Revisiting flotation mechanisms of the selective separation of alkali feldspars in the presence of NaCl

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Abstract: Selective separation of Na-feldspar ($NaAl_3SiO_8$) from K-feldspar (KAl_3SiO_8) by flotation appears to be the only alternative in commonly found mixed-type ore formations. For this purpose, various mechanisms in various studies have been proposed by which selective separation can be achieved in the presence of salt ions. These mechanisms under different flotation conditions are systematically discussed in this study. Literature review reveals that two adsorption mechanisms are operating in the presence of Na^+ ions and natural pH: Ion exchange and ion adsorption. In mixed feldspar systems, the mineral surface properties change due to ion exchange of counter ions on K-feldspar surface and become suitable for amine adsorption, while Na-feldspar surface is suppressed due to co-ion adsorption leading to limited amine adsorption. Similar mechanisms occur in acidic conditions with fluorine ions which increases the dispersion of particles and provides selectivity for K-feldspar by forming AlSiF-amine complexes. K-feldspar at alkaline pH with NaOH is activated with fluorine ions at the previous flotation stages and then floated with amine releasing K ions into the solution. The ion exchange/ion adsorption mechanism seems effective in alkaline as well as in natural and acidic conditions.

Keywords: feldspar, flotation, sodium chloride, selectivity, mechanism

1. Introduction

Na-feldspar (albite) and K-feldspar (orthoclase or microcline) are different feldspar minerals with similar crystal structures and close chemical and physical properties, mostly found in the same ore matrix. The selective recovery of these minerals from feldspar ore has become a necessity for commercial and technical reasons in the last two decades. Flotation technique is the most appropriate technique for the selective separation of Na-feldspar and K-feldspar. Therefore, studies on selective separation have focused on flotation in the literature.

The first studies on the selective separation of Na and K feldspars are followed by two in Russian (Yanis, 1968; Klaychin, 1969) and one in American patents (Katayanagi, 1974). In the related patents and studies carried out by various researchers in the same years, the separation of Na-K feldspar was typically carried out by cationic flotation in hydrofluoric acid (HF) medium using various salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, etc.) (Kovalenko, 1967; Strakova, 1968; Tröndle, 1968; Revnivtzev et al., 1968; Marius and Laura, 1970; Sheliko, 1972; Yanis and Gorelik 1973; Klünker, 1974). At the end of the 60s and the beginning of the 70s, Manser (1975) believed that there was no need for the Na-K feldspar separation because of rich deposits containing Na and K feldspars. Due to this idea, a limited number of studies on this subject were carried out in the literature until the 2000s. The increase in the demand for K-feldspar in the Turkish porcelain industry in the late 1990s and early 2000s has revealed the necessity of evaluating the mixed type feldspars, which are quite common in Turkey. For this reason, Dr. Çelik and his research group brought up the issue of selective separation of Na and K feldspar from feldspar formations. Thus, the subject abandoned in the 70s was systematically revisited since the beginning of the 2000s (Demir et al., 2000, Gülgönül et al., 2004, Karagüzel et al., 2005).

