THE EVAPORATION OF POTASSIUM FROM PHLOGOPITE

M. Khalighi and *P. Minkkinen*

DEPARTMENT OF CHEMICAL TECHNOLOGY, LAPPEENRANTA UNIVERSITY OF TECHNOLOGY, P. O. BOX 20, SF–53851 LAPPEENRANTA, FINLAND

The evaporation of potassium from phlogopite was investigated by roasting phlogopite with different chemical reagents. The possible reactions between reactants and the sample at different temperatures were investigated by thermogravimetry. Gypsum, calcite, sodium chloride, activated carbon, calcium chloride and fluoride were used as chemical reactants. Similar tests were carried out by batch experiments using muffle furnace and tube oven and finally the sample mixtures were heated in a vacuum. The use of a vacuum enabled an almost complete extraction of potassium in solid state at the lowest temperature so far investigated. The structure of phlogopite was shown to be destroyed by raising the temperature. The extraction of potassium from feldspar, a sample from Lohja, Finland was also investigated.

Raw material

The only possible potassium sources in Finland are mica, feldspar and nepheline, with a relative potassium content of 7–10%. The phlogopite-mica investigated in this work is produced as a by-product (>3 m.tpa) of the flotation process at Siilinjärvi apatite mine near Kuopio in eastern Finland. A carbonatite body which has been intruded by the granite-gneiss is a source of about 10% apatite, 19% carbonate, and 65% phlogopite.

The sample investigated in this work consists of 98–99% phlogopite with some impurities of calcite, dolomite, dark silicates, and apatite (prelimi-monoclinic system with a hardness of 2.5–3.0 in the Mohs scale and a specific nary data from Kemira OY). The chemical composition of the material is given in Table 1.

Table 1 Chemical composition of phlogopite-mica in the Siilinjärvi ore

	Weight %
Al_2O_3	10.8
K_2O	10.5
MgO	23.8
FeO, Fe_2O_3	10.0 as Fe_2O_3
SiO_2	40.5
F	1.0
H_2O	3.4
Impurities: Ti, Ca, Na, Mn, P	

Phlogopite has a pearly to submetallic lustre. It is crystallised in the monoclinic system with a hardness of 2.5—3.0 in the Mohs scale and a specific gravity of 2.76—2.90.

With an idealised formula of K_2 $(Mg, Fe)_6$ $[Al_2 Si_6 O_{20}]$ $(OH,F)_4$, which gives the number of ions in the unit cell, it is a trioctahedral mica, a mineral with a layered structure. The basic structural feature of mica is composite t-o-t layers in which a sheet of the octahedrally coordinated cations is sandwiched between two identical sheets of linket $(Si, Al)O_4$ tetrahedra.

Between these composite layers lie the interlayer cations, K^+ or Na^+. Octahedral sites are generally filled by Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Ti^{4+}, etc. The metallic ions in the octahedra are surrounded by four oxygen and two hydroxyl ions [1], the latter can be partly replaced by F-ions.

The potassium ions in the mica structure are arranged parallel to tetrahedral and octahedral sheets. The bonding of the potassium layer sandwiched between tightly linked (Mg, Al)-O and (Si, Al)-O sheets is relatively weak [2], which may explain the relatively easy exchangeability of potassium with other alkali or alkaline earth ions.

The bonding energy for potassium in dioctahedral micas such as muscovite is much higher than in trioctahedral ones such as biotite and phlogopite [3]. Furthermore, of these two trioctahedral micas, the Mg rich phlogopite has a higher bonding energy than the iron-rich biotite. This is probably the reason that the trioctahedral micas are less stable than the dioctahedral ones.

Previous work

As potassium is one of the most important elements for the growing of plants, mica minerals high in potassium content in soil and sediments have often been the subject of investigations in soil science. Investigations had been carried out into natural and induced weathering of different mica minerals. During weathering, the interlayer potassium of the mica can be replaced by alkaline and alkaline-earth cations and the structure of the original mineral may change to that of a vermiculite-like mineral [4].

