

Compound	Albite, %	Microcline, %
SiO ₂	66.02	65.30
Al ₂ O ₃	19.92	18.72
Fe ₂ O ₃	0.04	0.05
MgO	0.04	0.01
CaO	1.74	0.24
Na ₂ O	10.68	2.84
K ₂ O	0.42	11.81
TiO ₂	0.04	0.01
P ₂ O ₅	0.49	0.32
Cr ₂ O ₃	0.022	0.024

a very brief review is given by Manser (1975). Yanis (1968) claims that Mg and Ca ions in amine flotation with HF act as depressant for Na-feldspar and thereby concentrate K-feldspar. Starikova (1968) conducted differential flotation of Na-K by fluoride activation in the presence of 15-g/L NaCl and found an increase in the potassium content of the feldspar concentrate. Revnivitzev et al. (1968) reported that, while potassium and ions with similar radii (e.g., Rb, Cs and Ba) depressed the potassium feldspar, Na, Ca, Sr and Mg depressed the sodium and calcium feldspars. Treatment by HF was found to both increase the selectivity and decrease the concentration of required salt depressant. Marius and Laura (1970) tested Voineasa pegmatites containing equal amounts of Na and K feldspars using amine collector. The best results were achieved when Na-feldspar was depressed with NaCl. Demir et al. (2001) showed that sodium ions depress Na-feldspar during the flotation of alkali feldspar at natural pH in the presence of an amine-type collector called Genamin-TAP.

Despite fragments of such literature available on differential flotation of alkali feldspars, the statements are often unsubstantiated and contradictory. The aim of this study is, therefore, to systematically investigate the surface chemical properties of both Na- and K-Feldspars in the presence of monovalent salts and HF. An attempt is made to shed light on the mechanism of selective flotation of feldspar minerals in the presence of HF.

Experimental

Materials. The high-purity albite and microcline samples used in these experiments were obtained from the Cine region of Turkey. The chemical analyses of the samples, Table 1, together with the XRD analysis reveal that the samples consist of albite and microcline with albite impurity. The lump-sized material was crushed using a hammer and ground in an agate mortar. This was followed by wet screening to produce a sample (150 x 53 μm) for microflotation studies. The fine fraction (-53 μm) was further ground to obtain a -38-μm sample for zeta potential, solubility and adsorption measurements. The cationic collector, Genamin-TAP (G-TAP), is a commercial reagent manufactured by Clariant of Germany. The reagent is in the solid form and was prepared at pH 3, as recommended by the manufacturer. The pH was adjusted by HCl and NaOH. Distilled and deionized water was used in all experiments.

Methods. Microflotation tests were carried out in a 150-mL column cell (25 x 220 mm) equipped with a 15-μm frit and a

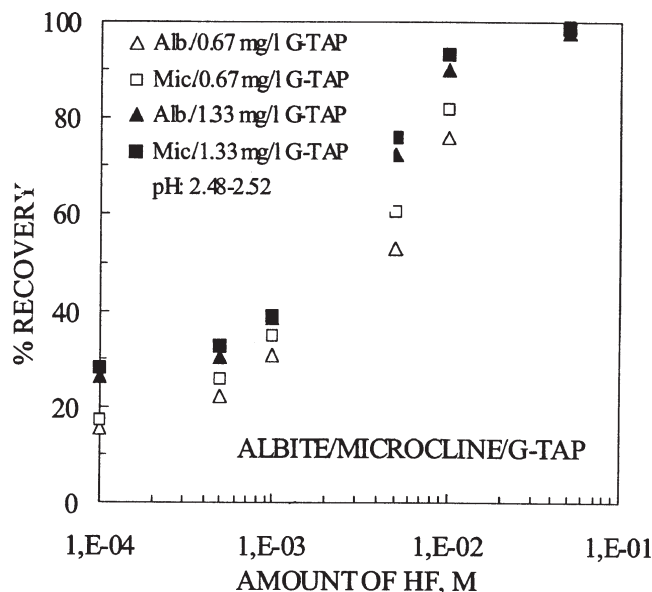


Figure 1 — Floatability of albite and microcline at HF medium.

magnetic stirrer. One-gram samples were conditioned for ten minutes in 150 mL of solution containing the desired collector. The sample was then floated for one minute with nitrogen gas at a flow rate of 50 cm³/min. The float and unfloat fractions were dried and weighed to calculate the percent floated.

