

A MICROWAVE-ASSISTED METHOD FOR THE RAPID REMOVAL OF K FROM PHLOGOPITE

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Abstract—The ability to remove K rapidly with a solution containing sodium tetraphenylborate (NaTPB) from the interlayers of naturally-occurring phlogopite using a microwave-assisted technique has been examined. Samples were equilibrated with a 1.0 N sodium chloride (NaCl) – 0.2 N NaTPB – 0.01 M disodium ethylenediaminetetraacetic acid (EDTA) solution at 60, 80 and 100°C under both conventional and microwave-assisted heating methods and for periods of time ranging from 1 to 3 h. The samples also underwent treatments of either continuous time periods or for successive treatments of 1 h with a washing step between each treatment.

Following sample treatment, the expansion of the *c*-axis value (d_{001}) from 10.0 to 12.2 Å indicated the presence of hydrated Na ions in the phlogopite structure. Under most treatment conditions the 10.0 Å peak remained even after treatment due to incomplete K removal. Chemical analysis and X-ray diffraction (XRD) revealed that samples heated using microwave radiation exchanged their interlayer K for Na much more rapidly than under conventional heating for all treatment times and temperatures. The successive treatments also degraded the mica more rapidly than the continuous treatments. The greatest amount of K (95%) was removed when the mica was treated three times for 1 h at 60°C. The results suggest that successive treatments of phlogopite mica heated under microwave radiation will rapidly remove K from the mica. Decreasing the amount of time required to prepare K-depleted phlogopite micas will make these materials more appealing as ion exchangers for separation of Cs from nuclear wastes.

Key Words—Ion Exchange, K-depleted Phlogopite, Mica, Microwave, Radioactive Waste Disposal.

INTRODUCTION

Radioactive ^{137}Cs is commonly found in nuclear reactor and military wastes and presents an extreme hazard for humans and animals. Many synthetic and natural ion exchangers have been proposed for the removal of radioactive ^{137}Cs from aqueous wastes and for the decontamination of accidentally released radioactive species (Amplett *et al.*, 1958; Bortun *et al.*, 1998; Komarneni and Roy, 1982a,b, 1988; Komarneni, 1985; Mercer and Ames, 1978; Nelson and Mercer, 1963). Inorganic ion exchangers are in general better suited to removal of radioactive ^{137}Cs from the nuclear waste stream because of their greater radiation stability than organic ion exchangers (Johnson, 1999). Komarneni and Roy (1988) showed that K-depleted phlogopite is not only highly selective for ^{137}Cs , but also immobilizes Cs at room temperature through electrostatic bonding and upon heating at ~100°C through collapse of the mica interlayers as H₂O is driven out. Bortun *et al.* (1998) later confirmed that K-depleted phlogopite was effective for Cs⁺ removal from both neutral and alkaline solutions.

Potassium-depleted mica is created by the topotactic leaching of naturally-occurring phlogopite mica (Komarneni and Roy, 1988). The removal of interlayer K can be increased by the use of chelating agents selective for monovalent cations such as cryptand [222]

(Bracke *et al.*, 1995) and sodium tetraphenylborate (NaTPB) (Reed and Scott, 1966) and by treating phlogopite samples hydrothermally in concentrated saline solutions (Bortun *et al.*, 1998). Due to the advent of new techniques for recycling tetraphenylborate anions precipitated from solution (Ponder and Mallouk, 1999), the most promising method for the large-scale production of K-depleted phlogopite appears to be that of Reed and Scott (1966).

Through a series of experiments, Reed and Scott investigated the removal of K from the interlayers of several mica-type minerals using NaTPB to precipitate K from solution (Scott *et al.*, 1960; Scott and Reed, 1962a,b; Reed and Scott, 1966). These researchers determined that phlogopite is readily degraded using this method. One problem associated with the production of K-depleted phlogopite is the length of time needed for the complete removal of all K from the interlayers of the mica. To enhance the kinetics of K removal, ultrasonic treatments were used previously (Smith and Scott, 1966; Srikanth *et al.*, 1992).

