Rate of Uranium Release from Calcium Meta-Autunite: Effect of Bicarbonate Solutions on the Dissolution - 14218

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ABSTRACT

Uranium is a key contaminant of concern at the 300 Area of the Hanford Site that poses risk to humans due to its chemical and radio toxicity. Injection of a soluble sodium polyphosphate amendment into uranium contaminated porous media has been shown to effectively remediate uranium (VI) by forming an insoluble uranyl-phosphate mineral, autunite $X_{1-2}[(UO_2)(PO_4)]_2 \cdot nH_2O$, where X is monovalent or divalent cations. The release of uranium from calcium meta-autunite occurs during the slow dissolution of the mineral structure. Carbonate is the major ion in the groundwater composition. According to the speciation modeling, uranyl ions (UO_2^{+2}) are predicted to form soluble uranyl-carbonate complexes such as $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$. Current knowledge on the uranium release from Ca-autunite is limited to the conditions involving pH and temperature; there is a need to assess the effect of bicarbonate on the release of uranium as a result of Ca-autunite mineral dissolution. The rate of uranium release from Ca-autunite in the presence of 0.5-3.0 mM bicarbonate solutions at pH 7-11 and temperature 23-90°C was evaluated via single-pass flow-through (SPFT) experiments. The presence of bicarbonate has been shown to influence the release of uranium from Ca-autunite. At pH 7, the uranium release rate increased 18 times; whereas, at pH 11, the release of uranium was 435 times greater than the release at pH 7. Activation energy values helped identify the rate limiting steps of the dissolution of uranium.

INTRODUCTION

Uranium contamination originated from the discharges at mining and processing sites and is the most common radiological contamination in soil and sediments [1, 13]. Quantitative predictions on the uranium movement in the groundwater are critical for future remediation technologies and disposal of radioactive waste. One of the notable uranium contaminated sites in the United States is the Department of Energy's (DOE) Hanford Site, which contains groundwater plumes contaminated with uranium (VI) that originated from unintended leakages and spills from nuclear production facilities [5]. Activities at the 300 Area of the Hanford Site led to the contamination of streams, soil and groundwater primarily with 58,967 kg of uranium, which poses risks to humans due to its chemical toxicity and risk of radiological exposure. Injection of a soluble sodium polyphosphate amendment into uranium contaminated porous media has been shown to effectively remediate uranium by forming an insoluble uranyl-phosphate mineral, autunite $X_{1-2}[(UO_2)(PO_4)]_{2-1} \cdot nH_2O$, where X is monovalent or divalent cations [16, 17, 19, 20]. Calcium is the most abundant metal in the earth's crust and, in Ca- rich environments typical for the western US, Ca replaces Na and the exchange takes place rapidly into Ca-autunite. Carbonate is the major ion in the groundwater composition at the 300 Area of the Hanford Site. According to the speciation modeling, uranyl ions (UO_2^{+2}) are predicted to form soluble uranyl-carbonate complexes such as $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ [19]. Current knowledge on the uranium release from Ca-autunite is limited to the conditions involving pH and temperature; there is a need to assess the effect of bicarbonate on the release of uranium as a result of Ca-autunite mineral dissolution. The objective of this research was to quantify the effect of bicarbonate

solutions (0.5-3.0 mM) on the rate of uranium release at varying pH (7-11) and temperature (23-90°C) conditions.

MATERIALS AND METHODS

Autunite Specimens

The natural Ca-autunite, $Ca[(UO_2)(PO_4)]_2 \cdot 3H_2O$, used in the experiments was obtained from Excalibur Mineral Corporation (Peekskill, New York). The autunite mineral was previously characterized by Wellman et al. (2006) by using ICP-OES, ICP-MS analyses, X-ray diffraction and SEM/EDS and confirmed to be 98-99% pure autunite. The autunite sample was powdered to have a size fraction of 75 to 150 μm (-100 to + 200 mesh) with an average surface area of 0.88 m^2 g^{-1}.