The vaporisation of alkaline at high temperatures starts at between 800 and 1000° and increases with higher temperature and longer heating time. Potassium oxide evaporates more easily than sodium oxide and the evaporation of alkalies decreases in the order of illite, mica, feldspar [5—7].

It was Sprengel [8] in 1830 who first suggested utilising the potassium content of silicate minerals and stones. Since then, numerous attempts to find an economical method of using this vast primary source of potassium in nature have failed. Gmelin Handbook [9], gives a wide survey of some of these attempts, which can be summarised as follows:

1— Raw materials used are: K-Al-silicates, feldspar, leucite, nepheline, mica, Georgia-schist, glauconite, etc., with less than 13.5% K_2O content.

2— Reactants used are: $CaCO_3$, CaO, CaC_2, CaF_2, $Ca(OH)_2$, $Ca_3(PO_4)_2$, $CaSO_4$, $CaCl_2$, NaCl, $NaHSO_4$, NH_4Cl, $POCl_3 + CaCl_2$, $FeCl_2$, FeS, FeS_2, S, C, etc.

3— Atmospheres in which the specimens were heated were given: air, N_2, Cl_2, SO_2, HCl, steam, etc.

4— The maximum temperature used was 2500°.

The potassium was then evaporated and condensed, leached, dissolved and precipitated by other chemicals in a more or less complicated way and up to 90% of the K-content could be recovered.

Some of these processes have been tested on phlogopite samples from Siilinjärvi. For comparison, feldspar from Lohja OY was also investigated.

Experimental

Thermobalance tests

Before starting the actual experimental tests, some thermogravimetric analyses have been carried out on the raw material and the reactants to investigate the possible mechanisms of the reactions. Tests were carried out in a dynamic air atmosphere with a Netzsch Thermobalance STA—409, capable for the simultaneous recording of TG, DTG and DTA curves. The heating rate was 10 deg/min, using open-type Al_2O_3 crucibles with 0.3 ml in volume and china clay as the reference material.

When two or more components were required as reactants, these were first mixed together, and then the ore was added to this mixture and mixed thoroughly to ensure intimate contact between the raw material and the reagents. The mixture was then transferred to the crucibles by means of glazed transparent paper.

Phlogopite heated alone shows a weight loss of 4% at between 1020— —1600°, which may correspond in part to dehydroxylation and the loss of some of its fluorine content (Fig. 1). For a more exact analysis of these
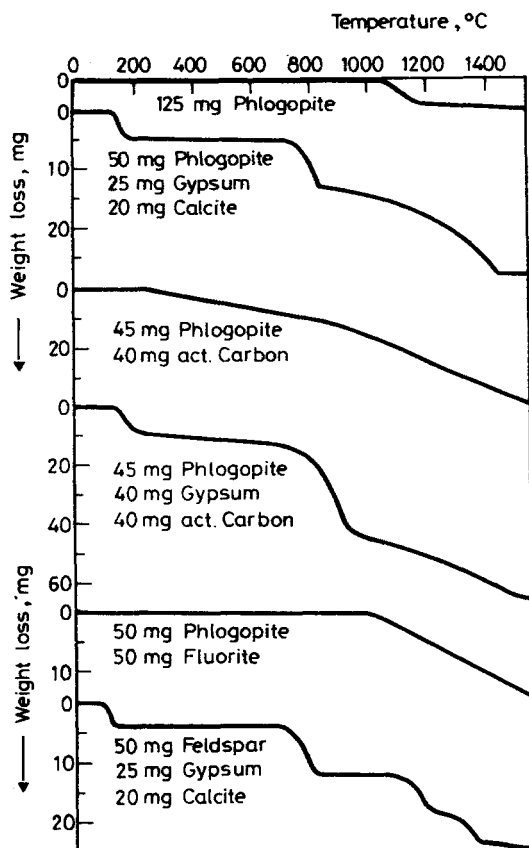
Fig. 1 Thermogravimetric curves of phlogopite or feldspar containing mixtures

evaporites an evolved gas analyser should be used. An X-ray fluorescence analysis of the residue left in the crucible showed no evidence of evaporation of the potassium. At higher temperatures the ferrous iron contained in phlogopite can oxidise to Fe^{3+} by taking oxygen from the air. Consequently the sample gains in weight. This can not be seen on the TG-curve because at the same time some water will be produced from hydroxyl groups which causes a loss in weight [10].