The objective of this study was to determine if a microwave-assisted method could be used to increase the exchange kinetics of K removal from a phlogopite mica. Microwave heating has been proven to be useful for the acceleration of inorganic reactions in aqueous media reducing reaction time from days to mere minutes. Microwave radiation has been used for the synthesis of hydroxyapatite (Vaidhyanathan and Rao, 1996), ceramic oxide powders (Komarneni *et al.*, 1992) and zeolites

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(Cundy, 1998); however, the mechanisms of microwave-assisted reactions are still unclear. Scientists have proposed that microwaves have the ability to transfer their energy directly to the chemical reactants through dielectric heating (Neas and Collins, 1988).

MATERIALS AND METHODS

Preparation of <45 μm phlogopite

A sample of phlogopite, $\text{KMg}_3\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ (ideal formula), was obtained from Ward's Natural Science Establishment, Inc. Previous experiments on this same phlogopite sample using ^{27}Al magic-angle spinning nuclear magnetic resonance indicated that all Al in the sample is tetrahedrally coordinated (unpublished). The large single-crystal micas were initially split into small pieces by hand, followed by further grinding in a blender in the presence of deionized water. The mica was wet sieved and the <45 μm particles were utilized in the following experiments. Since all of the phlogopite used in these experiments was ground in an identical manner, grinding had no effect on the comparison of treated and untreated samples.

Potassium removal

Potassium removal was accomplished using the method of Scott and Smith (1966) under both conventional and microwave-assisted heating conditions. The conventional experiments were carried out in 30 ml polyethylene centrifuge tubes. Ten milliliters of a 1.0 N NaCl–0.2 N NaTPB–0.01 M EDTA solution were added to each centrifuge tube. The centrifuge tubes were placed in a hot-water bath and allowed to reach the treatment temperature. The <45 μm phlogopite (0.5 g) was weighed, added to each tube and allowed to react for

the predetermined experimental times without shaking. Both continuous and successive treatments were performed on the sample. The successive 1 h treatments were repeated a maximum of three times at the 60°C temperature only. The sample identification and treatments are shown in Table 1. An additional sample was treated for a period of 168 h with the same leaching solution at room temperature, washed and the procedure was repeated a total of three times.

The microwave-assisted experiments were performed using a MARS5 (CEM Corp., Matthews, NC) microwave digestion system. The microwave operates at a frequency of 2.45 GHz with a maximum power of 1200 W. The experiments were carried out in double-walled digestion vessels having an inner non-reactive Teflon PFA liner and an outer Ultem polyetherimide shell of high mechanical strength. Temperature and pressure probes allow the reaction to be controlled by monitoring the temperature and pressure within a control vessel. The maximum operating temperature and pressure for the system are 240°C and 350 psi, respectively. For this set of experiments, the microwave used a maximum power of 600 W and the percentage of power used was varied automatically by the microwave system in order to keep the reaction at the proper temperature for the treatment times.

The <45 μm phlogopite was weighed (0.5 g) into the non-reactive Teflon vessels and 10 ml of a 1.0 N NaCl–0.2 N NaTPB–0.01 M EDTA solution was added. The treatments are given in Table 1. The temperature within the vessel was ramped from room temperature to the treatment temperature within 2 min, then held at the proper temperature for the treatment time.

After the reaction was complete the conventional and the microwave-treated samples were processed identi-

Table 1. Heating method, temperature and duration of sample treatments.

Sample number	Conventional or microwave	Temperature (°C)	Time (h)	Treatments
60-1x1c	Conventional	60	1	1
60-2x1c	Conventional	60	1	2
60-3x1c	Conventional	60	1	3
60-1x2c	Conventional	60	2	1
60-1x3c	Conventional	60	3	1
80-1x1c	Conventional	80	1	1
100-1x1c	Conventional	100	1	1
60-1x1m	Microwave	60	1	1
60-2x1m	Microwave	60	1	2
60-3x1m	Microwave	60	1	3
60-1x2m	Microwave	60	2	1
60-1x3m	Microwave	60	3	1
80-1x1m	Microwave	80	1	1
100-1x1m	Microwave	100	1	1
Extended	Conventional	25	168	3

