



Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of aqueous bicarbonate ions

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ABSTRACT

This research evaluated the effect of aqueous hydrogen carbonate solutions on the uranium rate of release from natural Ca-autunite and quantified the process kinetic rate law for a better prediction of the stability of autunite-group minerals. Testing was accomplished via a single-pass flow-through (SPFT) apparatus using buffered aqueous bicarbonate solutions (0.0005 to 0.003 M) at temperatures of 23–90 °C and pH values of 7–11. The release rate of uranium from Ca-autunite was directly correlated to increasing concentrations of hydrogen carbonate solutions and showed strong pH dependency. Ca-autunite kinetic rate law parameters were compared to the values obtained for synthetic Na-autunite. The power law coefficient and intrinsic rate constant were higher at pH 9–11 for Ca-autunite than for Na-autunite. The lower stability of Ca-autunite was attributed to the high Ca-autunite surface cracking, fractures and basal plane cleavages as compared to Na-autunite and the combined effect of the formation of aqueous uranyl-carbonate and calcium uranyl carbonate species as a driving force for uranium(VI) detachment and the formation of secondary Ca-P hydroxyapatite and uranyl phosphate mineral phases as a driving force for phosphate and calcium detachment controlling the net release of elements.

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1. Introduction

Globally, uranium (U) occurs as an essential component in different minerals and the majority of naturally occurring uranium deposits are oxides, silicates, vanadates, and phosphate minerals such as autunite (Burns, 1999). Uranium is one of the most frequently found radionuclides in groundwater as a result of reactor operations, nuclear fuel production and waste reprocessing (Riley et al., 1992). Autunite minerals $\{(X^m)_{2/m}[(UO_2)(PO_4)]_2 \cdot xH_2O\}$ are an important group known for their low solubility that largely controls the mobility of U in the subsurface. The autunite-group is very diverse, permits a wide range of cation and anion substitutions, and varying degrees of hydration (Burns, 1999). Many arid and semi-arid environments, including areas used for the storage of high-level radioactive waste at the U.S. Department of Energy (DOE) sites, contain elevated concentrations of sodium that in the presence of phosphorus (P) and uranium U(VI) rapidly form sodium uranyl phosphate phases. Injection of a soluble sodium tripolyphosphate amendment into the uranium contaminated groundwater and soil have been shown to effectively sequester uranium through the formation of insoluble Na uranyl phosphate solid phases. A sodium analog of autunite has

been found in nature. Chernikov et al. (1957) conducted characterization of the hydrated sodium meta-autunite discovered in the Kuruk uranium deposit of northern Tajikistan and found that it is similar in properties to the autunite group. Mills et al. (2012) reported that metanatroautunite from the Lake Boga granite, Victoria, Australia, was similar to synthetic Na $[(UO_2)(PO_4)](H_2O)_3$ and featured identical corrugated polyhedral sheets as the meta-autunite-group minerals, consisting of corner-sharing uranyl square pyramids and phosphate tetrahedra.

Calcium, as one of most abundant metals in the earth's crust, promotes the formation of calcium-autunite, $Ca[(UO_2)(PO_4)]_2 \cdot (H_2O)_{11}$. This phase has been recognized as the dominant form of autunite (Burns, 1999). The crystal structure contains the well-known autunite type sheet with composition $[(UO_2)(PO_4)]^-$, resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra. The calcium atom in the interlayer is coordinated by seven H₂O groups and two longer distances from uranyl ion oxygen atoms (Locock and Burns, 2003).

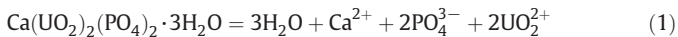
Fairchild (1929) showed that in artificial autunites sodium was replaced by calcium and the exchange reactions take place rapidly in Ca-rich environment with compounds of the autunite type. According to Anthony et al. (2000), two distinct changes occur during the exchange of sodium for calcium in the autunite structure. Primarily, two sodium cations are exchanged for the calcium ion to maintain the

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charge balance of the structure. The exchange of sodium for calcium is also associated with an increase in waters of hydration (Wellman et al., 2005). These changes in the chemical and structural composition of autunite raise questions on the impact of environmental factors on the stability of autunite-group minerals.

