Asian Journal of Chemistry Vol. 10, No. 4 (1998), 690–706

REVIEW

Feldspar for Potassium, Fertilisers, Catalysts and Cement

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INTRODUCTION

Feldspar is the most abundant rock-forming mineral in nature and makes up an estimated 60% of the earth's crust. The feldspars comprise a group of minerals consisting of the silicates of aluminium with varying amounts of potassium (orthoclase and microcline: $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), sodium (albite: $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), or calcium (anorthite: $CaO{\cdot}Al_2O_3{\cdot}6SiO_2$). The mineral has wide applications in the glass and ceramic industry with its production going up remarkably over the years. In the United States of America the production increased from 580,000 metric tons in 1991 to 870,000 metric tons by 1995. Italy, the largest feldspar-producing country in 1994, had an estimated output of 1.6 million metric tons. Many other countries also produce feldspar. India, with its known recoverable resources of 16 million metric tons, produces less than 100, 000 tons annually and the demand is increasing every year.

Among the various feldspars, potassium feldspar is the most common and contains upto 13% potassium as K_2O. Interestingly, feldspar is considered only a secondary source of potassium as the potassium-bearing brine and the underground deposits of soluble minerals constitute the primary source of commercial potassium. Potassium is a strategic metal signified by its use in agriculture as well as in defence, both of which contribute to the progress of a country. India, with its vast agricultural base, meets its entire requirement (*ca* 150,000 tons per annum) of fertiliser-potassium through imports. Though the need for processing feldspar for potassium was felt in the first quarter of this century, the resulting innumerable patents did not seem to have enthused later researchers. Moreover, feldspar can be converted into a fertiliser, catalyst or cement and thus becomes a very attractive raw material for industrial use. This article attempts to examine the status of feldspar as a source of potassium and for producing fertiliser, catalyst or cement since the beginning of this century.

Meffert[1] reviewed the occurrence and importance of feldspar while Sharp and Lyle[2] described feldspar as a raw material. Extraction of potassium from feldspar was the subject matter of discussion[3] as early as in the year 1913 and a process[4] with special emphasis on costs and returns was described by 1915. Newman and Draisbach[5] gave numerous references to the literature and a complete list of patents for recovering K_2O from feldspar while reporting on a feldspar of Norwegian origin for obtaining potassium on a technical scale. Holter[6] presented his critical observations along with economic considerations on K_2O, manufactured from feldspar, for agricultural needs. In a monograph, Johnstone[7] dealt with the sources of the world's supply of potassium and considered the feldspars of Canada as important. He mentioned a process for the extraction of potassium from feldspar, which was on trial at the works of National Portland Cement Co., Ontario. Turrentine *et al.*[8] described a process used by the experimental plant of the Bureau of Soils, at Summerland in California. Johnson[9] had presented an extensive review on the patent and journal literature of potassium extraction from feldspar, and considered all proposed chemical processes as uneconomical because high-grade feldspar commanded a price higher than that of its potassium content. Feldspar seldom occurred as a pure mineral in large masses and no effective method of concentration was known. Recently Rogers[10] presented in a nutshell the aspects of processing, application and uses of feldspar.

Feldspar as a Potassium Source

Feldspar contains considerable amount of potassium. It is therefore not surprising if a number of attempts, from time to time, have been made on feldspar to explore several methods such as heat treatment, fusion, volatilisation, leaching, electrolysis and dialysis, decomposition by microorganisms for obtaining potassium. The work has been examined in detail and reviewed in the following lines.

Heat Treatment

Feldspar is a reasonably stable silicate. Several workers have studied its behaviour at varying and high temperatures. Seki and Kennedy[11] investigated the breakdown of feldspar at high temperature and pressure and noted its apparent stability even at 1000°C and 60 kilobars. Urusov[12] studied the concept of crystal lattice energy with respect to feldspars. Karpov and Pampura[13] determined the thermodynamic properties of feldspars at varying temperatures. Filonenko *et al.*[14] studied the phase transformations in feldspar at 1100–1500°C by X-ray diffraction, IR spectroscopy and electron microscopy; the final product formed at 1300–1500°C consisted mainly of acid-soluble leucite. Rosenholtz and Smith[15] observed 11 abrupt changes while investigating the thermal properties of feldspars. Peacock[16] melted feldspar in an electric furance at 1400–1500°C and then disintegrated it by a blast of air or by allowing the molten mass into a stream of water. Henshaw[17] heated at 950–1000°C the feldspar containing CaF_2 to sublime off the fluorine as KF. La Rue and Scofield[18] converted the crystalline feldspar into an amorphous form by heating at 1350–1400°C. Soluble potassium compounds were formed after heating the amorphous sample with KOH. In another method[19] hot feldspar was disintegrated by directly treating with H_2SO_4 or firsh with water and then with H_2SO_4. Alexander[20] injected pulverised feldspar with fuel and air into a combustion and reaction chamber in order to obtain soluble potassium compounds. Kohl[21] used dilute HCl to decompose feldspar ignited at 750°C; Nayak *et al.*[22] used H_2SO_4, HNO_3 and H_3PO_4 also. Rebuffat[23] had quenched the heat-treated feldspar in water, pumped the slurry into an autoclave and subjected to up to 20 atm hydraulic pressures; soluble salts of potassium were produced by treating the solution at 2 atm with CO_2 or SO_2.