Adsorption tests were carried out in 40-mL Teflon-capped glass vials. For each test, a one-gram sample of the feldspar was mixed in 20 mL of surfactant solution at a solid to liquid ratio of 0.05. The vials were shaken for one hour on a shaker and centrifuged for 15 min. The supernatant was analyzed for its amine content using picric acid in the presence of chloroform (Sabah, 1998). The adsorption density was calculated by

$$G = (C_i - C_r)V/1,000S \quad (1)$$

where

C_i and C_r represent the initial and residual surfactant concentrations in mg/L,

V is the volume of the solution in mL,

S denotes the amount of solids in grams and

G is the adsorption density in mg/g.

Results and discussion

Sodium and potassium feldspars show the same crystal-chemical properties. Subtle differences are respectively amplified by the presence of Na⁺ and K⁺ ions in their crystal lattices. The surface-charge characteristics of the feldspar mineral surface mainly depends on the ratio of the cations and dissociated silanol groups as a function of pH. Increasing the pH leads to an increase in the negative centers. Similarly, a decrease in pH results in positively charged centers.

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. Surface potential calculations made by Demir et al. (2001) show that microcline is only 9 mV more negative than albite. This confirms the flotation data obtained in Fig. 1, where both minerals in the presence of an amine (G-TAP) and HF exhibit identical floatability. Similar

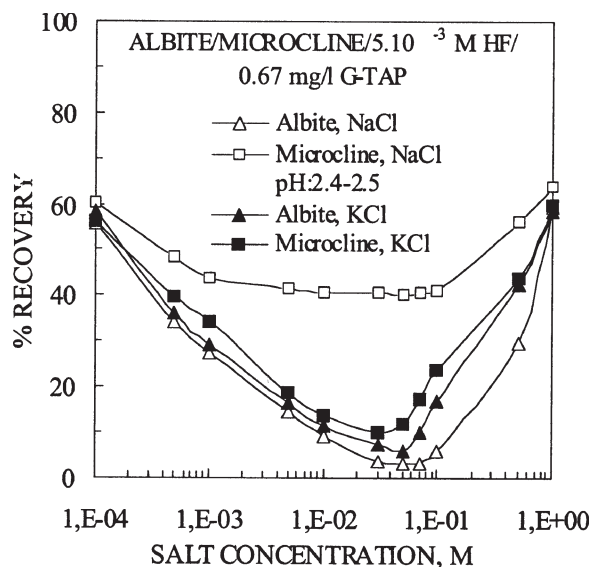


Figure 2a — Floatability of albite and microcline vs. salt concentration with 0.67 mg/L of G-TAP and 5.10^{-3} M HF addition.

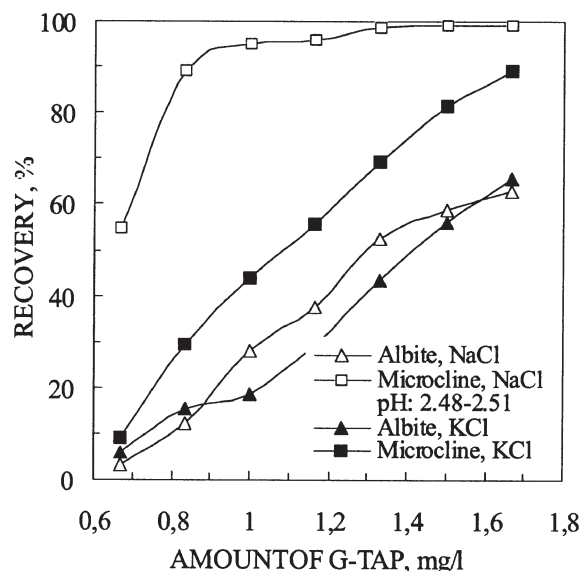


Figure 3a — Floatability of albite and microcline against amine concentration at 5×10^{-2} M of salt and 5×10^{-3} M HF additions.