Demir et al. (2000) used different salts in micro-flotation and Denver flotation studies with pure minerals with a cationic reagent at natural pH and stated that especially NaCl and CaCl$_2$ provided selectivity between feldspar minerals. Gülgönül et al. (2004), on the other hand, investigated the effect of different salts on the selectivity of a large number of pure albite, orthoclase, and microcline samples with fundamental tests (electrokinetic, adsorption, solubility, SEM, ESCA, etc.) along with the micro-flotation experiments. These studies revealed that the impurities formed in the form of spots on pure mineral surfaces due to mineralization could change the flotation behavior of minerals. Additionally, it was stated that monovalent salts were very effective in selective separation, and a mechanism including ion exchange between uncommon ions and adsorption of common ions created differences in the surface charge of albite and microcline (Gülgönül et al., 2004; 2008). On the other hand, Karagüzel et al. (2005) dealt with the subject of both fundamental studies and flotation experiments involving real ore samples. Karagüzel et al. (2005) determined that the free surface energy measured on the surface of orthoclase in the presence of NaCl was higher than that of albite, in their studies where they calculated the surface energies of albite and orthoclase. Karagüzel et al. (2006) showed that concentrates with a K content of >10% could be obtained with a cationic reagent in the presence of HF under acidic conditions, in the step-wise flotation tests performed on a pegmatitic ore sample. The use of sulfuric acid (H$_2$SO$_4$) instead of HF acid to control the pH was found less effective. In addition to these studies, Ociepa (1994) stated that NaCl depressed albite and floated microcline, while KCl was not effective in selective separation. On the other hand, Uhlig (1985), determined that although the flotation behavior of 19 single-mineral feldspar samples with different compositions was the same at acidic pH, they exhibited differences in the collector consumption. Gülsoy et al. (2005) differentially floated orthoclase from albite in NaCl solution (20 kg/Mg) at pH 2.5–3 (controlled with HF acid) using tallow amine acetate (ArmacTD) as a collector. Larsen et al. (2021) stated that K-feldspar could float better than Na-feldspar in alkaline conditions using 2-3.10^{-3} mol/dm^3 NaOH (pH: 11) and HF on the feldspar concentrate obtained from the classical feldspar-quartz separation.

Studies on Na-K feldspar separation with ore and pure samples have shown that selective separation takes place under different conditions (acidic, natural, alkaline), and the proposed mechanisms vary depending on the type of mineral and methodology involved. In this study, the surface properties and flotation behavior of Na and K feldspars were examined and the mechanisms proposed in the literature for their selective separation were evaluated.

2.   Surface properties of Na-feldspar and K-feldspar

Feldspar surfaces consist of the cationic center such as K$^+$ ion in microcline/orthoclase and Na$^+$ ion in albite and anionic center such as polar silanol groups or relatively non-polar siloxane groups (Abramov et al., 1992), the ratio of which determines the surface charge character of feldspars as a function of pH. Increasing pH increases the negative species ($\equiv$Si-OH + OH$^-$ → $\equiv$SiO$^-$ + H$_2$O). Conversely, the positive charges increase with decreasing pH ($\equiv$Si-OH + H$^+$ → $\equiv$Si$^+$ + H$_2$O). The surface potential values determine the extent of adsorption and flotation which then depend on the concentration of Na$^+$ ion and K$^+$ ions (Me$^+$) as well as the solution pH following Eq. (1) (Demir et al., 2001):

$$3Si + Me^+ + Al(OH)_3 + 5H_2O \rightarrow MeAlSi_3O_8 + 13H^+ + 12e^- \tag{1}$$

Fig. 1 shows the result for the zeta potential measurements of albite, orthoclase, and feldspar samples in the absence and presence of fluoride media. As seen from Fig. 1, while the surface charge of Na feldspar (albite) and K feldspar (orthoclase) was similar in the absence of fluoride ions, feldspar samples showed a very negative surface charge at acidic pH (2-3) in the presence of fluoride ions. Demir (2001) stated that albite and orthoclase give exchangeable alkali and alkaline earth alkaline ions to water and have a constant negative charge at all pHs in a fluoride-free environment. In addition to this, Demir (2001) expressed that aluminum oxide and silicon oxide contribute to the surface charge density of these minerals. Ütine (1985) indicated that the potential determining ions (PDI) for feldspar would be all Al and Si-containing hydroxyl complexes and H$^+$ and OH$^-$ ions in the solution. Gülgönül (2005) stated that there may be differences in the surface charges because the amounts of ions such as Na$^+$, K$^+$, and Ca^{2+} released from feldspars with different sodium and potassium oxide contents and their adsorptive tendencies will be different. For this reason, it was determined that Na-feldspar (albite) was slightly more negative than K-feldspar in the zeta potential measurements for different samples carried out by

