



Synthesis and characterization of 1:1 layered uranyl silicate mineral phases

Nathalie A. Wall, Sue B. Clark*, Jeanne L. McHale

Department of Chemistry, Washington State University, Pullman, WA 99164-4630, United States

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ABSTRACT

Sodium boltwoodite ($\text{Na}[(\text{UO}_2)(\text{SiO}_3\text{OH})] \cdot x \text{H}_2\text{O}$), uranophane ($\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot y \text{H}_2\text{O}$), and sklodowskite ($\text{Mg}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot z \text{H}_2\text{O}$) were synthesized in our laboratory using an optimized procedure described herein. Mineral identities were confirmed using powder X-ray diffraction. We also characterized our uranophane using Raman spectroscopy. The surface area of each material we produced was determined by two methods. We used the standard BET approach (gas phase absorption, N_2), and we also estimated surface areas in solution using sorption of methylene blue. These two techniques provided markedly different results, possibly due to the collapse of the mineral structure under the vacuum necessary for the BET analysis. In aqueous suspensions, the surface areas are 83 ± 10 , 72 ± 7 , and $47 \pm 4 \text{ m}^2/\text{g}$, for sodium boltwoodite, sklodowskite, and uranophane, respectively, using the methylene blue sorption method. The amount of water associated to each mineral was determined by thermogravimetric analysis. Results showed that minerals that had been dried in a desiccator contained less structural water than samples that had been allowed to set in aqueous suspension. The numbers of water for dry sodium boltwoodite, uranophane, and sklodowskite were found to be $1.5 (\pm 0.1)$, $2.8 (\pm 0.6)$, and $6.0 (\pm 0.6)$, respectively. The zeta potentials in suspension of 0.1 M NaClO_4 were similar for all three minerals, decreasing from -20 mV to -45 mV from pH 5 to 12, and remaining stable over a 10 day time period. The combination of a large surface area and negative zeta potential implies that these solids will behave much like clay minerals, serving as important sinks for other dissolved radioactive cations present in radioactive waste repositories.

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1. Introduction

The 35,000 MT of used nuclear fuel from commercial power plants in the United States is currently destined for geologic disposal in an engineered repository (Stucker and Stanley, 1995). To assess the performance of the repository for the isolation of the radioactivity, knowledge of the source term and its geochemical behavior are needed to estimate the release of contaminants from the repository. These estimates must span the regulatory time period of the repository, currently 10^6 years as defined by the US Nuclear Regulatory Commission (Vawter, 2006). Consequently, it is important to understand the parameters that might increase or decrease the radioisotope migration.

The US high level radioactive waste repository is expected to be under oxidizing geochemical conditions. Under these conditions, the used nuclear fuel alters from tetravalent U as UO_2 to hexavalent U, or uranyl, solids (Johnson and Shoesmith, 1988). Many groundwaters contain dissolved silicate; this, in combination with dissolved uranyl, is expected to result in the formation of uranyl silicate minerals, such as sodium boltwoodite ($\text{Na}[(\text{UO}_2)(\text{SiO}_3\text{OH})] \cdot x \text{H}_2\text{O}$), uranophane (Ca

$[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot y \text{H}_2\text{O}$), and sklodowskite ($\text{Mg}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot z \text{H}_2\text{O}$) (Wronkiewicz et al., 1992; Leslie et al., 1993; Wronkiewicz et al., 1997; Finch and Murakami, 1999). These minerals are layered U(VI) silicates that behave much like clay minerals. The layers are composed of sheets of uranyl cations coordinated to silicate anions in a 1:1 stoichiometry (Burns and Finch, 1999). These sheets have a net negative charge; in the three-dimensional solid, the sheets stack up with cations in the interlayer spaces to provide charge balance within the structure. The location of the uranyl cation in the two-dimensional sheet could be occupied by other non-uranyl cations (e.g., Burns et al., 2004; Douglas et al., 2005), similar to cation substitution in the sheets of aluminosilicate clay minerals. Also, other cations can be substituted into the interlayer spaces via ion exchange (e.g., Burns, 1999b). The sorption of radionuclides onto clay materials has received extensive study over the past four decades (e.g., Weaver and Pollard, 1973; Parker and Rae, 1998). Clay minerals offer high surface areas for radionuclide sorption, and also the possibility of ion exchange into interlayer sites within the mineral structure (Weaver and Pollard, 1973).