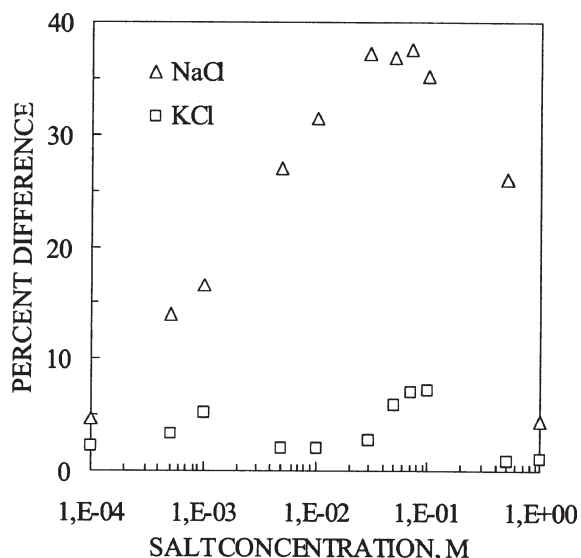


Figure 2b — Percent difference in the floatability of albite and microcline as a function of salt concentration under the conditions of Fig. 2a.

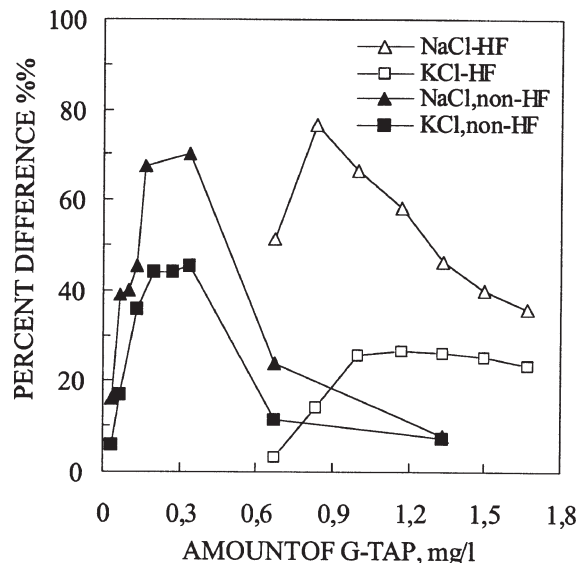


Figure 3b — Percent difference in the floatability of albite and microcline as a function of salt concentration under the conditions of Fig. 3a.

results were previously obtained in the absence of HF and were explained as follows: 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, creates a favorable profile for the adsorption of cationic collector onto different feldspar minerals (Demir et al., 2001).

Figure 2a shows floatability of albite and microcline at constant amine addition of 0.67 mg/L and 5×10^{-3} M HF concentration. Interestingly, albite and microcline systems exhibit a distinct minimum around 5×10^{-2} M salt addition as that of natural pH presented elsewhere (Demir et al., 2001) and provide the widest window of separation. The percent difference (%) against salt concentration given in Fig. 2b further illustrates that the selectivity between albite and mi-

crocline is optimum around 5×10^{-2} M salt addition with better results obtained in the presence of NaCl.

Figures 3a and 3b illustrate the flotation recovery of albite and microcline with constant salt levels of 5×10^{-2} M and 5×10^{-3} M HF but varying G-TAP additions to explore whether the window of selectivity can be improved. Examination of Fig. 3a clearly shows that the flotation profile of microcline, as in Fig. 2a, remains practically the same in the presence of both NaCl and KCl. This vividly exemplifies that the flotation behavior of microcline has not changed much but the floatability of albite has been retarded or depressed in the presence of salt — more significantly with NaCl. The reason for the depression of albite can be ascribed to the inability of albite to undergo an effective ion-exchange process with NaCl and KCl and thereby remain less negatively charged on the sur-