Gülgönül (2005). Dai et al (1996) stated that K^+ or Na^+ at the edge of feldspar is dissolved in the water solution, leaving positive charge holes, leading to a negative charge. On the other hand, it has been stated that fluoride ion changes the surface charge of the mineral by breaking the Al-O and Si-O bonds on the feldspar surface (Buckenam and Rogers 1954-55; Shimoizaka et al. 1964; Smith, 1965; Warren and Kitchener, 1972; Thornton, 1988; Duan et al 2019). The results of the study by Rattanakawin and Thacom (2019) have been adapted to Fig. 1, where it was observed that the surface charge of feldspar in the presence of HF as a variable was more negative at acidic pHs without a definitive zero point of charge (zpc). Whereas albite and orthoclase were estimated to exhibit iep around pH 1. Rattanakawin and Thacom (2019) explained the effect of fluoride ions on surface charge by adsorption of fluorosilicate ions ($AlSiF_6^{2-}$) on feldspar surfaces at acidic pH as stated in the literature (Fuerstenau et al., 1985). Morever, Wang et al. (2018) stated that feldspar samples pretreated with HF showed more negative surface charge leading to better particle dispersion.
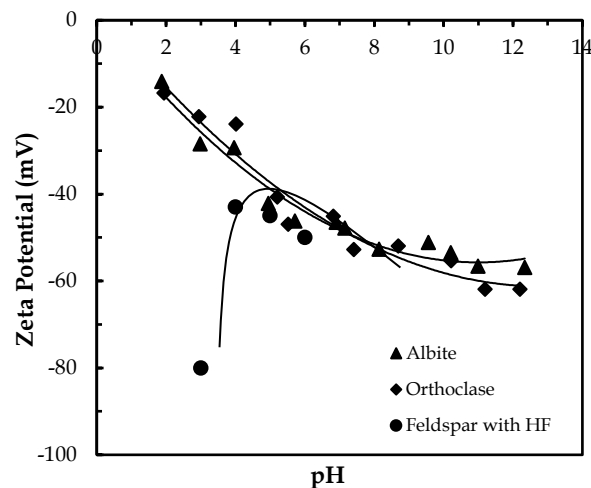

Fig. 1. Zeta potential-pH profile of feldspar minerals (Karagüzel, 2005; Rattanakawin and Thacom, 2019)

The surface properties of these two minerals with similar surface charges were also investigated with different techniques. Karagüzel (2005) carried out contact angle and free surface energy measurements using the wettability tests of minerals with hydrophobic and hydrophilic liquids. The contact angles and surface energies of both minerals determined by the thin layer wicking technique were found to be 43°, 45°, and 56.66, 52.20 mJ/m², respectively. These results of Karagüzel (2005) once again confirmed the similarity in surface properties of the two minerals. However, Gülgönül et al. (2005) detected surface stains on the surfaces of different feldspar minerals through X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) analyses. They reported that the changes in the surface properties of feldspar minerals due to these stains, which are the subject of this study, are envisaged to have occurred by either mineralization or contamination in the fractures and cracks of the ore.

3. Flotation behaviour of Na-feldspar and K-feldspar

Feldspar flotation is based on the activation of feldspar with fluoride ions and flotation with a cationic reagent at low pH (O'Meara et al., 1939; Buckhenham and Rogers, 1954; Joy et al., 1966; Kovalenko, 1967; Yanis, 1968; Starikova, 1968; Tröndle, 1968; Revnivtzev et al., 1968; Marius and Laura, 1970; Sheiko, 1972; Yanis and Gorelik 1973; Katayanagi, 1972; Klunker et al., 1974; Ociepa, 1994; Rao and Forssberg, 1985; 1993; Demir et al., 2001; Demir et al., 2003; Karagüzel et al., 2006; Gülgönül et al., 2008; Gülgönül and Çelik, 2018). To date, many researchers have proposed various mechanisms for the flotation system. Dean and Ambrose (1944) stated that reactive adsorption occurred as a result of cleaning the amorphous layer on the feldspar surfaces by dissolving and removing it in acidic conditions containing fluoride. It was reported in the literature that SiF_6 or SiF_6^{-2}-amine complexes were formed in the solution in the flotation medium and that feldspar flotation took place by the adsorption of these complexes on the aluminium atoms or ions on the mineral surfaces (Smith, 1965; Smith and Smolik, 1965; Suliin and Smith, 1966; Smith and Akhtar, 1976). It was also stated that aluminium fluoride complexes formed on

the mineral surface and amine adsorption occurred on these sites (Buckenham and Rogers, 1954; Schubert and Abido, 1967; Warren and Kitchener, 1972). Manser (1975) took these considerations into account and stated that the amine adsorption occurred and feldspar floated when potential-determining polyvalent cations form fluoride complexes in solution.