Fusion

Normally, fusion methods are employed to break the silicate structures for reliability in analysis. Sereval workers have attempted to extend the fusion technique for potassium extraction using a variety of metal salts as fluxes and as presented in the following lines.

With Sodium Salts

One of the first attempts to obtain potassium from feldspar employed the fusion method using sodium bisulphate and sodium chloride with good yields up to 90% after water leaching followed by crystallisation of the sodium and potassium sulphates[24–26]. NaCl alone had shown considerable promise.[27, 28] Ashcroft[29] heated feldspar in the absence of air and moisture and proposed the following equation:

$$2NaCl + K_2O \cdot Al_2O_3(SiO_2)_6 \rightleftharpoons Na_2O \cdot Al_2O_3(SiO_2)_6 + 2KCl$$

He described an emergency plant with costs of operation on British conditions. Rhodin[30] carried out the fusion in a reverberatory furnace along with a mixture of SO_2, steam and air. Blummenberg[31, 32] could bring down the fusion temperature to 650 to 800°C by using $NaNO_3$; he employed mineral acids for leaching the alkali salts. In another experiment[33] feldspar was first heated at 815°C and then dropped into water. The disintegrated mass was then heated at 535°C with excess $NaNO_3$ for 6–8 h. Water leaching under pressure (4 atms) resulted in up to 80% yield of KNO_3. Bassett[34] employed a 3 : 2 Na_2CO_3–NaCl mixture for fusion. The water-leached solution was carbonated to separate aluminium, then treated with NaOH to convert the respective sodium or potassium bicarbonates into carbonates. Na_2CO_3 and NaCl could be recovered for recycling. Alternately, the leach solution was treated[35] with a mixture of NaOH, iron oxide and CaO to effect the separation of aluminium and recovery of potassium. Blummenberg[36] heated finely ground orthoclase with twice its weight of Na_2CO_3 in a closed retort, at 800 to 900°C until complete fusion, with the total removal of CO_2. Hirota[37] found it convenient to heat the feldspar with Na_2CO_3 in 10:7 ratio to dull red heat for 1 h to leach out the sulphates of potassium and aluminium with excess H_2SO_4 at 100°C for 90 minutes. Nayak *et al.*[38] reported 80% water-extractable potassium after heating a 5 : 1 feldspar and Na_2CO_3 mixture at 900°C. The fusion temperature could be brought down to 600°C by replacing 50% of the sodium salt with that of lithium though the potassium extraction also dropped to 50%. While employing $NaHSO_4$, Bassett[39] used fluorides of sodium or calcium to bring down the reaction temperature to 480–540°C. However, higher temperatures are sometimes convenient to reduce the reaction time drastically. Thus, a 25:15:5 mixture of orthoclase, Na_2SO_4 and sulphur was fused and held at 1150–1250°C for 8–10 min to obtain soluble potassium salts[40].

With Potassium Salts

Hart[41, 42] fused a 4:4:2 mixture of feldspar, K_2SO_4 and carbon. In another method[43], feldspar was melted with an alkali sulphate followed by treatment of the molten mass with gaseous sulphur-oxygen compounds in the presence of steam or air. K_2CO_3 was used by Swenarton[44, 45] as well as Scholes and Brenner[46] in equivalent amount with finely ground feldspar for fusion at 800–1200°C for 1 h; Na_2CO_3 was equally effective[47–49]. Stover[50] suggested addition of 1.5 times as much K_2CO_3 as feldspar and powdered coal to assist the fusion. KOH or K_2O and Na_2CO_3 [51] could also be used in place of K_2CO_3. Ashcroft[52] first suspended feldspar in a fused bath of sodium and/or potassium chlorides. The suspension was then treated with chlorine gas (using Fe, Mn or Cr salts as chlorine carriers) and reducing agents (carbon or Na, K, Zn, Pb or Fe sulphides) in a converter at 800 to 1100°C. Potassium chloride was separated by lixiviation. In addition, use of catalyst carriers such as ferrous or manganese salts was also reported[53]. Morse[54] treated feldspar with caustic alkali and then heated in a current of SO_2 at 250°C to specifically react will potassium and not aluminium.