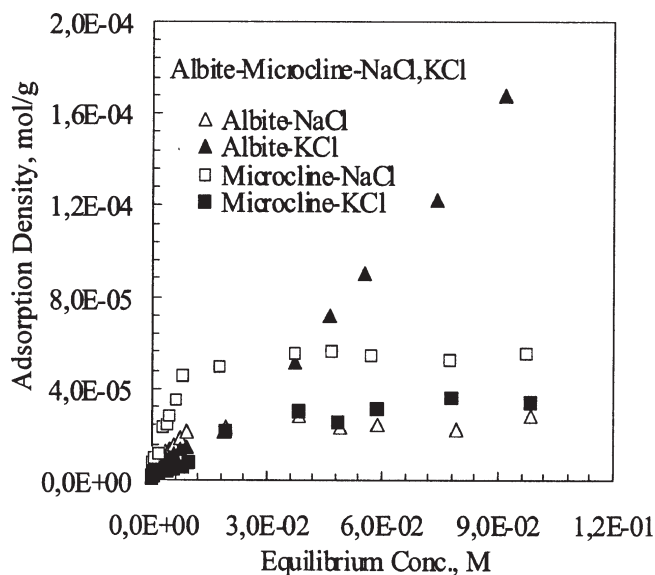


Figure 4 — Adsorption isotherms of albite and microcline in monovalent salts suspensions at natural pH.

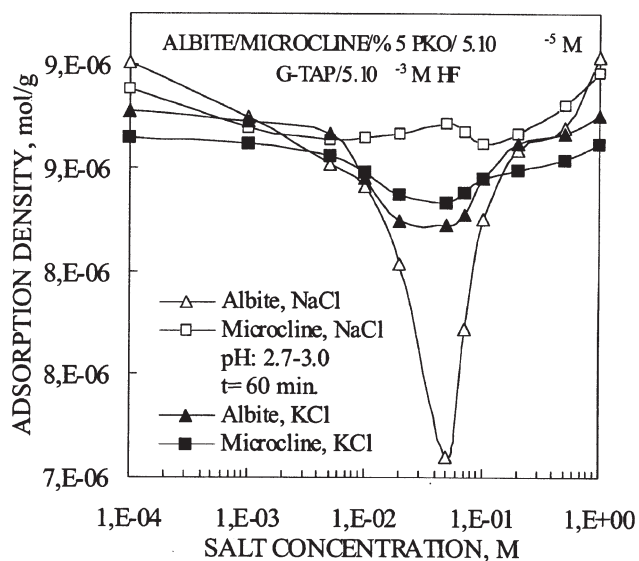


Figure 5 — Adsorption density of amine as a function of added salt concentration in the presence of HF.

face, on which the adsorption of cationic collector is relatively hindered (Demir et al., 2001).

The percent difference (*%e*) between the floatability of albite and that of microcline in the absence and presence of HF, Fig. 3b, shows that at about 0.83 mg/L of G-TAP addition, a maximum difference of about 77% is achieved with NaCl; under the same conditions, KCl imparts a difference of approximately 14%. Under similar conditions, the data in the absence of HF at 0.30-mg/L G-TAP concentration yield an optimum percent difference of about 71% with NaCl and 44% with KCl. Despite the concentration difference of about three times (0.30 vs. 0.83 mg/L), the overall results in HF and non-HF systems show about the same results with NaCl, but KCl salt performs better in the case of natural system. Research is in progress to find out whether these results will translate in the same scale when applied to actual ores.

Results presented in Fig. 3b for HF and non-HF media indicate that the former system requires about three times higher amine levels for the same flotation recovery. This has been well illustrated in a study where flotation of quartz with amine is reported as a function of pH (Takeda and Usui, 1987). It is shown that the required amine concentration for the same flotation recovery increases considerably with decreasing pH. The adsorption and flotation of amine is respectively found to exhibit a minimum and maximum in the vicinity of pH 10, where ion molecular complexes form. In this study, the adsorption of amine in the presence of HF decreases with a decrease in pH in line with the above findings.

