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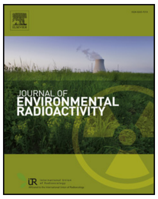

Quantification of kinetic rate law parameters for the dissolution of natural autunite in the presence of aqueous bicarbonate ions at high concentrations

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ABSTRACT

Uranium is a key contaminant of concern in the groundwater at U.S. Department of Energy (DOE) facilities within the United States and is a potential source of groundwater contamination and a risk to human health and the environment through discharges to surface water. Dissolved inorganic carbon (bicarbonate/carbonate) has a high affinity for complexing with uranium that is present as sorbed or unique uranium-bearing mineral phases within the sedimentary matrix. This process can result in the formation of soluble uranyl carbonate aqueous species, which are mobile under circumneutral pH conditions. This study was conducted to quantify the rate of release of uranium from the autunite mineral, ($Ca[(UO_2)(PO_4)]_2 \cdot 3H_2O$), that was formed during polyphosphate injection to remediate uranium; the dissolution of uranium was studied as a function of the aqueous bicarbonate concentration, ranging from 25 to 100 mM. Experiments were carried out in the pH range from 7 to 11 in the temperature range of 23–90 °C via single-pass flow-through testing. Consistent with the results of previous studies (Gudavalli et al., 2013a, 2013b), the rate of uranium release from autunite exhibited minimal dependency on temperature, but was strongly dependent on pH and increasing concentrations of bicarbonate in the solution. Data obtained during these experiments were compared with results of previous experiments conducted using a low-concentration range of bicarbonate solutions (0.5–3.0 mM). An 8- to 30-fold increase in the rate of uranium release was observed in the presence of high bicarbonate concentrations at pH 7–8 compared to low bicarbonate values, while at pH 9–11, there was only a 5-fold increase in uranium rate of release with an increase in bicarbonate concentrations. The rate of uranium release was calculated to be between 5.18×10^{-8} and 1.69×10^{-7} mol m^{-2} s^{-1}. The activation energy values at high and low bicarbonate concentrations were similar, with ratio values in the range of 0.6–1.0.

1. Introduction

Uranium U(VI) is a key contaminant of concern commonly found in groundwater as a result of uranium mining, processing of uranium ores, and production and disposal of radioactive materials (Riley et al., 1992). In the presence of phosphate and under favorable conditions, U(VI) forms a series of highly insoluble phosphate minerals such meta-autunite (Raicevic et al., 2006). Autunite minerals $\{(Xm)_{2/m}[(UO_2)(PO_4)]_2 \cdot xH_2O\}$ 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 has varying degrees of hydration (Burns, 1999).

Uranium is a very reactive element that readily combines with many elements to form a variety of complexes. The aqueous speciation of U(VI) includes many different species, and the uranyl ion (UO_2^{2+}) forms soluble complexes with naturally abundant groundwater anions and can easily combine with Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-} (Langmuir, 1997; Finch and Murakami, 1999; Guillaumont et al., 2003). Dissolved inorganic carbon present in soil and groundwater is one of the primary factors controlling uranium aqueous speciation. In carbonate-rich conditions, the most significant dissolved complexes are with carbonate: UO_2CO_3 (aq), $UO_2(CO_3)_3^{4-}$, $(UO_2)_2(OH)_3CO_3^-$, and $UO_2(CO_3)_2^{2-}$ (Langmuir, 1978). In the calcareous subsurface environment typical for arid regions throughout the western United States, porewater is at equilibrium with respect to calcite and contains significant concentrations of calcium. Bernhard et al. (2001) reported that, in conditions rich in carbonate and Ca, calcium-uranyl-carbonate complexes such as $Ca_2UO_2(CO_3)_3$ (aq) and $CaUO_2(CO_3)_3^{2-}$ are the predominant species of dissolved U(VI) in solutions with pH greater than 6.

Wellman et al. (2006, 2007) studied the effects of different environmental variables such as temperature and pH on the dissolution of

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autunite. Their data indicate that autunite dissolution is strongly dependent on the pH but is not dependent on temperature variations. Gudavalli et al. (2013a, 2013b) studied the dissolution of autunite as a function of bicarbonate solution concentrations ranging from 0.0005 to 0.003 M in the pH range of 7–11. Their results suggest that the rate of U (VI) release from Na-autunite in the presence of low bicarbonate concentrations was increased over 300 fold when compared with the rate of U(VI) release in the bicarbonate-free solution. In addition, the effect of bicarbonate surpassed the effect of pH and there was no quantifiable dependency of autunite dissolution on temperature (Gudavalli et al., 2013a, 2013b), which is in agreement with data obtained by Wellman et al. (2006, 2007). Zhou and Gu (2005) studied the effects of various bicarbonate concentrations on the extraction of uranium from contaminated soils. They reported that carbonate-free solutions were inefficient at extracting U(VI) from contaminated soil at a relatively low pH. However, even small quantities of carbonate/bicarbonate resulted in a rapid and significantly increased U leaching. They also observed that more than 50% of the total U(VI) could be extracted when the bicarbonate concentration was increased to around 30 mM. It is important to understand the extent of the effect of high bicarbonate concentrations on the autunite dissolution. This information is critical for the prediction of autunite stability and long-term assessment of the fate and transport of uranium in the subsurface.