With Calcium Salts

Calcium carbonate or CaO was heated to glowing in admixture with finely pulverised feldspar and the resultant mass was lixiviated[55–60]. The CaO was obtained by adding $CaCl_2$ solution to the mass and then decomposing with steam[61]. Calcium nitrate was used[62] for the fractional crystallisation of KNO_3 and Edison[63] described a suitable apparatus. Beckett[64] suggested chlorine recovery by interaction of lime with the ultimate KCl. Fusion also with $CaSO_4$ [65, 66] and $CaCl_2$ [67] has been reported for obtaining soluble potassium salts. Kirpatrick[68] conducted a fusion study on feldspar using calcite and magnesite. His studies indicate the absence of formation of any predominating compound in the series; feldspar was decomposed by CaO but not by MgO. Sudo and coworkers[69] investigated the reaction of pure feldspars with $CaCO_3$ and NH_4Cl in 2:3:2 weight proportion at different temperatures for 1 h. Eberhardt[70] used 10–20% CaF_2 as flux with 2–5% $CaSO_4$ to bring down the calcination temperature. Gypsum was used with or without limestone[71, 72] and with calcium hydroxide[73] or petroleum acid sludge[74]. In the acid sludge method, calcination temperature was 700–800°C only as the carbonaceous material in the acid sludge furnished part of the heat for the reaction. When $CaCO_3$ was used[75] in place of gypsum, the calcination temperature was 700–1000°C. Nayak *et al.*[38] studied the extraction of potassium from feldspar by roasting route using different fluxes individually or in combination; the roasted matter was leached under reflux with water. They reported potassium recoveries up to 80% with a 0.75 : 3 : 1 $CaSO_4$, $CaCO_3$, feldspar mixture heated at 900°C. Potassium recoveries decreased to 60% when $CaSO_4$ was replaced by $MgSO_4$ and a further drop to 18% resulted when $CaCO_3$ was replaced by $MgCO_3$. Lime with salt as flux was investigated by Cushmann and Coggeshall[76] and later by Auden[77, 78]. Edwards[79] used 60% NaCl (by weight) to fill the voids and then fused the mineral with hydrated lime or $CaCO_3$. Recovery of potassium was incomplete if Na_2SO_4 was used in place of NaCl. However, Gleaser[80] reported the beneficial effect of Na_2SO_4 to lime at 800°C in a closed chamber. Formation of water-soluble potassium and aluminium salts was found possible[81, 82] on sintering feldspar with CaO and Na_2CO_3. Basett[83] added Fe_2O_3 and NaCl to the above flux. Drury[84] heated the feldspar with CaO or $CaCO_3$ and iron oxide in a blast furnace. Gleaser[85] added 5% reducng iron oxide to a 1:1 mixture of feldspar and $CaCl_2$ and then heated to 900°C in non-oxidising atmosphere; iron or iron oxide and coke could also replace the reducing oxide[86]. Tomula established the catalytic effect of iron and manganese salts for the reaction between feldspar and lime[87] or $CaCl_2$ [88]. He attributed the solubilisation to nascent chlorine. In another experiment[89], feldspar was mixed with pyrite ore and a small amount of CaF_2, $CaCl_2$ or $MgCl_2$ before firing. Frazer and co-workers[90] suggested a new method in which finely ground feldspar was mixed with caustic alkali, first heated to dryness and then at 275–300°C for 1 h. Artificial leucite was formed containing all the potassium and aluminium of the feldspar. The leucite can yield its constituents one by one on treating with acids. Similarly, Rody[91] treated feldspar with K_2CO_3 or KOH to increase its potassium content. The product was then heated to sintering temperature with CaO or $CaCl_2$ in proportion to form orthosilicate of calcium and water-soluble combination of alkali and alumina. Bailey[92] gave the equilibrium of the reaction at one kilobar pressure:

$$\text{Orthoclase} + \text{Dolomite} + H_2O \rightleftharpoons \text{Phlogopite} + \text{Calcite} + CO_2$$

Drobot and Khazanov[93] observed that interaction of calcite with orthoclase occurred at 1145–1200°C, which is much above the temperature at which calcite begins to decompose.