Fig. 2 shows the results of flotation experiments for albite (Na-feldspar) and orthoclase (K-feldspar) as a function of reagent concentration at natural pH (Fig. 2a) and as a function of HF concentration at acidic pH (Fig. 2b).
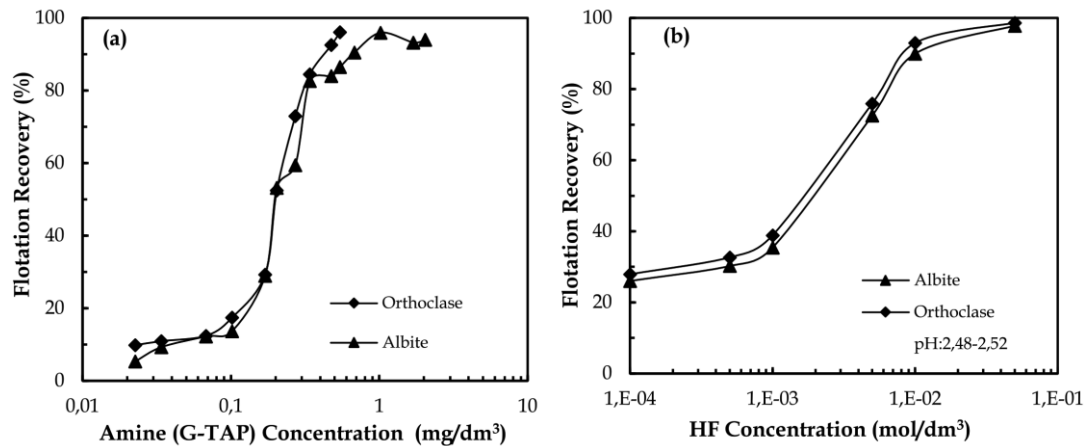

Fig. 2. Flotation behavior of albite and orthoclase (a) as a function of amine concentration at natural pH (b) as a function of HF concentration at acidic pH and 0.32 mg/dm^3 amine concentration (Demir, 2001; Karagüzel, 2005)

As seen in Fig. 2, Na and K feldspars with similar surface properties exhibit similar flotation properties at natural pH and in the presence of fluoride ions. Although the reason for the studies on the selective separation of these two minerals was not known exactly in the 60s, today it has become an economic and technological necessity to separately obtain Na and K feldspars from mixed type ore formations. The first studies on the selective separation of feldspar minerals coincide with the view that potential determining multivalent cations can be utilized by forming fluoride complexes with amine, as expressed in the literature (Manser, 1975). In this context, Na, K, Ca Mg, and Ba salts were used in the first studies for the separation of Na and K feldspars (Yanis, 1968; Starikova, 1968; Revnivtzev et al., 1968; Ociepa, 1994; Demir, 2001; Gülgönül, 2004). In summary of these studies, it was stated that while K, Rb, and Ba ions depressed K-feldspar, Na, Ca, Mg, and Sr depressed Na-feldspar.