Single-Pass Flow-Through (SPFT) Experiments

Dissolution of minerals is a complex process that involves a series of reactions occurring at the mineral-water interface. The dissolution process is also dependent on the rate limiting reaction [12, 13, 15]. Transition state theory (TST) is widely applied to estimate the reaction rates of elementary reactions. TST is based on the assumption that the dissolution is controlled by the desorption kinetics of an activated complex formed at the surface of a solid phase. A general form of the TST rate equation is centered on the prediction that the overall reaction rate is governed by the slowest elementary reaction, known as the rate-limiting step [11]. The reaction is given by

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

Where:

r = dissolution rate in g m^{-2} d^{-1},

k = intrinsic rate constant in g m^{-2} d^{-1},

v_i = mass fraction of element i,

a_j = activity of the jth aqueous species that acts as an inhibitor or catalyst,

E_a = activation energy in kJ mol^{-1},

R = gas constant in kJ mol^{-1} K^{-1},

T = temperature in °K,

Q = ion activity product,

K_g = pseudo equilibrium constant,

η = power law coefficient, and

σ = Temkin coefficient.

The Ca-autunite dissolution rate was measured via single-pass flow-through (SPFT) experiments at varying concentrations of bicarbonate (0.5 - 3.0 mM) in a pH range of 7 to 11 and temperature range of 23° to 90°C (Fig. 1). SPFT experiments are designed to measure reaction rates at the forward rate under tightly controlled conditions.

Fresh buffer solutions prepared with distilled, de-ionized water (DDIW) with 0.5 - 3.0 mM bicarbonate solutions buffered with 0.01 M *tris (hydroxymethyl) aminomethane* (TRIS) were used to investigate U(VI) release from a natural Ca-autunite mineral. Concentrated trace-metal grade nitric acid and lithium hydroxide were used to adjust the pH of buffer solutions in the range of 7-11. A 0.25 g sample of powered Ca-autunite was introduced into the reactor that came into contact with the buffered bicarbonate solutions. The effluent solutions from the SPFT reactor cells were continuously collected until steady state conditions were achieved. Effluent solutions were wet- and dry-ashed to reduce the interference of organic content on the analytical instruments. Dissolved concentrations of U(VI) were quantified using kinetic phosphorescence analyzer (KPA-11) and Ca and P concentrations were analyzed by means of ICP-OES (Optima 7300).
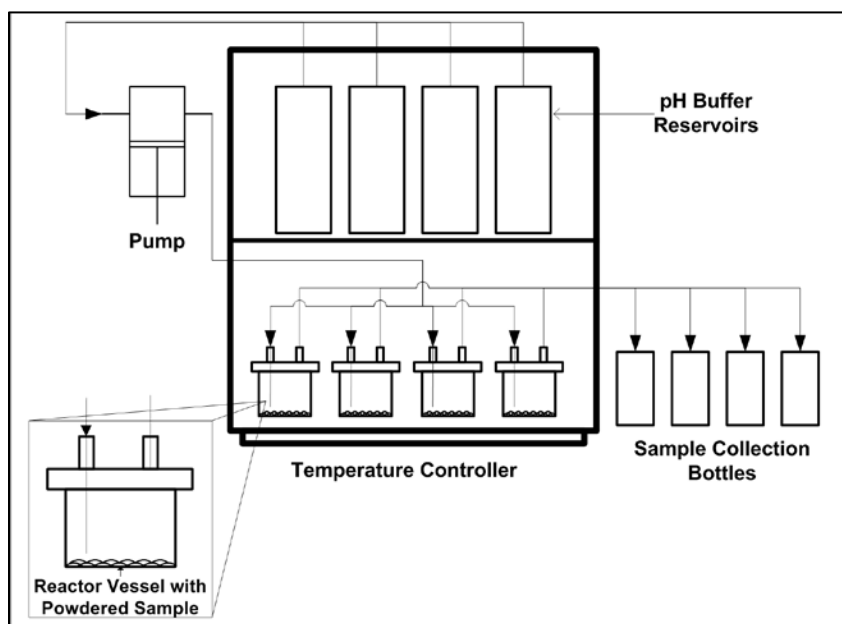

Fig. 1. Experimental Setup With Single-Pass Flow-Through Apparatus

Quantification of Dissolution Rate

The normalized dissolution rate of Ca-autunite solids was calculated from Eq. 2 when the system reached equilibrium [11].

$$R_i = (C_i - C_{ib}) \frac{q}{f_i S}$$
(Eq. 2)

Where:

R_i = normalized dissolution rate for element i (mol m^{-2} s^{-1}),

q = flow rate (L d^{-1}),

C_i = concentration of component i in the effluent (g L^{-1}),

C_{ib} = mean background concentration of component i (g L^{-1}),

f_i = mass fraction of the element in the metal (dimensionless), and

S = surface area of the sample (m^2).