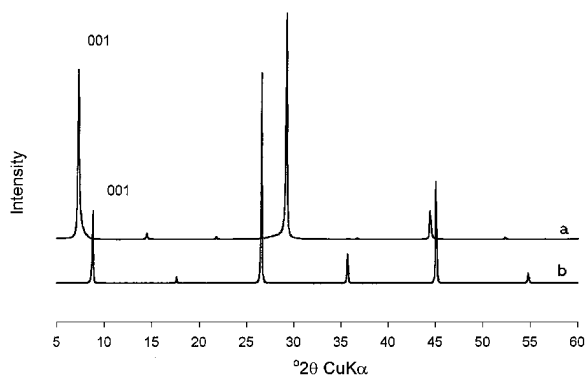


Figure 1. XRD patterns for untreated phlogopite and K-depleted phlogopite after three 168 h treatments with leaching solution: (a) K-depleted phlogopite; (b) phlogopite.

cally. The samples were suction filtered through Whatman 50 filter paper and the mica and KTPB precipitate were washed repeatedly with a solution containing 40 vol.% 0.5 N NaCl–60 vol.% acetone to dissolve the KTPB. The resulting K-depleted phlogopite was washed repeatedly with deionized H₂O to remove excess NaCl and allowed to air dry.

Chemical analysis of samples

Untreated and treated phlogopite samples were weighed (0.10 g) in triplicate into Teflon microwave reaction vessels. Fifteen milliliters of acid (20 vol.% 29 N HF and 80 vol.% 12 N HCl) were added to each reaction vessel. The vessels were sealed, placed in a MARS5 microwave and heated 15 min at 10% power per vessel and 600 W. The sealed vessels were allowed to cool overnight before opening. The digests were transferred to 100 ml volumetric flasks and brought to volume. The diluted digests were analyzed for K using atomic emission spectroscopy.

Characterization of samples

Powder X-ray diffraction (XRD) patterns were determined on the treated samples using a Phillips X'pert MPD diffractometer using graphite monochromated CuK α radiation. Samples were oriented preferentially using a wet-mount technique in order to enhance the 00 l family of lattice planes. By observing the increase in d_{001} , it was possible to determine the degree of K release for each treatment qualitatively.

RESULTS AND DISCUSSION

Treating phlogopite with the 1.0 N NaCl–0.2 N NaTPB–0.01 M EDTA leaching solution resulted in removal of K from the interlayers of the mica followed by replacement with Na ions and a monolayer of H₂O. The resulting K-depleted mica has an ideal formula of K_{1-x}Na_xMg₃Si₃AlO₁₀(OH)₂·nH₂O. When the interlayers of the mica are filled with hydrated Na⁺ the c -axis value d_{001} increases from 10.0 to 12.2 Å. This expansion is

readily seen when comparing the XRD pattern of the K-depleted phlogopite mica (Figure 1a) with that of untreated phlogopite (Figure 1b).

Although a significant amount of K was removed at all treatment temperatures, the XRD patterns for these samples showed both 12.2 and 10.0 Å peaks (Table 2). The 10.0 Å peak was highly prominent in all of the samples treated for 1 h. This indicates that a treatment time of 1 h is insufficient to remove large quantities of K from the phlogopite using any treatment temperature or heating method. Since some K remained in the mica under all treatment conditions, it is possible to compare the 12.2 Å peak intensity with the 10.0 Å peak intensity using an intensity quotient. This quotient can be used for semi-quantitative comparison of treatment effects (Table 2). Although no statistical analyses were conducted, the calculated ratios appear to correlate well with the chemical analysis of the samples.

Comparison of conventional vs. microwave-assisted heating

Although all sample treatments removed some K from the interlayers of the phlogopite, the extent of K removal was highly dependent upon the nature of treatment. In these experiments heating was done by either conventional or microwave-assisted techniques. Under all temperatures and treatment times the samples heated by microwave radiation released the most K. This result was substantiated by both wet chemical analysis and XRD analyses.

Chemical analysis indicated that the untreated K-phlogopite mica contained 2.11 meq K/g mica.

Table 2. XRD intensities and intensity quotients.