A critical finding in this study is whether the salt ions actually adsorb on feldspar minerals. Figure 4 illustrates that, except for the albite/KCl system, the adsorption isotherms reach plateau values at about 10^{-2} M equilibrium salt concentrations, which correspond to the inflection points in the flotation curves. Because ion-selective electrodes were not functional at relevant acidic pH medium, the measurements were conducted at natural pH. These results, although they require further explanation, indicate that both ion exchange and adsorption are taking place at the feldspar interfaces.

The adsorption of amine as a function of salt concentration in HF medium is given in Fig. 5. Interestingly, the adsorption

of amine exhibits a minimum for albite and maximum for microcline at salt concentrations in the region of 1×10^{-2} M to 5×10^{-2} M, which corresponds to the optimum salt concentration and flotation as well. The adsorption of amine on albite decreases considerably in the presence of salt. Such difference in adsorption for both salts is well reflected in the flotation of individual feldspar minerals.

This finding is in line with the zeta-potential measurements, where microcline had more negative charge and, in turn, a higher ability to interact with the cationic surfactant. Similarly, the ion-release measurements determined elsewhere indicated that K ion showed a maximum around 5×10^{-2} M salt concentration for microcline but no appreciable ion release was observed in the case of albite. The addition of salt beyond about 5×10^{-2} M exhibits a rather sharp increase in flotation recoveries for both albite and microcline. This enhancement was basically attributed to pseudo-hydrophobic effect at high salinity (Demir et al., 2001).

The literature results discussed above for the selective Na-K feldspar separation seems to employ only HF medium. The first mechanism on fluoride activation of feldspar at low pH was given by Buckenham and Rogers in 1954. They proposed that fluoride gives rise to sites of charged aluminum/fluoride complexes at the mineral surface on which cationic collectors adsorb. A second explanation was given by Smith (1965), who investigated the activation of beryl and feldspar with fluoride in cationic collector systems. Smith believed that fluoride attacked the surface silicic acid on the mineral resulting from the adsorption of the fluorosilicate ions on surface aluminum sites, giving rise to negatively charged sites that could attract cationic collectors. Smith (1965) also proposed an alternative mechanism involving the formation of RNH_3SiF_6 -complexes in solution, which then adsorb by replacing surface hydroxyls. The formation of negatively charged alumina-fluoride complexes at mineral surfaces is one of the reasons for fluoride activation.

The exclusive use of HF medium in differential flotation of Na-K feldspars in the literature was noted. Whether this is conscientiously done is not known at present due to difficulties in obtaining the full text of these references. Irrespective

of the mechanism of fluoride activation, the use of salt in HF medium appears to induce no significant selectivity when compared to natural pH. Because, fluoride ions seem to equally activate both feldspar minerals.

Conclusions

Selective flotation of Na- and K-feldspars using amine in HF medium in the absence of salt is not possible due to the similarities in their crystal and chemical properties. Microflotation data indicate that it is possible to separate Na-feldspar from K-feldspar using monovalent salts in HF medium at low pH levels. Adsorption measurements together with flotation recoveries in the presence of amine reveal an optimum salt concentration of 5×10^{-2} M. The most efficient separation of microcline from albite in HF medium is obtained in NaCl solutions with a difference of 77% between albite and microcline. A mechanism based on the adsorption of common ions, and ion exchange between the added salt of uncommon ions and those ions in the crystal matrix and the resultant surface modification is proposed to be responsible for the observed selective separation.

Although the use of HF is not encouraged because of environmental concerns, its success must be compared with other acids such as sulfuric acid. The authors' recent results on feldspar ores show that albite-microcline separation is not always induced at natural pH if extensive perthitic texture is present; the performance and limitation of each acid must be ascertained for commercial applications.