Literature data suggest the low solubility and high stability of many uranyl–phosphate minerals (Felmy et al., 2003; Gorman-Lewis et al., 2009). The solubility constant of the calcium form of autunite, $\log K_{sp}$, has been measured as -44.7 (Grenthe et al., 1992; Langmuir, 1997). A recent solubility study on natural Ca–U–P stability constant values for aqueous complexes yielded a $\log K_{sp}$ value of -48.36 with 2σ uncertainty values of ± 0.03 (Gorman-Lewis et al., 2009). Associated species of reaction are shown in Eq. (1).



Different environmental variables including temperature and pH have been extensively investigated (Wellman et al., 2006) on the dissolution of synthetic Na meta-autunite (herein designated as Na-autunite) and natural Ca meta-autunite minerals (herein designated as Ca-autunite). Their results indicated that meta-autunite dissolution kinetics is strongly dependent on pH and independent of temperature variation. Ca-rich carbonate-bearing subsurface environments, typical for the arid areas of the western U.S., afford the formation of aqueous calcium uranyl–carbonate and hydroxide complexes, which are mobile and promote U(VI) migration in natural waters (Clark et al., 1995; Kalmykov and Choppin, 2000; Bernhard et al., 2001). The strength of uranyl carbonate complexes makes the inorganic carbon species be the most effective extractant in terms of the dissolution rate and the extent of recovery of U from uranyl – bearing mineral phases (Perez et al., 2000; Sowder et al., 2001). Gudavalli, 2012, via single-pass flow-through (SPFT) experiments, investigated the rate of U(VI) release from Na-autunite, $\text{Na}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$, as a function of bicarbonate solution concentrations ranging from 0.0005 M to 0.003 M in the pH range of 6–11 and temperature between 5 and 60 °C. The rate of U(VI) release from Na-autunite in the presence of low bicarbonate concentrations was increased over 300 fold when compared to the rate of U(VI) release in the absence of bicarbonate. Quantification of kinetic rate law parameters for the dissolution reaction of sodium meta-autunite suggested that activation energies were unaffected by temperature and bicarbonate solution concentrations but strongly depended on pH conditions (Gudavalli, 2012). Considering rapid exchange reactions of sodium for calcium in the autunite structure, the study of the effect of aqueous bicarbonate concentrations on the rate of U(VI) release from Ca-autunite can be extended to better understand U(VI) mobilization in groundwater.

The objectives of this research were to (i) investigate the effect of low concentrations of bicarbonate solutions on the dissolution of U(VI) from Ca-autunite via SPFT experiments and determine the U(VI) rate of release, (ii) quantify the kinetic rate law parameters of Ca-autunite dissolution, and (iii) compare the results with the dissolution of Na-autunite for better prediction of the bicarbonate impact on the release of U(VI) and the dissolution process of the autunite-group minerals. This information is critical for the prediction of autunite stability and long-term fate and transport of uranium in the subsurface.

2. Materials and methods

2.1. Autunite specimens

Synthesis of Na-autunite, $\text{Na}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$, was followed by a modified direct precipitation method described by Wellman et al. (2005). Uranyl nitrate and sodium phosphate dibasic solutions were mixed in a volumetric ratio of 1:7.5 at 70 °C while stirring; heat was terminated after a yellowish green precipitate was formed. X-ray diffraction analysis was performed on the synthesized autunite mineral