$$4\,Fe^{2+} + 4\,OH^- + O_2 \longrightarrow 4\,Fe^{3+} + 4\,O^{2-} + 2\,H_2O$$
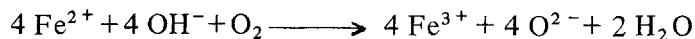
Phlogopite, gypsum and calcite were mixed at a ratio of 2:1:1 and heated to 1600° (Fig. 1). The weight loss at 110–170° corresponds to the dehydration of the gypsum and at 710–840° the loss of 9.0% corresponds

to the complete decarbonisation of the calcite. Anhydrous gypsum already starts to decompose at 900°. A loss of 15.5% at 900−1450° corresponds to the complete evaporation of potassium, and also to the partial evaporation of the Fe- and SO_2-contents, verified by analysing the fused mass. Some 3% S is still contained in the fused mass, which might be in the form of metal sulfide. The fluoride content of phlogopite might also evaporate in the form of HF, KF or even as SiF_4.

A mixture of phlogopite, gypsum and activated carbon was prepared and heated to 1600°. Dehydration of the gypsum appeared as usual on the weight-loss curve at 120−190° (Fig. 1). The gently inclined slope of the TG curve showed slow burning of carbon until 820°. The anhydrous gypsum was decomposed completely at 820−950° with a loss of 17.5% showing that the major part of the SO_2 had evaporated. At this stage another part of the released SO_2 reacts with part of the potassium released from the phlogopite forming K_2SO_4, which then decomposes and evaporates at higher temperatures. Between 950−1600° there is a loss of 19.5% in weight due to the complete evaporation of K_2SO_4 and the burning of the remaining carbon. In addition the hydroxyl and fluoride contents of phlogopite can partly evaporate at this last stage. An X-ray fluorescence analysis of the fused material showed no traces of sulphur left in the residue, but about 3% K which can only exist as a silicate.

Phlogopite mixed with fluorite at a weight ratio of 1:1 was heated to 1600°. The volatile components from the phlogopite already started to vaporise at 1000°. A loss of 13.5% at 1000−1600° recorded on the weight-loss curve is mainly due to the complete evaporation of potassium, tested by X-ray fluorescence analysis on the fused mass (Fig. 1).

A mixture of phlogopite with $CaCl_2 \cdot 2H_2O$ and activated carbon was prepared and heated to 900° at a rate of 20 deg/min (Fig. 2). Dehydration of the two molecules of water in $CaCl_2 \cdot 2H_2O$ occured completely at 110−−160°. Activated carbon was mostly burnt out at 360−840° and the evaporation of volatile gases like CO_2, CO and Cl as HCl, was less intense when the temperature was kept at a constant 900°. An X-ray fluorescence analysis of the residue showed that about 5% potassium and 8% chlorine still remained in the cake.