With Other Salts

Complete fusion was reported with 1:1 mixture of finely ground orthoclase and lead nitrate on heating at 650–815°C in a cast iron retort. After leaching with nitric acid, lead nitrate was regenerated for recycling. Nitrates of iron and manganese were also effective[94]. Ferric sulphate was found[95] to effect complete fusion at even lower temperatures, 400–500°C. However, Dasgupta and Chatterjee[96] reported temperatures as high as 1310°C for complete reaction when Fe_2O_3 was heated with feldspar of Indian origin. The yield of potassium during the heating cycle was found to increase with increased concentration of Fe_2O_3, and with time, temperature and concentration of CO_2 during the water-extraction cycle. Finely ground feldspar was heated with sulphurous gases to form potassium and aluminium sulphates[97, 98]. Investigations were carried out on B_2O_3, crude borax and H_3BO_3 as fluxes for fusion of feldspar[99, 100]. Hart[101] fused felspar, $BaSO_4$ and carbon in 1:1:2 proportion to form soluble K-Al alum for its easy separation from the insoluble constituents including SiO_2 and $BaSO_4$. Lindblad[102] observed the silicic acid component of the feldspar to wholly break down on heating feldspar in an electric furnace with coal and a metal such as iron or another reducing agent. The fusion temperature could be brought down to 650°C by using suitable fusible salts[103] such as $MgSO_4$, $NaNO_3$ or chlorides of Ca, Ba, Fe, Zn, Mn and Al. The salts can be used individually or in mixtures but the heating is to be effected under pressure. Nayak and co-workers[38] employed the rare earth salts as fluxes and found them ineffective. Fusion with rock phosphate in proper proportion to form K_3PO_4 followed by double decomposition of the sludge at 600–900°C by passing electric current was another convenient method[104]. Heating with $AsCl_3$ at 700–900°C followed by lixiviation was found to give good recoveries of KCl from feldspar[105–107]. Ravner[108–110] reported distintegration of feldspar through fusion with ashes of marine plants. Vandecaveye[111] studied the liberation of potassium from finely ground feldspar by the action of manure extracts and manure extracts plus acids. The dissolution did not improve further on sterilisation of the soil or addition of acids, $CaCO_3$ and $CaSO_4$.

Leaching

As feldspar is a silicate mineral, fusion methods are generally employed to open it up. However, systematic studies on its dissolution by various solvents had also been the subject of interest since long. A critical examination of such work has been presented in the following paragraphs.

Blum and Stilling[112] reviewed the dissolution kinetics of feldspar covering the aspects of mineralogy, surface chemistry during dissolution, experimental determination of dissolution kinetics and the limitations of modelling natural system with rates determined experimentally. Cushmann and Hubbard[113] authored the first report on leaching feldspar. From 100 g powdered orthoclase 400 mL water extracted 0.03 g, 15% NH_4Cl or 0.1 N HCl dissolved 0.27–0.29 g in cold and 0.48 g while hot; with hot concentrated HCl, the extraction increased to 0.67 g. Wet grinding improved extraction while more alkali was extracted by using the sulphates or hydroxides of calcium. Frank[114] studied the extraction behaviour with water over long periods ranging from a few hours to six months. Stephenson[115] observed that pure water did not attack feldspar up to 300°C. Parmelee and Monack[116] investigated the solubility of feldspar in water and noticed that increase in pH varied from 1.7 to 2.7 for different feldspars but bore no relationship to the K_2O/Na_2O ratio; the pH became constant after 48 h. Bazarov[117] determined the solubility of feldspar in aqueous medium under isothermal conditions and observed increased solubility with increase in the concentration of CO_2. Busenberg and Clemency[118] studied the dissolution kinetics of feldspars at 25°C and a CO_2 partial pressure of 1 atm.