The steady-state conditions were achieved after approximately eight reactor volumes were exchanged and the concentrations of uranium released from natural Ca-autunite became invariant with respect to time for all pH and bicarbonate ranges tested.

The standard deviation of the dissolution rate was determined according to the uncertainty associated with each parameter shown in Equation 2. Standard deviation for uncorrelated random errors is given by:

$$\sigma_f = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2 \sigma_i^2}$$

(Eq. 3)

Where: σ_f - standard deviation of the function f ; x_i - parameter i; and σ_i -standard deviation of parameter i.

Substituting Eq. 2 in Eq. 3 and converting to relative standard deviation 2, $\hat{\sigma}_r = \sigma_f / \overline{x}$, yields

$$\hat{\sigma}_r = \sqrt{\frac{\left(\hat{\sigma}_c C_i^{out}\right)^2 + \left(\hat{\sigma}_b C_i^{in}\right)}{\left(c_i^{out} + c_i^{in}\right)^2} + \hat{\sigma}_{fi}^2 + \hat{\sigma}_s^2 + \hat{\sigma}_q^2}$$

(Eq. 4)

Uncertainty associated with each parameter was considered when calculating the dissolution rate; relative errors included are final concentration (10%), background concentration (10%), mass distribution (5%), surface area (15%), and flow rate (5%). This error analysis results in typical 2σ uncertainties of approximately ±35% for SPFT-measured dissolution rates (or ±0.2 log units when reported as log10 rates) [17]. The experimental results were correlated by linear regression using SigmaPlot-11.2 (Systat Software Inc.).

Groundwater Modeling

Steady state elemental concentrations in the effluent solution after the system reached equilibrium were used to identify the predominant uranium species in the aqueous solution. The speciation modeling was performed by means of geochemical modeling software Visual MINTEQ v. 3.0, maintained by J. Gustafsson at KTH, Sweden, available at http://www.lwr.kth.se/English/OurSoftware/vminteq/ using thermodynamic data from Grenthe et al, (1992) and updated with the Nuclear Energy Agency's thermodynamic database for uranium (Guillaumont et al., 2003), calcium-uranyl-carbonate complexes (Dong and Brooks, 2006), and becquerelite dissolution data by Gorman-Lewis et al. (2008). The uranium speciation and solubility calculations are based on current knowledge and may have significant associated uncertainties.

RESULTS AND DISCUSSION

Influence of bicarbonate

The influence of bicarbonate on the dissolution of Ca-autunite was experimentally determined using Eq. 5:

$$\log(r) = \log(k) + \eta \log[HCO_3^-]$$ (Eq. 5)

Where:

r = dissolution rate (mol m^{-2} s^{-1}),

k = intrinsic rate constant (mol m^{-2} s^{-1}), and

[HCO$_3^-$] = concentration of pH-adjusted bicarboante solutions (mol L^{-1}).

A non-linear regression was performed for each temperature with dissolution rates as a function of the concentration of the bicarbonate solutions to determine slope and the power law coefficient, η. The resulting regression coefficient over the entire data helped to define the intrinsic rate constant, k (mol m^{-2} s^{-1}).

Data presented in Fig. 2 shows the change in the rate of release of uranium from Ca-autunite with the change in bicarbonate concentrations tested and the temperature range of 23 - 90 $^{\circ}$C. A strong influence of pH was displayed on the release of uranium from Ca-autunite which is in agreement with the results previously reported [16, 17]. An approximate 18-fold increase in the rate of uranium release was observed with an increase in the bicarbonate concentration from 0.5 to 3.0 mM; the resulting regression coefficients are η = 0.50 ± 0.12 and k = 1.09 × 10^{-09} (mol m^{-2} s^{-1}). The influence of bicarbonate concentration on the release of uranium from Ca-autunite was shown to increase with an increase in pH. At pH 8 - 11, the increase in the uranium release were 17, 65, 392 and 434 fold at pH 8, 9, 10 and 11, respectively, when compared to the values at pH 7. The values of the power law coefficient and the intrinsic rate constants at pH 7 - 11 are shown in TABLE I.