at 40 kV and 40 mA using a Bruker 5000D XRD instrument. Diffraction patterns were obtained using a copper radiation source with a tungsten filter. The sample was analyzed in the range of 2 to 35° for the 2-theta (2 θ) with a 0.04° step increment and a two-second count time at each step. The XRD diffraction patterns were consistent with PDF# 049-0432 for Na-meta-autunite I (mAut I), $\text{Na}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$, obtained from PNNL for comparison. The synthesized autunite solids were characterized by a JSM-5900-LV low vacuum scanning electron microscope (SEM) at 15 kV for identification of the particle sizes. The elemental composition and purity of the solids were determined via a Noran System Six Model 200 SEM energy dispersive X-ray spectroscopy (EDS). The Na:O:P:U atomic ratios of 1.08:5.69:1.00:1.04, determined by means of EDS analysis, corresponded to an ideal empirical formula of $\text{Na}[\text{UO}_2\text{PO}_4]$ as 1:6:1:1. Pre-experimental surface area analysis was conducted following the N_2 -adsorption BET method (Brunauer et al., 1938) by using a Micromeritics ASAP 2020 surface and porosity analyzer at Pacific Northwest National Laboratory (PNNL). The structure of synthesized autunite solids, characterized by JSM-5900-LV low vacuum scanning electron microscope (SEM) at 15 kV, exhibited a smooth surface without distinctive cleavage planes (Fig. 1a).

Natural Ca-autunite, $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$, obtained from Excalibur Mineral Corporation (Peekskill, New York), was previously characterized using ICP-OES, ICP-MS analyses, X-ray diffraction and SEM/EDS to confirm the mineral composition, structure, and morphology as 98–99% pure autunite (Wellman et al., 2006). Scanning electron micrographs of Ca-autunite illustrate the multilayer structure resulting from the negatively charged $[(\text{UO}_2)(\text{PO}_4)]_2^{2-}$ layers. The morphology features perfect (001) basal, cleavage producing planes characteristic of autunite minerals (Anthony et al., 2000). As illustrated in the scanning electron micrographs displayed in Fig. 1b and c, surface cracking, fractures, and basal plane cleavage tended to be greater in Ca-autunite, resulting in a greater surface area compared to the Na-autunite counterpart. The autunite sample was powdered to have a size fraction of 75 to 150 μm or -100 to $+200$ mesh with an average surface area of 0.88 $\text{m}^2 \text{g}^{-1}$.

2.2. Single-pass flow-through (SPFT) experiments

Mineral dissolution is a complex process consisting of a series of elementary reactions occurring at the mineral–water interface (Stamm and Wollast, 1990; Nagy, 1995; Sparks, 1999; Pablo et al., 1999). The release rate of elements from solids into solution is frequently controlled by kinetics. It has been accepted practice by geochemists to use the Transition State Theory (TST) that assumes that the dissolution rate is controlled by the desorption kinetics of an activated complex formed at the surface of solid phase (Lasaga, 1984). TST can be used to calculate the flux of elements released into the aqueous phase (Nagy, 1995). A general form of rate equation is based on the TST of chemical kinetics, centered on the prediction that the overall reaction rate is governed by the slowest elementary reaction, known as the rate-limiting step (Aagaard and Helgeson, 1982; McGrail et al., 1997). The reaction is given by

$$r = kv_i a_{H^+}^{\pm\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \frac{Q}{K_g}\right]^\sigma \prod_j a_j^{n_j}, i = 1, 2, \dots, N \quad (2)$$

where r is the dissolution rate in $\text{g m}^{-2} \text{d}^{-1}$, k is the intrinsic rate constant in $\text{g m}^{-2} \text{d}^{-1}$, v_i is the mass fraction of element i , a_j is the activity of the j th aqueous species that acts as an inhibitor or catalyst, E_a is the activation energy in kJ mol^{-1} , R is the gas constant in $\text{kJ mol}^{-1} \text{K}^{-1}$, T is the temperature in K, Q is the ion activity product, K_g is the pseudo equilibrium constant, η is the power law coefficient, and σ is the Temkin coefficient.

The dependence of the dissolution rate of the Ca-autunite mineral on bicarbonate concentration was quantified via single-pass flow-through (SPFT) experiments conducted over a temperature range of 23° to 90 °C and a controlled pH range from 7 to 11. This test is designed to

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