An evaluation of geologic materials of the Hanford Formation, one of the major stratigraphic unit underlining Tank Farm at the Hanford Site 200 area located within the Colombia Plateau of the southeastern Washington State, U.S., revealed the presence of calcium carbonate ($CaCO_3$) phases in the contaminated vadose zone (VZ) sediment. The bicarbonate concentration in the porewater composition in this area was found elevated up to 100 mM (Serne et al., 2008). Bicarbonate is one of the major anions affecting uranium mobility and currently there are no studies gauging the effect of elevated bicarbonate concentrations on the uranium release from uranyl phosphate minerals. This research evaluates the effects of pH levels between 7 and 11 and high bicarbonate concentrations (25–100 mM) on the dissolution kinetics of autunite mineral in a temperature range from 23 °C to 90 °C. The objectives of this research were to: (i) investigate the effects of high concentrations of bicarbonate, ranging from 25 to 100 mM, in the solutions on the dissolution of Ca-autunite and determine the U(VI) rate of release via single-pass flow-through (SPFT) experiments; (ii) quantify the kinetic rate law parameters of Ca-autunite dissolution for the tested conditions; and (iii) compare the results with values obtained for the dissolution of Ca-autunite at low bicarbonate concentrations ranging between 0.0005 and 0.003 mM (Gudavalli et al., 2013a) 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 to understanding the uranium geochemical cycle and the dissolution kinetics of uranyl phosphate phases given the high content of calcium carbonate minerals in soil and sediments typical for arid regions throughout the western United States. The results from the study can be applied for remediation of saturated and unsaturated zones of the subsurface environments.

2. Materials and methods

2.1. Autunite specimens

The natural Ca-meta-autunite, $Ca[(UO_2)(PO_4)]_2 \cdot 3H_2O$, used in the experiments was obtained from Excalibur Mineral Corporation (Peekskill, NY). The mineral was characterized using inductively coupled plasma optical emission spectroscopy, inductively coupled plasma mass spectroscopy analyses, X-ray diffraction, and scanning electron microscopy/energy dispersive X-ray spectroscopy to confirm the mineral composition, structure, and morphology as 98%–99% pure autunite (Wellman et al., 2006). The autunite sample was powdered and sieved to achieve a size fraction ranging from 75 to 150 μm (−100 to +200 mesh) with an average surface area measured as 0.88 $m^2\,g^{-1}$ (Wellman et al., 2006).

2.2. Single-pass flow-through experiments

The dissolution of minerals transpires via a series of elementary reactions that occur at the mineral-water interface, and the release of elements from solids into the aqueous phase is controlled by chemical kinetics (Stamm and Wollast, 1990; Nagy, 1995; Sparks, 1999; Pablo et al., 1999). Transition state theory (TST) has been widely used to quickly estimate the reaction rates of a variety of processes (Jiulin Du, 2012). Lasaga (1984) reported that the dissolution rate is controlled by the desorption kinetics of an activated complex formed at the surface of the solid phase. TST is used to calculate the flux of elements released into the aqueous phase. Several authors previously reported that the general rate equation is based on TST of chemical kinetics, helping to predict the overall reaction rate. The rate of reaction is governed by the slowest elementary reaction controlling the dissolution, known as the rate-limiting step (Aagaard and Helgeson, 1982; Nagy, 1995; McGrail et al., 1997). The reaction is given by

$$r = k \;\; \nu_i \;\; a_{H^+}^{\pm\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \frac{Q}{K_g}\right]^{\sigma} \prod_j a_j^{n_i},\ i = 1,2,\ ....N \tag{1}$$

where r is the dissolution rate in g m^{-2} d^{-1}, k is the intrinsic rate constant in g m^{-2} d^{-1}, ν_i is the mass fraction of element i, a_j is the activity of the jth 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 kJ mol^{-1} 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 SPFT apparatus was used to quantify the dependence of the dissolution rate of the Ca-autunite mineral on the bicarbonate concentration. Several authors have previously described the SPFT apparatus in detail (McGrail et al., 1997; Pierce et al., 2005, 2008; Icenhower et al., 2006; Wellman et al., 2006). Mixing is accomplished by the solution convection flow from fluid transfer Teflon lines that protrude through two separate ports (1/4") at the top of the reactor allowing influent and effluent solutions to enter and exit, respectively. This setup minimizes the potential for particles to become entrained in flow currents. Entrainment of particles may result in artificially faster dissolution rates due to collisions with other particles or the reactor walls generating additional surface area (Wellman et al., 2007). So, particles stirring is not recommended since it can affect surface area during the test. In addition, the design of SPFT reactors prevents fluid from being pumped directly through the sample and bubbles that could potentially form in the fluid transfer tubing do not entrain in the sample altering the exposed surface area.

In the current experiments, the dissolution rate of Ca-autunite was quantified over a temperature range of 23 °C to 90 °C and a controlled pH range from 7 to 11. This test was designed to measure reaction rates under tightly controlled, dilute solution conditions by performing experiments at the forward rate, which is far from equilibrium conditions (McGrail et al., 1997). The SPFT test was designed to limit the accumulation of reaction products using a sufficient ratio of flow rate to surface area of the mineral sample (q/S) to ensure the maximum dissolution rate or forward rate was achieved. Therefore, by design, the SPFT experiment prevents the progressive accumulation of reaction products that would affect element release rates (Pierce et al., 2010). The forward rate is then used to independently determine the effect of all other environmental variables on release rates. These conditions allow the chemical affinity term, Q/K_g, to be maintained at a value near zero in Eq. (1). By observing changes in the dissolution rate over the range of experimental parameters tested, k, Ea, and η can be easily calculated via standard non-linear regression.

The experimental setup (Fig. 1) consisted of a syringe pump that

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