As the reaction between phlogopite and the reactant is related not only to the temperature but also to the time, the following two tests were carried out while keeping the temperature constant for a set period of time. Phlogopite was mixed with $CaCl_2$ and heated to 800, 900, 1000 and 1100° with a 20 deg/min heating rate (Fig. 2). Dehydration of $CaCl_2 \cdot 2H_2O$ occured at 100−160°. The loss in weight at 730−800° is due to the expulsion of Cl
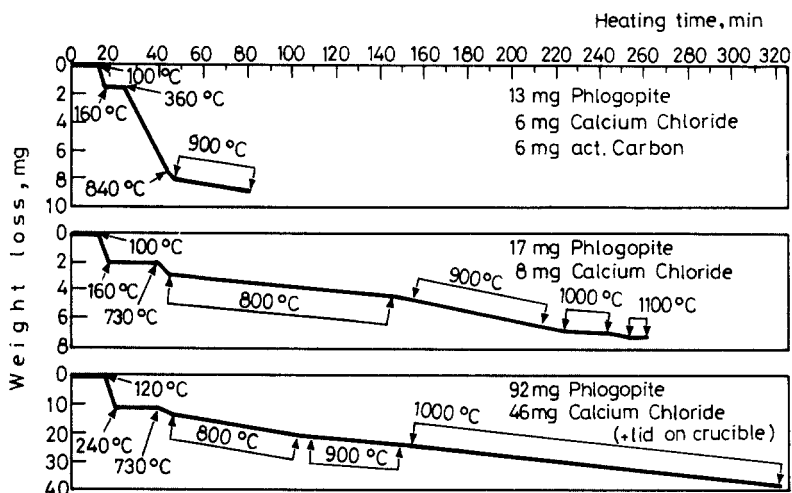
Fig. 2 Effect of heating time on the evaporation of volatile components in some phlogopite/reactants mixtures

as HCl, which then continues to volatilise slowly when the temperature is kept at a constant 800° for about 100 minutes. A small part of potassium also evaporates during this latter stage, this becoming more intense at 900° with the remainder evaporating at 1000°. No further loss in weight was recorded on the TG curve at 1100° and an X-ray fluorescence test of the residue showed complete evaporation of the potassium and chlorine.

The experiment described above was repeated while keeping the furnace closed to any air intake. The crucible was filled to the brim with a phlogopite-calcium chloride mixture and was covered with an Al_2O_3 lid, so that the reaction could occur without any air moisture being admitted from outside. The mixture was heated to 800, 900, and 1000° at a rate of 20 deg/min. Dehydration of calcium chloride was delayed until 120–240°. At 730° Cl^- reacts with H^+, taken probably from the hydroxyl content in phlogopite, and evaporates as HCl more rapidly as the temperature rises to 800°. By maintaining the temperature at a constant 800° for about one hour the evaporation of the HCl was gradually slowed down showing a more gentle incline on the slope of the TG curve (Fig.2).

The gentle slope of the weight-loss curve remained almost constant when the mixture was heated for about 40 minutes at 900° and about 160 minutes at 1000°. Two samples were taken from the residue for X-ray fluorescence analysis. The one taken from the upper part of the cake showed

no potassium left but about 0.1% chlorine still remained. The other sample taken from the bottom of the cake showed both a higher content of potassium (0.3%) and chlorine (0.8%).

Roasting tests in a muffle furnace

Mixtures of fine grained phlogopite or feldspar ($\sim$ 50 μm) and the reactants were transferred to the porcelain boats and placed in the furnace at 800, 900, or 1000° and heated for 30 minutes. After the heating process, the components were leached, filtered, dried and checked with X-ray for the potassium content in the residue.

Evaporation tests in a tube oven

Two main reasons for the use of the tube oven were 1) the ore-mixtures could be brought into closer contact with air or some other atmosphere, 2) the vaporised components could be recollected and checked for their quality.

The effect of different atmospheres and heating times on the volatility of potassium in a series of different ore and reactant mixtures was examined with the help of a tube oven. A "Heraeus" oven with a maximum temperature of 1100° and a heating rate of about 50 deg/min was used. The porcelain tube of the oven was 60 cm long with an inside diameter of 3 cm.

A kind of collecting flask with heavy walls was tightly joined to one end of the porcelain tube, so that the flying fragments could be condensed and tested by X-ray fluorescence. Air or gas was blown into the tube from the other end at a flow rate of about 70 l/h.