Fig. 3 shows the flotation recoveries albite and orthoclase in the presence of NaCl, which is known to be the most effective salt in the literature, at natural pH and in the presence of acidic pH 2.5 with HF (Demir, 2001; Karagüzel, 2005).
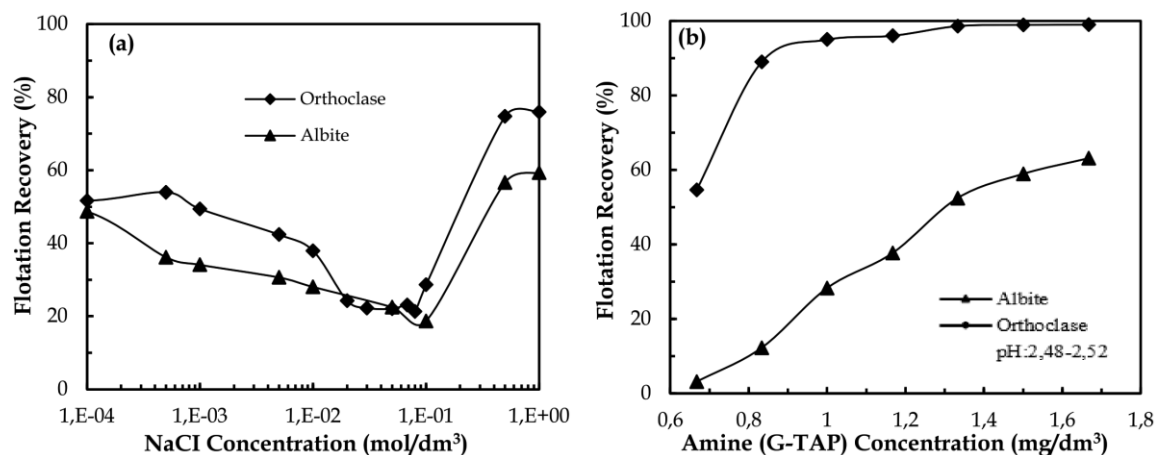

Fig. 3. Flotation behavior of albite and orthoclase (a) as a function of NaCl concentration at natural pH and 0.32 mg/dm^3 amine concentration (B) as a function of amine concentration at acidic pH (pH: 2.5; 5.10^{-3} mol/dm^3 HF concentration) and 5.10^{-2} mol/dm^3 NaCl concentration (Demir, 2001; Karagüzel, 2005)

As seen in Fig. 3a, in the presence of NaCl at natural pH, Na-feldspar was depressed around 1.10^{-3} mol/dm³ NaCl concentration and some selectivity was achieved. It was observed in Fig. 3b that the selectivity between the two minerals in the presence of HF in acidic conditions was higher than that at natural pH with a selectivity reaching 80%, especially in the presence of HF around 0.8 mg/dm³ G-TAP concentration. Revnivtzev (1968) stated that while selective separation at high salt concentrations was possible without HF, similar recovery was found with HF even at lower salt concentrations.

Various studies have been carried out in the literature to understand the mechanism of selective flotation in the presence of NaCl at natural pH. Gülgönül et al. (2012) stated from the solubility, adsorption, and electrokinetic tests that ion exchange and ion adsorption mechanisms, which primarily affect the mineral surface charge, occurred between Na-Feldspar and K-feldspar minerals and the flotation medium. They further stated that with increasing NaCl concentration, there was a K^+ ion transition from K-feldspar to the environment, and this situation continued until 1.10^{-2} mol/dm³ NaCl concentration, where there was no change in the zeta potential in this region; but after this concentration, the zeta potential decreased towards zero. On the other hand, in Na-feldspar, it was determined that the surface charge decreased continuously towards zero upon Na^+ ion adsorption (Fig. 4a). Ion exchange and ion adsorption capacities in the presence of Na-feldspar and K-feldspar with NaCl are presented in Fig. 4b. As seen in Fig. 4b, ion exchange takes place on microcline and whereas ion adsorption occurs on albite. Karagüzel (2005) repeated the same experiments in the albite/NaCl system and found that Na^+ ion added to the solution prevented the ion transfer from the albite surface to the medium, therefore, the adsorption of amine onto the albite surface was more limited than that of K-feldspar. Accordingly, the first mechanism in selective separation is ion exchange in K-feldspar, ion adsorption in Na-feldspar, and formation of new mineral surface character that prevents cationic amine adsorption on Na-feldspar but is conducive to K-feldspar, as seen in Figs. 5a and 5b. Another mechanism proposed by Karagüzel (2005) was that selective separation was realized by hindering amine adsorption since Na^+ ion was a structure maker ion for the albite surface.