TABLE I Experimentally determined data for Ca-autunite dissolution

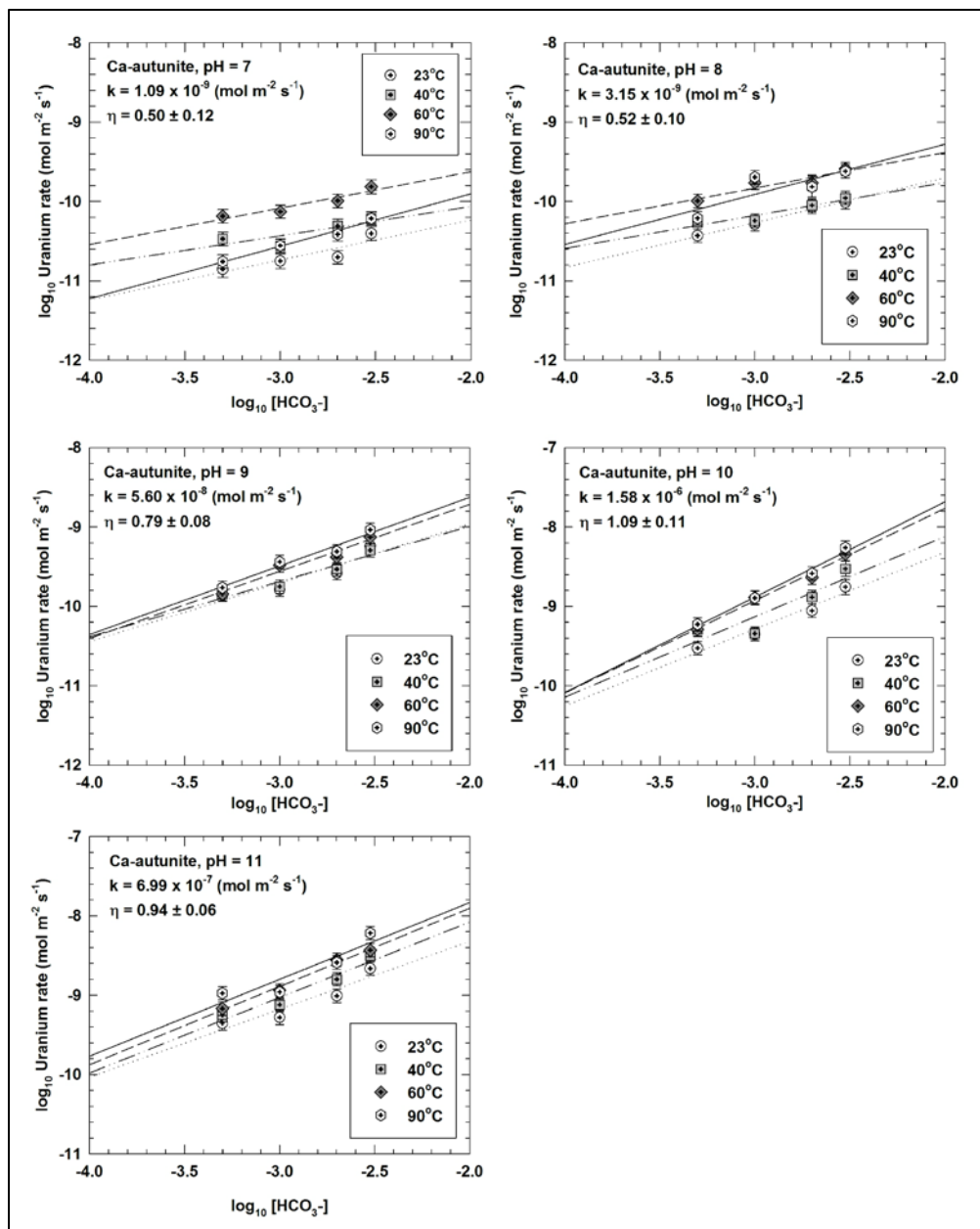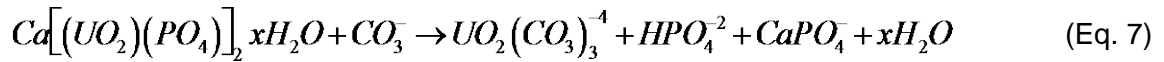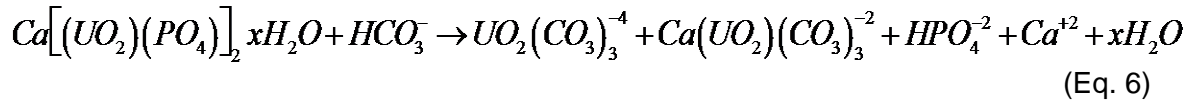| pH	Ca-autunite			
	η	k (mol m^{-2} s^{-1})	K$_g$	ΔH (kJ mol^{-1})
7	0.50 ± 0.12	1.09 x 10^{-09}	0.65	28.58
8	0.52 ± 0.10	3.15 x 10^{-09}	0.79	11.83
9	0.79 ± 0.08	5.60 x 10^{-08}	4.20	11.90
10	1.09 ± 0.11	1.58 x 10^{-06}	25.97	15.88
11	0.94 ± 0.06	6.99 x 10^{-07}	27.75	13.84