Roasting tests in a vacuum

A metal tube made of stainless steel was used, with a diameter that could just fit inside the porcelain tube in the oven (Fig. 3). One side of the metal tube was welded to a 50 cm long copper pipe connected via a filter flask to the water-jet-pump [12]. From the other end, a sample carrier boat was placed into the tube and the pressure was reduced to about 6 kPa. The sample was heated to 800 and 900° for 30 minutes and to 1000° for 15 minutes. After the heating process the sample was cooled in a vacuum to about 200° and then it was removed and cooled further to room temperature. The potassium content in the cake before and after the leaching process was checked by X-ray method and the results are shown in Fig. 4.
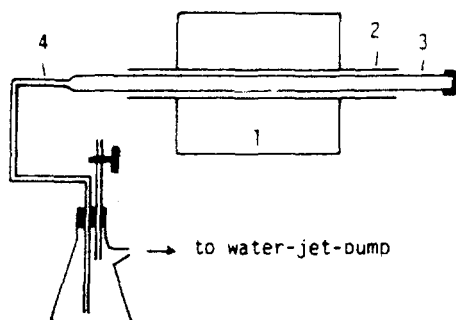
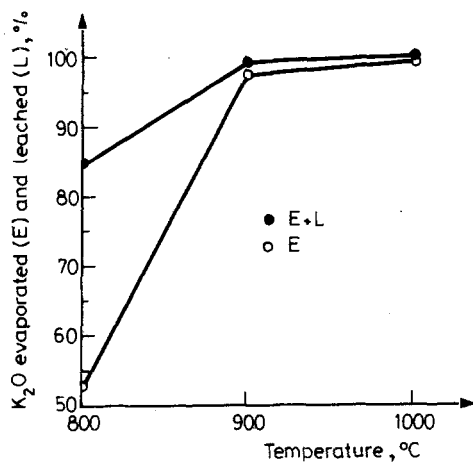Fig. 3 Schematic diagram of experimental apparatus. 1 Tube oven, 2 Porcelain tube, 3 Metal tube, 4 Copper pipe

Fig. 4 Evaporation and leaching of potassium from phlogopite mixed with $CaCl_2 \cdot 2H_2O$ and heated in a vacuum at a pressure of about 6 kPa

Results and discussion

Extensive removal of potassium from phlogopite and feldspar was observed in muffle furnace tests when the raw material was mixed with calcite and calcium chloride and heated to 800 or 900°. The chemistry of the reaction might be summarised as being that the reactants decompose at 800° the produced CaO combines with the attacked part of phlogopite or feldspar to form water-insoluble Ca-silicates or Ca-Al-silicates [13]. The released potassium will form KCl, which partly evaporates or remains in the cake and

can be easily leached out. The unattacked part of the raw material may contain the small amount of potassium still in the cake.

Feldspar behaved quite differently when it was mixed with calcium chloride and heated to 1000° in muffle furnace. When the temperature rose rapidly, some feldspar particles were apparently surrounded by a hard layer of semi fused Ca-Al-silicate that prevented the ore from further attack. However, calcium chloride was the most active reactant on phlogopite at 1000° and was capable of releasing up to 99% of its potassium content.

Although the structure of phlogopite is considered to be stable when heated with gypsum [14], these tests showed that by 1000° it is mostly destroyed (Fig. 5). Yet gypsum was not a good reactant for potassium extraction. The almost complete destruction of the phlogopite structure was observed when it was mixed with $CaCl_2$ and heated to 1000° for 30 minutes. Considering that in these reactions at high temperature Ca-salt reacts with ore to form Ca-silicates or Ca-Al-silicates (see above), the phases present in leached residue may appear as grossular, $Ca_3Al_2[SiO_4]_3$, monticellite, $CaMg[SiO_4]$ and olivine $(Mg, Fe)_2[SiO_4]$.
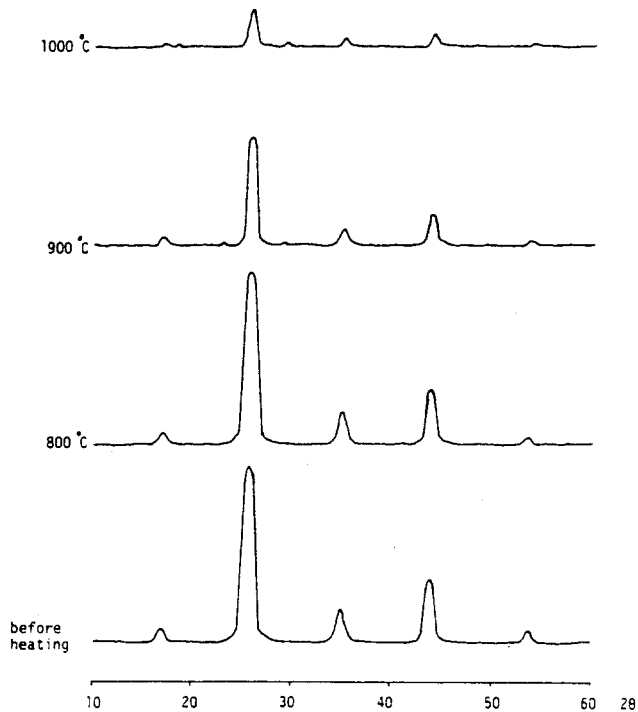