The steady state composition of the surface layer had a 2 : 1 ratio of silicon to aluminium for the potassium feldspars. Whyte[119] treated a water mixture of finely ground feldspar, with a continuous stream of CO_2 or SO_2 at the boiling temperature of the solution under ordinary or increased pressures, and reported extraction of 5% of the total K_2O present. Knauss and Wolery[120] measured the dissolution rates of feldspars as a function of pH and time at 25 and 70°C in a single-pass flowthrough leaching apparatus. Feldspars leached at low and high pH at 70°C showed extensive development of prismatic etch pits demonstrating a surface reaction-controlled dissolution process. Helgeson and coworkers[121] analysed experimental data reported in literature, with the aid of irreversible thermodynamics and transition state theory. They suggested that at ≤ 650°C, the rate of both congruent and incongruent feldspar hydrolysis in aqueous solutions was a function solely of effective surface area and pH at constant pressure and temperature. The rate became pH dependent at lower pH. Here, the rate-limiting step is related to breakdown of a protonated configuration of the atoms on the surface of the reactant feldspars while at higher pH the rate is limited by decomposition of an activated surface hydrous feldspar. Near equilibrium, the rate is proportional to the chemical affinity of the overall hydrolysis reaction regardless of pH. Malyshev[122] observed increased alkalinity in suspensions of varying amounts of feldspar in water (30 mL) due to dissolution of the mineral. Kotov and co-workers[123] studied the hydrothermal behaviour of feldspar at 100 MP_a and observed increased exchange of potassium with the vapour phase with increased temperature. Kitto and Patterson[124] studied the rate of solution of orthoclase particles of 0.2–2.0 μ at pH 8–11 and observed higher intrinsic solubility of the finest particles even when the disturbed outer surface was removed. Although Nagai and Nagaeda[125] reported the near insolubility of feldspar in HCl or H_2SO_4, there was sufficient evidence to support their utility. Splichal[126] studied the dissolution of the feldspars by acids of various concentrations at room temperatures over a period of 8 weeks and found a regular increase in solubility as the composition approaches the anorthite end from that of a plagioclase.

Haslup and Peacock[127] dissolved finely comminuted feldspar with H_2SO_4 at 200–300°C in a closed vessel. Katorcha[128] presented solubility data on feldspar in aqueous 0.5–1.0 N H_2SO_4 at 200–300°C and 3000 kg/Cm^2; Zverev and co-workers[129] related its solubility in 10% H_2SO_4 to the energy of crystal lattice reduced to a single oxygen atom. Guo *et al.*[130] studied the dissolution of feldspar in aqueous dilute HCl at pH 4.0 and observed the rate as proportional to the grain specific surface. The rate was, however, inversely proportional to the mean grain size of feldspar. Such weathering studies were also conducted for HNO_3 [131]. Robertson[132] used phosphoric acid to dissolve feldspar at 100–130°C for several hours to obtain soluble potassium salts. Alternatively, the mineral and phosphoric acid mixture was heated to a sufficiently high temperature to volatilise the potassium salts produced. Radaelli and Martelli[133] used 0.1–0.3 M phosphate solutions of Na, K, NH_4, Mg or Ca at 20 and 80°C. They found that calcium phosphate was highly effective in dissolving the mineral while sodium and magnesium phosphates were particularly effective at higher concentrations. Van der Leeden[134] studied the effectiveness of acetic acid for feldspar dissolution. Ilchenko and Guimaraes[135] treated feldspar with 0.2 N acetic acid and observed a pH rise of 3.46–3.90 in 24 h and a 25% by weight dissolution in 32 days; they found that acetic acid was more effective than alkalies. Stephenson[115] investigated the dissolution of feldspar in alkaline solutions and noted that fluorides and borates in small amounts did not influence as mineralisers in the presence of other substances. Thomisaka[136] studied the solubility of feldspars in acid, neutral and alkaline solutions and suggested a feasible alkali-feldspar system supported by the thermodynamic and reaction kinetic theories. Swayze[137, 138] mixed amorphous feldspar, prepared by heating the feldspar mineral, with caustic potash and heated the mixture in a closed vessel under pressure to obtain potassium silicates and aluminates.