Sample number ¹	Intensity, d_{001} value		Intensity quotient ² (%)
	12.2 Å	10.0 Å	
60-1x1c	38124	10022	79.2
60-2x1c	142402	8860	94.1
60-3x1c	217529	3487	98.4
60-1x2c	41826	9343	81.7
60-1x3c	107096	29798	78.2
80-1x1c	30040	6771	81.6
100-1x1c	35933	11985	75.0
60-1x1m	25664	3210	88.9
60-2x1m	99116	4142	96.0
60-3x1m	125442	630	99.5
60-1x2m	72394	4923	93.6
60-1x3m	49245	7301	87.1
80-1x1m	17480	1975	89.8
100-1x1m	16509	3297	83.4
Extended	246523	74	100

¹ See Table 1 for treatment conditions

² Intensity quotient = intensity (12.2 Å)/[(intensity (12.2 Å) + intensity (10.0 Å)] × 100

Table 3. Potassium analysis of mica samples for temperature and heating-method treatments.

Heating method	Temperature (°C)	K in mica (meq K/g)	K removed (% ± S.D. ¹)
Microwave	60	0.721 ± 0.031	65.9 ± 1.5
	80	0.558 ± 0.010	73.6 ± 0.5
	100	0.606 ± 0.078	71.3 ± 3.7
Conventional	60	1.401 ± 0.005	33.7 ± 0.2
	80	1.019 ± 0.005	51.8 ± 0.3
	100	0.956 ± 0.009	54.8 ± 0.4
Untreated mica		2.114 ± 0.077	

¹ S.D. = standard deviation

Table 3 contains the K analysis for samples treated for 1 h at 60, 80 and 100°C using both conventional and microwave heating techniques. Microwave treatment increased the kinetics of K exchange under all treatment temperatures (Table 3). The amount of K removed increased by ~20% when samples were heated using microwave radiation. Under most treatment conditions the amount of K removed increased with increasing equilibrating temperature. Microwave heating of the samples at 60, 80 and 100°C resulted in K removals of 65.9, 73.6 and 71.3%, respectively (Table 3). Conventional heating of the samples at the same temperatures resulted in 33.7, 51.8 and 54.8% K removal, respectively (Table 3). The amount of K removed was slightly lower for the samples heated by microwaves at 100°C than those heated at 80°C. This may be due to decomposition of the tetraphenylborate anion under microwave-assisted conditions at elevated temperatures or due to increased solubility of the KTPB under microwave-assisted conditions. The intensity quotients for the samples heated at 100°C were also lower than for those heated at 80°C using both heating methods (Table 2). Future work on this project should evaluate the stability of the tetraphenylborate anion and the solubility of KTPB under both heating methods and over a range of temperatures and reaction times. More experiments are also needed to determine the ideal

temperature for maximum K removal under microwave-assisted conditions.

Although these experiments indicate a significant effect due to microwave heating, they unfortunately do not aid in the understanding of the causes of these effects. The observed rate increase under microwave heating may be explained by the generation of localized hot spots during microwave heating (Neas and Collins, 1988). The localized hot spots may accelerate the diffusion of ions into and out of the interlayers of the mica, thus increasing the rate of K removal.

Successive vs. continuous treatment

The samples which underwent successive treatments showed increased rates of K removal. Analysis of the sample prepared at room temperature with three successive 168 h treatments (extended treatment) showed that the mica contained 0.168 meq K/g mica after treatment, resulting in 92% K removal (Table 4). The conventionally-heated samples lost 50.6% K when treated continuously for 3 h and 82.7% K when subjected to three successive treatments of 1 h each (Table 4). The microwave-heated samples released 71.0 and 95.2% K under continuous and successive treatments, respectively, as above. The conventionally-heated samples released 47% when treated continuously for 2 h and 63% K when subjected to two successive 1 h treatments (Table 4). The microwave-heated samples released 74.3% K by the 2 h continuous treatment and 84.9% K by the two successive 1 h treatments (Table 4).

