

Uptake of cesium and strontium cations by potassium-depleted phlogopite

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Abstract

Phlogopite mica was equilibrated with 1.0 N sodium chloride (NaCl)–0.2 N sodium tetraphenylborate (NaTPB)–0.01 M disodium ethylenediaminetetraacetic acid (EDTA) solution at room temperature resulting in an almost complete removal (92%) of the mica's interlayer K. X-ray powder diffraction analysis provides additional evidence that hydrated Na⁺ ions had almost completely replaced the interlayer K⁺. Following equilibration, the *c*-axis spacing of the mica increased from 10.0 Å to approximately 12.2 Å. Cesium and Sr ion exchange isotherms indicate that K-depleted phlogopite is highly selective for both elements, the Cs⁺ exchange capacity is 1.26 meq/g or 65% of the theoretical cation exchange capacity and the Sr²⁺ exchange capacity is 1.94 meq/g or 100% of the theoretical exchange capacity of the mica. Kielland plots indicated that the mica was selective for Cs⁺ when the equivalent exchange capacity of Cs⁺ in the exchanger phase (\bar{X}_{Cs}) was <0.66 and selective for Sr²⁺ when \bar{X}_{Sr} < 0.41. At equivalent fractions greater than these levels, layer collapse and/or steric effects limit the diffusion of these ions into the interlayers of the mica. Analysis of the Cs⁺ equilibrated mica utilizing XRD indicated that a collapse of the *c*-axis spacing had occurred. Based on the high selectivity of <45- μ m K-depleted phlogopite for Sr²⁺ and Cs⁺, this material may prove useful as an inorganic ion exchanger for these radioactive isotopes.

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1. Introduction

Re-processing of nuclear fuels has resulted in the generation of large amounts of nuclear wastes containing the fission products ¹³⁷Cs and ⁹⁰Sr. These high-level radioactive wastes are often stored in underground stainless steel tanks at locations such as the Department of Energy Hanford Site. Over time, some of these tanks

have leaked, allowing radionuclides to enter the surrounding soils and groundwater. One potential method for remediation is to pump groundwater from the contaminated aquifer followed by treatment with ion exchange materials selective for these fission products. In order to consolidate the radionuclides into a waste form suitable for long-term storage, these materials must also be capable of withstanding intense radiation and elevated temperatures. Many classes of inorganic materials have been proposed for this purpose: zeolites (Mercer and Ames, 1978; Komarneni, 1985; Dyer et al., 1999;

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Sylvester and Clearfield, 1999), titanates (Nenoff et al., 1996), zirconium phosphates (Amphlett et al., 1958; Komarneni and Roy, 1982a,b), phyllosilicates (Sawhney, 1965; Komarneni and Roy, 1988; Bortun et al., 1998; Suzuki et al., 2000), and pillared clays (Sylvester et al., 1999). Potassium-depleted micas, a type of phyllosilicate, have also shown promise as ion exchangers (Komarneni and Roy, 1988; Bortun et al., 1998).

Micas are ideal candidates for use as ion exchangers due to their large layer charge and thermal stability. Most naturally occurring micas contain K within their interlayers, keeping the micas in a collapsed state (*c*-axis spacing $d_{001}=10.0$ Å). This collapsed state limits ion exchange to the edges of the mica flakes and causes the exchange reactions occurring between the interlayer K and other cations to proceed at a very slow rate. Even though reaction kinetics are limited, $^{137}\text{Cs}^+$ is mainly retained in the micaceous fraction (biotite, muscovite, and vermiculitized biotite) of contaminated sediments (McKinley et al., 2001). In order for micas to be useful as industrial ion exchange materials, their interlayer K must be replaced with small hydrated cations such as Na, which can easily undergo ion exchange, resulting in an expansion of their d_{001} spacing and an increase in surface area.

Many procedures have been reported for the removal of K from the interlayers of micas. Much of the research in this area has concentrated on the use of compounds that selectively precipitate K, such as sodium tetraphenylborate (NaTPB) (Scott et al., 1960; Scott and Reed, 1962a,b; Reed and Scott, 1966; Scott and Smith, 1966, 1967), cryptand [222] (Bracke et al., 1995), and sodium cobaltinitrite (White, 1950). Other scientists have succeeded at removing K from the interlayers of micas by reacting them with molten salts (White, 1954) or exposing them to concentrated saline solutions under hydrothermal conditions (Bortun et al., 1998).

Production of K-depleted phlogopite for use as an inorganic ion exchanger for radioactive ions has become more economically feasible due to a novel technique using the sodium tetraphenylborate method of Scott and Smith (1966) and microwave-assisted heating (Stout and Komarneni, 2002). Use of microwave radiation decreases the amount of time needed for almost complete removal of K from the interlayers of phlogopite micas from days to mere minutes (Stout and Komarneni, 2002). Microwave radiation may increase the reaction kinetics by increasing the rate of K diffusion out of the interlayers. The production costs for the preparation of K-depleted phlogopite may also be reduced through the use of new methods for recycling the tetraphenylborate anion (Ponder and Mallouk, 1999).

Previous research indicated that K-depleted phlogopite <20 μm showed promise for use as a sorbent for removal of Cs^+ from nuclear wastes and contaminated groundwaters (Komarneni and Roy, 1988). Even though the mica excels at Cs^+ removal, few scientists have investigated its ability to uptake other cations. After using a hydrothermal method to leach K from phlogopite and biotite, Bortun et al. (1998) investigated the ion exchange behavior of these micas towards Li^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Pb^{2+} , Hg^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , and Zn^{2+} . The objective of the research reported here was to determine the uptake characteristics of <45- μm K-depleted phlogopite following extended leaching using the method of Scott and Smith (1966) for both Cs^+ and Sr^{2+} through the creation of ion exchange isotherms and Kielland plots. Cesium and Sr ions were studied due to the need for the removal of their radioactive isotopes from nuclear-waste-contaminated groundwater.

2. Materials and methods

2.1. Preparation of the K-depleted phlogopite

Large single crystals of phlogopite mica were obtained from Ward's Natural Science Establishment, Inc. The crystals were broken into small pieces by hand followed by grinding in a household blender in the presence of de-ionized water. After grinding, the mica slurry was wet-sieved and the <45- μm size fraction was collected for use in this study. Powder X-ray diffraction patterns obtained before and after grinding the phlogopite indicate no decrease in crystallinity.

Potassium was removed from the phlogopite mica flakes using the procedure described by Scott and Smith (1966). The <45- μm mica (5 g) was equilibrated with 100 ml of a solution containing 1.0 M sodium chloride (NaCl)–0.2 N NaTPB–0.01 M disodium ethylenediaminetetracetic acid (EDTA) for 168 h at room temperature. This procedure was repeated for a total of three times to ensure the maximum removal of K from the interlayers of the mica. The samples were suction-filtered through Whatman 50 filter paper and washed repeatedly with a solution containing 40% 0.5 N NaCl–60% acetone (*v/v*) to remove the precipitated KTBP from the sample. After the initial washings, the K-depleted phlogopite was washed with a large volume of de-ionized water under vacuum to remove all entrained NaCl and allowed to air-dry.

2.2. Characterization of the K-depleted phlogopite

Powder X-ray diffraction (XRD) patterns were obtained for the unaltered mica and the K-depleted phlogopite using a Scintag PAD X θ – 2θ diffractometer utilizing $\text{Cu K}\alpha$ radiation and a germanium solid-state detector. The samples were mounted in a side drift cavity in order to reduce preferred

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