The mechanisms explained above are usually valid in relatively pure samples. However, as stated by Gülgönül (2004) the proposed mechanisms do not work and the selective separation is not sufficiently realized due to various metal ions causing surface contamination on the surfaces. On the other hand, Karagüzel (2005) stated in his study with pegmatite samples that selective separation could not be achieved under the recommended conditions at natural pH, but selective separation could be achieved in flotation experiments using HF. Similarly, in previous studies with real ore samples (plagioclase and pegmatite), it was stated that samples activated with fluorine ion depressed Na-feldspar in the presence of NaCl (Starikova, 1968; Revnivtzev et al., 1968; Marius and Laura 1970; Gülsoy et al., 2005). The opinion of the researchers working on the Na-feldspar K-feldspar separation on the selective separation is listed in Table 1.
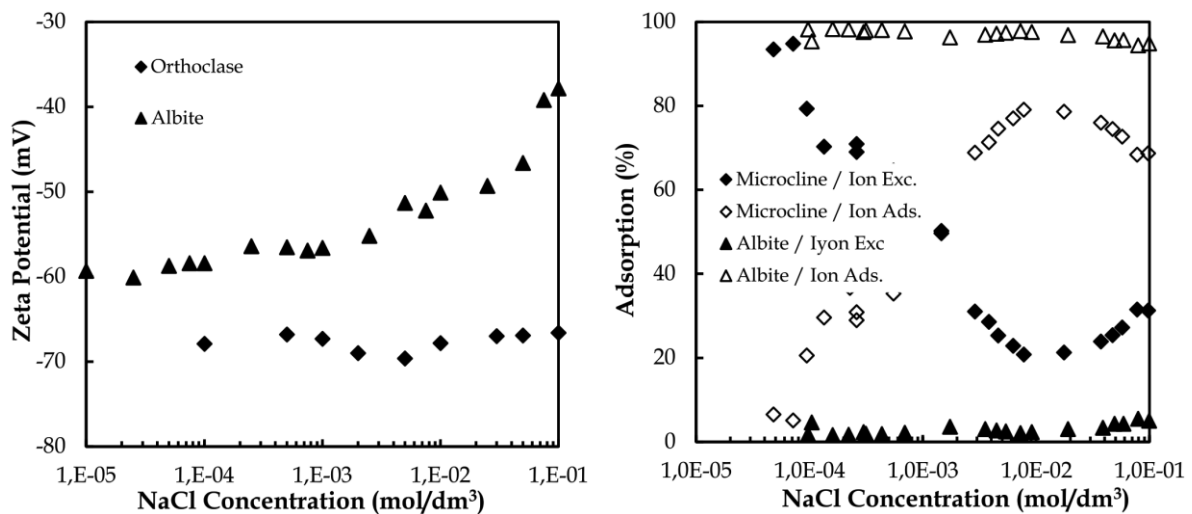

Fig. 4. (a) Zeta potential of albite and microcline as a function of NaCl (b) Ion adsorption/exchange capacity of albite and microcline as a function of NaCl (Demir, 2001; Gulgonul et al., 2012)

Contrary to Gülgönül (2004), though contamination on the mineral surfaces, it is considered that in the presence of fluoride, fluorine-amine complexes occur on the surfaces, especially for the K-feldspar surface, and for Na-feldspar, less amine adsorption occurs as a result of suppression due to Na$^+$ ions. Thus, selective flotation can occur even in ore samples sheltering Na and K feldspars in the same matrix (Figs. 5c and 5d).