References

- Ardha, N., and Atangsaputra, K., 1998, "Tests of new flotation technique for feldspar-quartz separation from feldspatic sand," Mineral Technology Research and Development Center, Bandung, Indonesia.
- Buckenham, M.H., and Rogers, J., 1954, "Flotation of quartz and feldspar by dodecylamine," *Trans. of Inst. of Mining and Metallurgy*, Vol. 64, pp. 11-30.
- Cheng, Z., Lu, W., Tang, J., and Sun, B., 1995, "Study on the separation of silicate minerals from quartz with collector mixture," Ch. 45, *XIX Int. Min. Process. Congr.*, pp. 263-266.
- Demir, C., Abramov, A.A., and Çelik, M.S., 2001, "Flotation separation of Na-feldspar from K-feldspar by monovalent salts," *Minerals Engineering*, Vol. 14, pp. 733-740.
- Katayanagi, T., 1974, "Flotation separation of feldspar," U.S. Pat. No. 3,844,939.
- Liu, Y., Gong, H., Qui, J., and Zhang, K., 1993, "A new flotation technique for feldspar-quartz separation," *XVIII Int. Min. Process. Congr.*, Parkville, Australian Inst. Min. Metall., Vol. 4, pp. 857-862.
- Malghan, S.G., 1981, "Effect of process variables in feldspar flotation using non-hydrofluoric acid system," *Mining Engineering*, Nov., pp. 1616-1623.
- Manser, R.M., 1975, *Handbook of Silicate Flotation*, Warren Spring Lab., Stevenage, England.
- Marius, C., and Laura, H., 1970, "Dressing of mica ores and separating potassium feldspars from the sodium ores from pegmatites by flotation," (CA: 74,102590n), *Cercet-Miniere*, Vol. 11, p. 331.
- O'Meara, R.G., Norman, J.E., and Hammond, W.E., 1939, "Froth flotation and agglomerate tabling of feldspars," *41st Annual Meeting, American Ceramic Society*, Chicago, Illinois, Vol. 18, No. 8, pp. 286-292.
- Rao, H.K., and Forssberg, K.S.E., 1993, "Solution chemistry of mixed cationic /anionic collectors and flotation separation of feldspar from quartz," *XVIII International Mineral Proc. Congress*, Sydney, Australia, 23-28 May.
- Revnitzev, V.I., Putrin, A.M., and Archangelskaya, I.N., 1968, "Flotation separation of minerals of the isomorphous group of feldspars," in *Proceedings of 8th International Mineral Processing Congress*, Leningrad, Vol. D-7, pp. 1-8.
- Sabah, E., 1998, "Adsorption Mechanism of Various Amines onto Sepiolite," Ph.D. thesis, Osmangazi University, Eskisehir, Turkey, 245 pp.
- Shimoiizaka, J., Nakatsuka, K. and Katayanagi, T., 1976, "Separation of feldspar from quartz by a new flotation process," in *World Mining and Metals Technology*, A. Weiss, ed., Port City Press, pp. 428-438.
- Smith, R.W., 1965, "Activation of beryl and feldspars by fluorides in cationic collector systems," *Transactions of Society of Mining Engineers of AIME*, Vol. 232, pp. 196-204.
- Suliin, D.B., and Smith, R.W., 1966, "Hallimond tube investigations of fluoride activation of beryl and feldspar in cationic collector system," *Trans. Instn. Min. Metall.*, C.75, pp. 333-336.
- Starikova, L., 1968, "Production of feldspar concentrate with a high $K_2O:Na_2O$ ratio," *Proekt. Inst. Rudodubiv Obogat*, Vol. 7, No. 7, pp. 93-96.
- Takeda, S., and Usui, S., 1987, "Adsorption of dodecylammonium ions on quartz in relation to its flotation, Colloids and Surfaces," Vol. 23, pp. 15-28.
- Tang, J., Mao, J., and Sun, B., 1988, "A new acidless and fluoless flotation method of silica sand," *XVI Int. Min. Process. Congr.*, E. Forssberg, ed., Vol. 10B, pp. 1529-1536.
- Yanis, N.A., 1968, "Froth Flotation Procedure for Separating Potassium Feldspar from Sodium Feldspar, USSR Patent 227,234.