Scofield and La Rue[139] heated feldspar with 90% KOH at 275–325°C and obtained soluble potassium salts by treating the solution with CO_2 under pressure; Wildman[140] used SO_2 in place of CO_2. Charlton[141] digested feldspar with milk of lime and a small proportion of KOH of NaOH at > 160°C and 2000 lbs/in^2 in an autoclave. Peacock[142] treated a mixture or feldspar and a magnesium silicate such as serpentine rock or dumite with sufficient H_2SO_4 at 200°C for 24–48 h. Jackson[143] obtained soluble alkali metal compounds by heating feldspar, CaO and water in 1 : 1 : 5 under pressure at 200°C and corresponding steam pressure. Tregan[144] conducted solubility studies on feldspar (500 mg), using a mixture of 0.1 M Na_2CO_3 and $NaHCO_3$ (20 mL) in a closed tube at 20°C, and observed a rapid decrease in the solubility during the first hours of extraction. Later the reaction tended to reach equilibrium; heating reduced the solubility rates. Alekseyev *et al.*[145] measured the Gibbs free energies and reaction rates of feldspar dissolution in bicarbonate solutions on the paths to equilibrium, at 300°C, 88 bars and pH 9.0. Andrews[146] applied the counter current principle for potassium extraction and introduced feldspar and caustic lime with the digester at one end of the series. This was treated with liquor from the next preceding digester. The latter was fed with sludge from the first digester and with weak liquor from the third digester. Charlton[147] obtained soluble potassium salts by heating feldspar with a mixture of lime, $CaCO_3$ and water under 200 lb/in^2. In another method[148], feldspar was digested with lime and water at an appropriate temperature and 200–350 lb/in^2 by continuously forcing through a pipe cell. Halvorsen[149] heated feldspar with $CaCN_2$ to obtain soluble potassium compounds. Asaoka and Ando[150] recommended bittern with a small amount of $MgSO_4$ for calcination with feldspar at 800°C. Blackmore[151, 152] heated finely divided feldspar with a solution of $Al_2(SiF_6)_3$, Fe_2SiF_6, Na_2SiF_6, $(NH_4)_2SiF_6$ or $MgSiF_6$ at 175°C and 200 lbs/in^2 to obtain soluble potassium compounds. This method was advantageous in avoiding the corrosive action of HF on the apparatus as might occur when H_2SiF_6 was used. Anderson[153] decomposed feldspar by heating with a solution of 5% HF and 95% H_2SO_4 under 50–75 lbs/in^2 at 135–175°C.

McIlhiney[154] treated feldspar with aqueous HF and heated the product, potassium silicon fluoride, with $CaSO_4$ to produce K_2SO_4. Foote and Scholes[155] could obtain near 90% decomposition by heating 10 g finely ground feldspar with 10 g H_2SO_4, 10 g water and 1 g CaF_2 in a sealed tube at 140–150°C for 20 h. Chiba and Takijima[156] studied the effects of sucrose addition on feldspar under water-logged condition. Gogolev[157] reported that citric acid at pH 3.3 and calcium citrate at pH 6.5 decompose feldspar intensely at first; after two months an organomineral film was formed on the mineral grains and the reaction stopped. Leleu *et al.*[158] found that the dissolution of feldspar in oxalic acid was incongruous and accompanied by an increase in surface area. Song and Haung[159] found the rates of potassium release to vary with the nature of organic acid, chemical composition at bonding, crystal structure and formation sequence of the mineral. Bevan and Savage[160] measured the rates of dissolution at 70 and 95°C at pH 1.0, 4.0 and 9.0 in aqueous solutions with and without oxalic acid at

50 MP_a using direct sampling autoclaves. Oxalic acid increased the dissolution rate at pH 4.0 and 9.0 but the rate decreased at pH 1.0. The dissolution mechanism was not through preferential complexation of Al, but by an increase in the overall solubility of feldspar. Suvorov[161] observed that organic acids such as fulvic acid and humic acids decomposed soil minerals through destruction of crystal lattice; layerised minerals decomposed faster than the skeleton minerals. Tan[162] discussed the degradation of soil minerals by humic acids and pointed out that a 100–1000 nm diffusion layer is formed on the mineral surface and acts as a diffusion barrier to slow down further diffusion.

Volatilisation

One of the important techniques of potassium extraction from feldspar employs treatment at higher temperatures to separate the potassium salts by volatilisation. Though the technique needs equipment that is not simple, the simplicity of the process might have drawn the attention of many a researcher to find sufficient information in literature which is presented in the following lines.