Table 1. Other results and comments from the literature on Na-K Feldspar selective separation

Explanations	References
The same ions in the crystal structure (Na$^+$ for Albite and K$^+$ for Microcline) decrease the selectivity, whereas the selectivity of Microcline in a solution containing NaCl and of albite in a solution containing KCl increases selectivity rapidly and effectively.	Revnivtzev et al. (1968)
Microcline and albite do not need to be separated from each other because they are obtained separately from the rocks they are rich in.	Manser (1975)
Since plagioclases float more difficult than sodium and potassium feldspars, they are obtained in scavenging cycles rather than coarse flotation cycles.	Revnivtzev et al. (1968)
HF activation of albite with HF is easier than that of calcium feldspar.	Manser (1975)
Under the same conditions, less amine is adsorbed on microcline than albite, but microcline has greater floatability.	Yanis and Gorelik (1973)
Although feldspars with high potassium content are less wettable, they are difficult to separate from different feldspars with very close chemical content and crystal structure in the presence of collectors. It is difficult in this sense to separate K-feldspar (microcline) from Na-feldspars or plagioclases.	Yanis and Gorelik (1973)
In amine flotation, K$^+$ ions have a depressive effect on potassium feldspars, and Na$^+$ and Ca^{2+} ions have a depressive effect on sodium feldspars.	Yanis and Gorelik (1973)
In zeta potential measurements depending on the amine concentration, K-feldspar is affected faster and more and the negativity decreases, while Na-feldspar is not affected much. Amine ions show a low reaction on Na-feldspar surfaces.	Ociepa et al. (1994)
At pH 5.8, microcline floats better than albite depending on the amine concentration. This situation is explained with; a. Hydration differences of potassium, sodium, and calcium ions on feldspar surfaces, b. Diameter of potassium cation and RNF^{3+} amine ion polar groups are almost the same diameter, therefore potassium cations are replaced by RNH^{3+} amine polar groups and K-feldspar has higher floatability.	Ociepa et al. (1994)
The stability of the air bubble-feldspar aggregate does not depend only on the dodecylamine hydrochloride solution. It also depends on NaCl and KCl solutions, the chemical content of feldspars, and crystal structures.	Ociepa et al. (1994)
It is possible to obtain products with high K and Na content in flotation cycles that include scavenging and cleaning stages.	Karagüzel et al. (2006)

Studies on the separation of Na-feldspar and K-feldspar were mostly carried out in the presence of HF at acidic pH or natural pH. It is observed from the literature that there have been not enough studies at alkaline pH for selective separation. Yanis (1968) stated for the first time in a Russian patent that the amine sodium silicate mixture increased the selectivity for the cationic flotation of Na-K feldspar in the presence of HF. However, Karagüzel et al. (2006) performed several experiments on a sample of pegmatitic feldspar at pH 9.5 but did not get successful results on selective separation. Bultovic (2015), on the other hand, made a pre-treatment using NaOH in the slime removal stage before the cationic reagent with NaCl in acidic conditions. Larsen et al. (2019) based on this idea, discussed the issue in more depth and stated that K-feldspar selectively floated from Na-feldspar at pH 10.5–11.6 with NaOH as pH adjuster/modifier and Brij58 as a frother, without any additional collectors except fluorine and amine already adsorbed from the feldspar-quartz separation of the three-stage flotation system. In the