Fig. 5 X-ray diffractograms of unheated phlogopite and phlogopite-gypsum mixtures being heated at different temperatures for 30 minutes

Change in the heating time was not found to be a major factor affecting vaporisation of KCl from the ore. Neither did the use of steam accelerate the reaction but on the contrary, it reduced the volatilisation of KCl in a mixture containing phlogopite, calcium chloride and activated carbon.

The well known effect of grain size on the volatility of potassium was examined on phlogopite which was mixed with calcite and gypsum and heated in a muffle furnace for 30 minutes. After the leaching- and drying -process, the sample was checked by X-ray fluorescence and showed only a 43% extraction of potassium for the grain size of about 1500 μm, as opposed to the 97% when fine-grained (~ 50 μm) phlogopite was treated the same way.

The required amount of water for the reaction $CaCl_2 + H_2O \longrightarrow CaO + 2\ HCl$ may be taken partly or completely from the hydroxyl content in phlogopite.

The production of HCl always preceded KCl formation, because hydrogen has a higher propensity to react with chlorine than potassium. It also became clear that the produced HCl on its own had no effect on the ore with regard to the volatility of potassium. This was tested by blowing HCl-gas into the tube above a phlogopite sample and heating it at $1000°$ for 30 minutes. It was found that no potassium could be extracted from the ore.

The use of a vacuum should reduce the reaction temperature and raise the yield [15]. In order to test the effect of a vacuum on the volatility of potassium from phlogopite, a mixture of this and Ca-chloride was heated in the apparatus demonstrated in Fig. 3 at 800 and $900°$ for 30 minutes, and $1000°$ for 15 minutes. The results seemed to be more interesting than the other tests carried out in this work.

Up to about 52% of the potassium content of phlogopite had already evaporated at $800°$, in comparison with only 2% in the tube oven tests. The total amount of potassium that could be released at this temperature was about 85% of the potassium content in phlogopite. Part of this was evaporated as mentioned above and the difference could easily be leached out. These amounts were much higher at 900 and $1000°$ with less difference between the evaporated and leachable parts of the potassium (Fig. 4). Complete extraction of potassium from phlogopite took place at $1000°$ after a heating period of 15 minutes.

Some of the advantages of using a vacuum were: 1) The temperature inside the tube does not decrease as no gas flows into the tube. 2) Because no gas is being applied to the tube in the tests carried out in a vacuum, the temperature both at the surface and bottom of the sample mixture in the

boat will be the same. Consequently heat losses are minimised and the reaction proceeds at its maximum rate. 3) Because there is no gas flow, the vaporised KCl will not be carried out of the tube. 4) At 900° 99.5% of the potassium content can be released, of which 97% is evaporated and condensed in the tube and the rest could be leached out if economically feasible. 5) It enables the highest possible extraction of potassium in solid state at the lowest possible temperature so far investigated.