Schneider[163, 164] removed the potassium content of feldspar by volatilisation in a blast furnace using coke as fuel. Only sodium accompanied while the rest comprising salts of Ca, Mg, Al, Fe and SiO_2 remained. Peacock[165] heated feldspar with carbon at less than atmospheric pressure and 2000°C to form volatile carbides. Similar treatment in a non-oxidising atmosphere containing a large percentage of nitrogen at above 1600°C resulted in the formation of K_2CN_2 and $Al_2C_3N_6$. These products yielded NH_3, K_2CO_3 and Al_2O_3 on treatment with superheated steam under a pressure of 4–5 atm[166]. Brown[167, 168] used $CaCl_2$ to volatilise potassium as its chloride. On the other hand Huber and Reath[169] employed CaF_2 to volatilise potassium as its fluoride and treated the KF with $CaSO_4$ to regenerate the CaF_2. Schmidt[170] roasted feldspar with lime in the presence of SO_2 and oxygen to separate the volatile potassium compounds by condensation. Reid[171] used $CaCl_2$ while heating the system by internal action of an electric current; KCN was produced by replacing $CaCl_2$ with calcium carbide and nitrogen[172]. Benham[173] did similar experiments by mixing feldspar with coal, $CaCl_2$ and limestone in a blast furnace at 900, 1000 and 1600°C. More than 90% of the total K_2O was volatilised from up to 110 tonnes of the above mixture. Hurst[174] described an apparatus for volatilisation of alkalis through forcing powdered feldspar by an air blast or a current of steam along a field tube and through an inverted U-tube heated to 1500–1800°C by a bath of molten metal.

Electrolysis and Dialysis

It had been reported[113, 175] that electrolysis in the presence of a small quantity of HF extracted 87% of the total K_2O present in feldspar. The authors[113] considered the action of electrolytes to set free the basic ions adsorbed by the colloid decomposition products. Anderson[176] produced KOH by mixing feldspar with carbon and electrifying the mixture in a solution of H_2SiF_6. Solubility of feldspar was found to increase in aqueous suspension after subjecting to A.C. and D.C. for 148 h[177]. Armstrong[178] could extract over 50% of the alkalis present by grinding feldspar to 0.1 μ under water and electrodialysing the suspension in an agate mortar. Taylor and Bond[179] proposed that dissimilar mineral pairs such as granite-orthoclase in contact with an electrolyte acquire surface potentials at the interphase boundary affecting dissolution of the mineral on short-circuiting. They discussed the possible application to electropotential changes in soil profiles.

Decomposition by Microorganisms

Wagner[180] investigated on 43 mineral samples to isolate a few microorganisms utilising oxalate in the disintegration of the minerals. *Flavobacterium extorquens, Pseudomonas* species, *Alkaligenes faecalis, Alkaligenes* species, *Agrobacterium radiobacter* and *Vibrio* species assimilated crystals of calcium oxalate to obtain optimum growth in liquid medium at 0.5–1.0% oxalate concentration; concentrations of over 25 inhibited growth. All these species were able to obtain the necessary metallic ions from several minerals including orthoclase. Wagner and Schwartz[181] studied the effect of bacteria on the surface of feldspar and their role in erosion. Eckhardt[182, 183] investigated the effect or pure cultures of yeast strains and filamentous fungi at room temperature and reported only moderate degradability for feldspar. Yeast strains induced the least degradation while *Aspergillus niger* had shown the lowest pH and the highest cation concentration. Mishustin *et al.*[184] observed that β-*mucilagnosis* removed *ca.* 15% K_2O while *Azotobacterchrocium* removed only < 7% of feldspar in a medium of 0.5% sucrose. Zahra *et al.*[185] observed that soil inoculation had a positive effect on the release of potassium and silicon from potassium-bearing minerals and increased plant uptake of the elements. Mansour *et al.*[186] studied the susceptibility of orthoclase to biological weathering by *Bacillus circulars* and *Arthrobacter tutmescens*.

Fertiliser from Feldspar

Feldspar was considered[187] a better source for manufacturing potash fertilisers owing to its favourable composition and higher rates of extraction of K_2O and Al_2O_3. Solberg's[188] experiments on plastic feldspar and clay showed much less satisfactory effects than the micas for improvement of the soil. Metson and Saunders[189] found calcined feldspar to give only a slight response as a potassium source to white clover crop. The response was relatively greater on a potassium-deficient soil though less effective than KCl. De Turk[190] applied 2 tonnes of feldspar per acre to limed peat soil and found an increase in the yield of buckwheat from 20 to 35%. Hartwell[191] observed that under nutrient conditions believed to be sub-optimum for only potassium, feldspar (from Maryland) was slightly more efficient than high-grade muriate of potassium sulphate when supplying the same amount of water-soluble potassium. Haley[192] conducted detailed studies on the availability of potassium for buckwheat plants grown in sand cultures. Fifty grams portion of feldspar supplied potassium at a sufficiently rapid rate to satisfy the requirements for a 7% larger yield of dry matter than was obtained with the complete nutrient solution. The total amount of potassium adsorbed from feldspar was in no case as large as with the complete nutrient solution but it was apparently utilised more economically. Carbonate or sulphate of calcium increased the potassium availability; sodium salts had only slight effect while dextrose and starch reduced the weight of dry matter as well as the amount of potassium-absorption. Jiang and Luo[193] determined the slowly available potassium in feldspar by boiling with nitric acid. The total amount released from the mineral varied with particle size with the largest amount coming from the $< 2\mu$ fraction.