same study, in which fluoride measurements were performed, the authors showed that segregation could result from the preferential desorption of fluorine-amine complexes from the Al and Na domains of Na-feldspar, but only from the preferential desorption of K-feldspar from the Al domains.
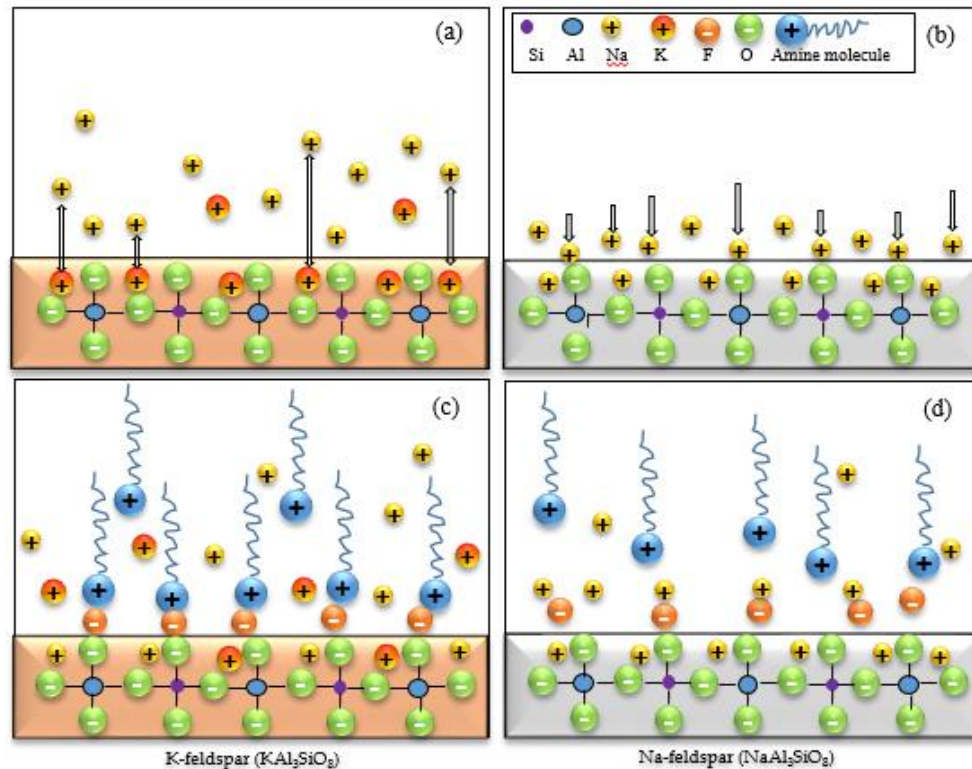

Fig. 5. Ion activities and selective separation mechanism on K- and Na-feldspar surfaces (a) ion-exchange mechanism on K-feldspar surface (b) ion adsorption mechanism on Na-feldspar surface (c) Amine adsorption on F activated K-feldspar (resurfacing with Na-K ion exchange) (d) Amine adsorption on F activated Na-feldspar (resurfacing with ion adsorption)

4. Conclusions

In the history of flotation, there have been periods in which studies on the selective recovery of Na and K-feldspar from mixed-type feldspars by flotation technique accelerated due to industrial needs. In the first period, studies were mostly focused on flotation applications. In this period, researchers aimed to produce K-feldspar concentrate. In the following periods, with the development of science and technology, studies on the mechanism of separation with high selectivity discrimination have increased.

The separation mechanism of Na-K feldspar in the presence of salt (Na) is highlighted in Fig. 5 as proposed in the previous studies. According to the mechanism described in Fig. 5:

1. K-feldspar gives some K^+ ions to the solution by ion exchange with Na^+ ions at all pH (Fig. 5a). Under these conditions, the surface charge of K-feldspar becomes more negative.
2. On the other hand, the ion (Na^+) adsorption occurs on the Na-feldspar surface (Fig. 5b). In this case, the Na-feldspar surface charge remains constant.
3. In the presence of fluoride ions, SiAlF-amine complexes are formed on the surface of K-feldspar, giving rise to a more negative surface charge with resultant ion exchange (Fig. 5c).
4. As the Na-feldspar surface is suppressed by ion adsorption, amine adsorption becomes very limited even in the presence of fluoride (Fig. 5d).

Consequently, the main mechanism providing selective flotation of Na-feldspar and K-feldspar is ion-exchange/ion adsorption. At natural pH and in the presence of fluoride ions, flotation occurs with amine adsorption after ion exchange in K-feldspar, while amine adsorption is inhibited due to Na^+ ion adsorption on Na-feldspar. In this case, especially in the presence of F, SiAlF-amine complexes are formed on the K-feldspar surface leading to flotation of K-feldspar while Na-feldspar is depressed. On the other hand, literature data reveal that in alkaline conditions K-feldspar activated with fluoride ions

in early flotation cycles float in the presence of NaOH. The proposed mechanism for this case is that K-feldspar forms SiAlF-amine complexes on the surface releasing K^+ ions to the solution due to the Na^+ ion in the medium. Accordingly, it is understood that the mechanism that ensures selectivity in all conditions, including alkaline conditions, is dominated by the ion exchange/ion adsorption mechanism.

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