Uranyl silicates have been studied extensively over the past 10–15 years (Burns, 1998a,b; Burns and Finch, 1999). Methods have been developed to easily identify them (Weier et al., 2005). Studies of process waste streams have been performed to determine the conditions in which their formation is not favored to reduce the total liquid waste volume and avoid fouling liquid evaporators (Oji et al.,

* Corresponding author.

E-mail address: s_clark@wsu.edu (S.B. Clark).

2006). The incorporation of non-uranium radionuclides into their structure has been evaluated (Burns, 1999b, 2004; Douglas et al., 2005; Klingensmith and Burns, 2007); and *ab-initio* calculations were developed to model the impact of substitutions on the uranophane structure and overall stability (Wander and Clark, 2008). Sodium boltwoodite, uranophane, and sklodowskite have been synthesized by this group and others (e.g. Honea, 1961; Stohl and Smith, 1981; Nguyen et al., 1992; Vochten et al., 1997; Douglas et al., 2005; Oji et al., 2006), but key details are often missing in the literature, rendering synthesized solids difficult to reproduce. This paper presents a detailed, optimized technique to synthesize these three uranyl silicates. In addition, we carefully characterized the materials we produced by determining their stoichiometric compositions, surface areas, hydration, zeta potentials, and Raman spectrum in the case of uranophane.

2. Experimental

2.1. Synthesis of sodium boltwoodite

All the solutions were prepared in degassed distilled deionized water (DDIW), with reagent grade chemicals, and at room temperature, except when specified. The first step of the synthesis was performed under constant vigorous stirring, using a magnetic bar, in a 50 mL polypropylene conical centrifuge tube: 30 mL of a 0.01 M uranyl acetate (Kodak) solution was added at once to 3 mL of 0.1 M sodium acetate (Aldrich). The solution pH was slowly adjusted to a value between 9 and 9.5, by adding carbonate-free saturated NaOH solution (Baker); NaOH was added by micro-drops and the pH was allowed to reach equilibrium between each NaOH addition. As NaOH was added, the formation of a yellow precipitate could be observed. 3 mL of freshly prepared 0.1 M sodium metasilicate (Johnson Matthey Cat.), previously adjusted to pH 10, was added at once to the yellow slurry. It was important that the sodium metasilicate solution be previously adjusted to pH 10; without such precaution, its pH was between 12.5 and 13, which rendered sodium boltwoodite synthesis impossible. The resulting slurry pH was adjusted to 10 ± 0.1 , by slowly adding micro-drops of carbonate-free saturated NaOH. The plastic screw cap was placed on the vial, but it was not tightly closed and the polypropylene vial was placed upward, in a tall beaker, for 2 days in a 100 °C oven. Some water evaporated during this process, but not enough to dry the sample. During this process, the color of the solid became slightly brighter yellow. To remove any unreacted cations, anions, or organic ligands, the slurry was centrifuged for 20 min at 4000 rpm, the supernatant decanted and discarded, and 30 mL DDIW was added; this process was repeated three times. The resulting 30 mL slurry was placed in the Teflon insert of a 45 mL Parr bomb at 135 °C for 1 week. The Parr bomb was allowed to cool down to room temperature before being opened. The resulting bright yellow solid was filtered using a 25 mm 0.2 µm pore size Tuffryn® membrane filter (Pall Life Science). All of the solid was collected and rinsed by washing the Parr Bomb Teflon insert several times with DDIW and filtering the rinsate; the filtrate was discarded.

The identity of the solid was confirmed by X-ray diffraction (XRD), using an Siemens Kristalloflex diffractometer coupled with the MDI Datascan control and data acquisition system (Materials Data, Inc, version 3.2.41); the diffractograms were processed and identified with the MDI Jade 8 software (Materials Data, Inc., version 8.09), which uses the International Center for Diffraction Data (ICDD) database. The diffractogram of the solid was measured immediately after it had been filtered by adhering the membrane filter with the associated solid to a glass slide. In some cases, the solids were allowed to dry in a dessicator before completing X-ray diffraction (data not shown); the diffractograms presented in this paper were obtained with solids that had not been dried.