Figure 2 shows the XRD patterns for the samples heated at 60°C for continuous and successive 3 h time periods under both microwave and conventional heating methods. The XRD patterns for the samples receiving the continuous treatments showed the 10.0 Å peak indicating that these samples retained more interlayer K (Figure 2a,c). The pattern shows an almost complete disappearance of the 10.0 Å peak for the samples receiving successive treatments (Figure 2b,d). The XRD patterns for the samples prepared from the 2 h treatments exhibit similar behavior to those treated for 3 h (data not shown).

Table 4. Potassium analysis of mica samples for successive vs. continuous treatments at 60°C.

Treatment Method	Time	Microwave		Conventional	
		K in mica (meq K/g)	K removed (% ± S.D. ¹)	K in mica (meq K/g)	K removed (% ± S.D. ¹)
Successive	2 × 1 h	0.319 ± 0.01	84.9 ± 0.4	0.781 ± 0.03	63.0 ± 1.4
	Continuous	2 h	0.543 ± 0.01	74.3 ± 0.5	1.121 ± 0.01
Successive	3 × 1 h	0.102 ± 0.01	95.2 ± 0.3	0.367 ± 0.007	82.7 ± 0.3
	Continuous	3 h	0.613 ± 0.03	71.0 ± 1.4	1.045 ± 0.002
Extended Treatment	3 × 168 h			0.168 ± 0.01	92.0 ± 0.6

¹ S.D. = standard deviation

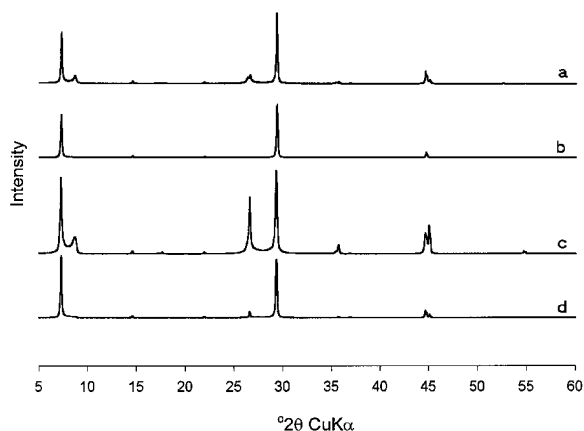


Figure 2. XRD patterns for selected continuous and successive treatments: (a) 3 h continuous microwave; (b) 3 h successive microwave; (c) 3 h continuous conventional; (d) 3 h successive conventional.

The results reported here agree with the preliminary experiments by Scott *et al.* (1960) indicating that the K in mica was removed more effectively by successive extractions rather than by continuous extractions for greater time periods. Bortun *et al.* (1995) also found successive treatments to be highly effective in the removal of interlayer K when treating samples hydrothermally at 180°C in 2 M NaCl. The presence of even low concentrations of K in solution will inhibit further removal of K from the interior of the mica flakes (Reed and Scott, 1962). This is apparently due to the collapse of the flake edges thus blocking the removal of K from the interior of the flakes. By washing the precipitated KTPB out of the equilibrating solution with acetone followed by replacement with fresh leachate solution, the amount of K being leached from the mica is increased.

Scott *et al.* (1960) stated that the discrepancy between amounts of K removed from successive and continuous treatments is probably due to ionization of some of the KTPB when acetone is added during the washing step, not due to solubility of KTPB in water. The solubility of KTPB is 1.5×10^{-4} M at 20°C and this would account for some residual K being present in solution. However, if the residual K was causing the samples with continuous treatments to remove less K than those with successive treatments then we might also expect the amount of K removed to decrease by increasing the equilibrating temperature under both conventional and microwave heating since solubility of KTPB is greater at higher temperatures. However, in this study a slight decrease in the removal of K was observed at 100°C compared to that at 80°C (Table 3) under microwave-assisted conditions only.

SUMMARY

The use of microwave-assisted heating in the presence of NaTPB will rapidly remove K from the

interlayers of phlogopite creating a K-depleted phlogopite mica. With successive treatments the majority of K (95% K) can be removed from the interlayers of the mica with as few as three 1 h treatments at 60°C. Although treatment times of <1 h and successive treatments at temperatures >60°C were not attempted, it can be postulated, based on these results, that using shorter successive treatment times at temperatures >60°C can produce a 100% Na-exchanged phlogopite ion sieve in <3 h.

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