Many efforts have been made to convert the feldspar into a fertiliser. These employ heating in reduced atmospheres[16, 109, 110, 194–196], fusion with sodium salts[40, 197] and calcium salts[71, 72, 76, 102, 198–204] and as described earlier under these heads. Andre[205] ground feldspar with 1% solution of NaCl, $CaCO_3$, $Ca_3(PO_4)_2$, $NaNO_3$, $(NH_4)_2SO_4$ and $CaSO_4$ for 130 h in an agate mortar and obtained 2–7% of K_2O into the suspension. Breckenridge[206] outlined his own efforts to render potassium in feldspar soluble. Jackson[207] prepared a fertiliser after digesting feldspar at 95°C for 6 h with an excess of lime and six times as much water. Richardson[208] mixed CaF_2, cryolite or other fluorides with ground feldspar and added sulphuric acid to generate HF for converting the potassium content into a soluble one. Vanatta[209] noticed a beneficial effect on plant growth after treating with feldspar containing added organic matter in the form of blue grass. Available K_2O was furnished by the blue grass either on its decay or by liberating potassium from the feldspar. Otherwise, the potassium content of the feldspatic rock was of little value in furnishing readily available plant food especially for wheat and clove[210]. Mansour *et al.*[186] studied the susceptibility of feldspar to biological weathering by two strains of *Bacillus circulars* and one strain of *Arthrobacter tutmescens*. These strains were effective enough to make it the system slow-release fertiliser; they found the latter strain as the most effective.

Feldspars as Catalysts

Rebuffat[211] observed that the solid residues obtained by the selective extraction of potassium from feldspar became excellent carriers for catalytic materials after suitable treatment. Some of them possessed adsorbent and catalytic properties useful for the cracking of petroleum[23]. Bridger and Harboard[212] prepared a catalyst for steam reforming of hydrocarbons by impregnating a metal such as nickel on to feldspar. Siegel and Siegel[213] investigated on the enzyme-like catalytic behaviour of 27 silicates including feldspar and observed catalase activity for H_2O_2 decomposition in all cases. Shindo and Huang[214] examined the catalytic effect of feldspar for the polymerisation of hydroquinone; manganese-bearing silicates showed higher catalytic activity in comparison to feldspar. Pugh[215] studied the surface chemical sites on several fillers such as feldspar by adsorption of well defined acidic probes from cyclohexane solutions. The adsorption data emphasised the wide range of site heterogeneity, acidic probes adsorbed on all the minerals indicating a predominance of basic over acidic sites.

Cement from Feldspar

Cement was prepared by heating feldspar with calcium compounds[57, 71, 78, 147, 167, 169, 216–219] and collecting the residue after separating the alkali compounds. Jungner[220] liberated the alkali salts by facilitating their volatilisation through addition of 4% finely divided coal to a mixture of limestone and feldspar and heating to 1250–1450°C. Langlois and Langlois[221] made a cement by grinding 100 parts of Portland cement and 32.6 parts of powdered feldspar through crushing and tearing action to convert the SiO_2 into 3.5 SiO_2–4 CaO and the Al_2O_3 into $Al_2O_3 \cdot CaO$. Rhodin[30] heated a mixture of ground feldspar and a small amount of NaCl in a reverberatory furnace and reacted upon with a mixture of SO_2, steam and air. The solid material remained after leaching out the K_2SO_4 was suitable for use in making white Roman or Portland cement.

Conclusion

The importance of feldspar as an industrial raw material is ever growing. If attention is diverted to its potassium content, the mineral can be successfully explored to extract this strategic metal. In addition, the characteristics of feldspar point to its promise as a fertiliser or catalyst and for cement. Explorative work on feldspar, which began in the early part of this century, is yet to attract the industry. It is hoped that the past presented in this article may impress many researchers in the field to draw a future line of action for feldspar to be utilised to its full potential and total promise. Work has already been initiated at the Regional Research Laboratory, Bhubaneswar, India in this direction.

ACKNOWLEDGEMENTS

The authors thank Dr. S.B. Rao, Head, Inorganic Chemicals Division for suggesting the work and Prof. H.S. Ray, Director for the facilities.

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(*Received:* 1 April 1998; *Accepted:* 15 April 1998) AJC-1468