After X-ray diffraction, a small amount of the damp solid (ca. 0.02 g) was weighed before and after drying in a dessicator for 1 week to quantify

the amount of water lost due to desiccation. We define this water loss as “labile” waters of hydration. The remaining solid was weighed and added to 15 mL DDIW; it was kept as a stock solution. This process allowed an exact determination of the g/L concentration of the mineral in the stock solution, which was ca. 4 g/L, for sodium boltwoodite.

2.2. Synthesis of uranophane

Uranophane synthesis was exactly as described for sodium boltwoodite, except that 3 mL of 0.1 M calcium acetate (Baker) was used during the first step of the procedure, instead of 3 mL of 0.1 M sodium acetate. The resulting stock solutions of uranophane had concentrations of ca. 7 g/L.

2.3. Synthesis of sklodowskite

The synthesis of sklodowskite was exactly as described for sodium boltwoodite, except that 3 mL of 0.05 M magnesium chloride (Baker) was used, during the first step of the procedure, instead of 3 mL of 0.1 M sodium acetate. The resulting stock solutions of sklodowskite had concentrations of ca. 6 g/L.

2.4. Mineral characterization

Raman spectra of pressed pellets of uranophane were recorded with 568.2 nm and 647.1 nm excitation from a krypton ion laser (Spectra Physics Beamlock 2060) in backscattering geometry. The incident light was passed through a holographic laser bandpass filter (Kaiser Optical) to eliminate plasma lines and focused onto the sample with a cylindrical lens. For excitation at 568.2 nm, the scattered light was passed through a notch filter (Kaiser Optical) to eliminate elastically scattered radiation, and focused onto the entrance slit of a single monochromator (Acton Spectra-Pro 2300i) and detected by a thermoelectrically cooled CCD camera (Roper Scientific Spec 10:256E). The Raman spectra excited at 647.1 nm were recorded using a scanning double monochromator (Spex 14018) equipped with thermoelectrically cooled photomultiplier detector. Our first attempt to obtain Raman data with a yellow laser line (568.2 nm) did not provide satisfactory data, because of the interference of the uranyl photoluminescence; only two peaks could be observed at 795 and 964 cm^{-1} . A red excitation at 647.1 nm led to a better spectrum definition, but the uranyl photoluminescence allowed us to acquire satisfactory data only between 1200 and 150 cm^{-1} .

For electron microscopy, a small amount of each solid was adhered to a standard scanning electron microscopy (SEM) stub using double-sided tape, and subsequently gold-coated using a 208HR Cressington high resolution sputter coater equipped with a rotary-planetary-tilting stage. A Hitachi S-570 SEM was used (30 kV accelerated voltage). SEM images were collected with a Hitachi digital camera (Quartz Imaging Corporation) coupled via Quartz PCI software.

The elemental composition of the uranyl silicates in Na, Ca, Mg, Si, and U was measured by inductive coupled plasma optical emission spectrometry (ICP OES), using a Perkin-Elmer Optima 3200RL instrument coupled with the WinLab32 Instrument Control software. Known amounts of the minerals sodium boltwoodite, uranophane, or sklodowskite stock suspension were added to 1 mL 10% HNO_3 and 3.9 mL DIW, to obtain a final concentration of 0.22 g mineral/L; this amount of acid is sufficient to ensure that the total dissolution of the solids. Na, Ca, Mg, Si and U contents were measured at wavelengths 330.237 nm, 396.848 nm, 279.553 nm, 251.611 nm, and 367.007 nm, respectively. The instrument was previously calibrated with dilutions of 1000 ppm Na, Ca, Mg, Si and U standard solutions (Inorganic Ventures, Fisher, and UFS Chemicals).

The surface area of each solid was measured using the Brunauer, Emmett, and Teller (BET) gas adsorption technique. The BET instrument (Flowsorb II, Particle and Surface Sciences, Pty limited) was calibrated with the injection of 1 mL of a 10% N_2 gas mixture,

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