Conclusion

The potassium content of phlogopite-mica could be completely extracted in a solid state in an evacuated environment. Yet the utilisation of the methods introduced in this work have to be evaluated economically. Taking into consideration that other kinds of mica besides phlogopite are found at many places in Finland as quarry remains. And also bearing in mind that their potassium contents are sufficient for the demand in Finland, these methods may become commercially feasible with the depletion of richer raw materials, even though they are not in the current market.

References

1 R. P. Tripathi, U. Chandra, R. Chandra and S. Lokanathan, J. Inorg. Nucl. Chem., 40 (1977) 1293.

2 J. T. Iiyama and M. Volfinger, Mineral. Mag. 40 (1976) 555.

3 S. Feigenbaum, R. Edelstein, and I. Shainberg, Soil Sci. Soc. Am. J. 45 (1981) 501.

4 K. Krausz, Can. Mineralogist, 12 (1974) 394.

5 C. Goes, Schriftenr. der Zementind., Heft 24 (1960) 79.

6 F. G. Banit and A. V. Vasilik, Tsement, 6 (1972) 17.

7 V. Johansen, N. H. Christensen and F. L. Smidth, Szilikatip. Szilikáttud. Konf., 3 (1981) 97.

8 C. Sprengel and J. Erdmann, J. techn. Ökonom. Ch., 8 (1830) 220, (Ref. Gmelins Handbuch der Anorg. Chem., 8. Aufl., Syst. No 22, p. 1232).

9 Gmelins Handbuch der Anorganischen Chemie, 8. Aufl., Teil B, Syst. No. 28, p. 676 and p. 688 and Syst. No 22, 1938, pp. 1305.

10 A. C. D. Newman, Clay Minerals, 7 (1967) 215.

11 E. Aitta, M. Leskelä, J. Moilanen and K. Jyrkäs, J. Chem. Techn. Biotechnol. 37 (1987) 73.

12 M. Khalighi and P. Minkkinen, Publication No. 5. Lappeenranta University of Technology, Lappeenranta 1984.

13 W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, 2nd ed., J. Wiley and Sons, New York 1953.

14 E. Aitta, M. Leskelä and L. H. J. Lajunen, Kem. Kemi, 6 (1981) 411.

15 L. Hackspill and H. J. Pinck, Soc. Chim., 4 (1931) 55.

Zusammenfassung — Beim Abrösten von Phlogopit mit verschiedenen chemischen Stoffen wurde das Verdampfen von Kalium aus Phlogopit untersucht. Die möglichen Reaktionen zwischen der Probe und der Reaktionspartnern bei verschiedenen Temperaturen wurden mittels Thermogravimetrie untersucht. Als Reaktant wurden Gips, Kalzit, Natriumchlorid, Aktivkohle, Kalziumchlorid und -fluorid verwendet. Ähnliche Untersuchungen wurden in Reihenexperimenten mittels Muffel- und Röhrenofen und letztlich durch Erhitzen der Proben im Vakuum durchgeführt. Die Anwendung von Vakuum ermöglicht bei den niedrigsten der angewendeten Temperaturen einen fast vollständigen Auszug des Kaliums aus dem Feststoff. Durch Erhöhen der Temperatur wurde die Struktur von Phlogopit nachweislich zerstört. Die Extraktion von Kalium aus einer Feldspatprobe aus Lohja, Finnland, wurde ebenfalls untersucht.

Резюме – Выделение калия из флогопита было изучено путем обжига флогопита с различными химическими реагентами. Методом ТГ были исследованы возможные реакции между реагентами и образцом. В качестве реагентов были использованы гипс, кальцит, хлористый натрий, активированный уголь, хлорид и фторид кальция. Подобные испытания были проведены периодической загрузкой , используя муфельную и трубчатую печь, а также нагреванием смесей в вакууме. Использование вакуума позволило установить, что полное выделение калия в твердом состоянии происходит при самой низкой температуре, исследованных до сих пор. Показано, что при повышении температуры структура флогопита нарушается. Изучено также выделение калия из полевого шпата месторождения Лохья /Финляндия/.