Fig. 2. Uranium Release Rate With The Change In Bicarobnate Concentrations At pH 7-11

At pH 7, the geochemical modeling data indicated that the possible uranyl secondary phase minerals (beta-$UO_2(OH)_2$ and schoepite) are under-saturated, suggesting that the release of U(VI) is solely due to the dissolution of Ca-autunite. At pH 8 and 9, the increase in aqueous bicarbonate concentrations correlated with a decrease in the saturation indices of potential secondary phases as schoepite and β-$UO_2(OH)_2$, suggesting a faster release of U(VI) from autunite under these conditions. At pH 9-11, hydroxyapatite became supersaturated at all bicarbonate concentrations along with other secondary Ca-P minerals controlling the net release of uranium. The increase in the uranium release rate with increasing pH could be explained by the increase in CO_3^{2-} as the distribution of dissolved inorganic carbon depends on

pH. The increased availability of CO_3^{2-} helped to form strong and highly soluble uranyl-carbonate and calcium-uranyl-carbonate complexes.

The predominant uranyl species at all pHs tested was $UO_2(CO_3)_3^{-4}$, accounting for approximately 70% of the total uranyl species. $H_2PO_4^{-2}$ was the major phosphate species, accounting for nearly 60% at all pH conditions tested. Calcium species distribution showed the dependency on pH. At pH 7, the system was dominated by Ca^{2+} ions while the $CaUO_2(CO_3)_3^{-2}$ species became predominate at pH 8 to 10, representing approximately 95% and 80% of the total Ca species, respectively. At pH 11, 85% of Ca was found in the form of $CaPO_4$. Based on the information obtained from the Visual MINTEQ geochemical modeling software, the following elementary reactions are proposed for dissolution reactions at pH 7-10 (Eq. 6) and pH 11 (Eq. 7):

$$Ca\left[\left(UO_2\right)\left(PO_4\right)\right]_2 xH_2O + HCO_3^- \rightarrow UO_2\left(CO_3\right)_3^{-4} + Ca\left(UO_2\right)\left(CO_3\right)_3^{-2} + HPO_4^{-2} + Ca^{+2} + xH_2O$$
(Eq. 6)

$$Ca\left[\left(UO_2\right)\left(PO_4\right)\right]_2 xH_2O + CO_3^- \rightarrow UO_2\left(CO_3\right)_3^{-4} + HPO_4^{-2} + CaPO_4^- + xH_2O \qquad \text{(Eq. 7)}$$

The release of uranium from an autunite mineral is a surface mediated reaction that occurs in several steps [12, 15]. It starts with the fast attachment of a reactant to the surface of the mineral through the surface cracks, followed by the rate-limiting detachment of metal species from the surface. The release of uranium from autunite mineral under the influence of bicarbonate is expected to take place via a two-step process of surface coordination of bicarbonate/carbonate ion followed by the detachment of uranyl carbonate/calcium uranyl carbonate.

Activation energy, E_a, is a unique parameter that describes the nature of the reaction; faster reactions have small activation energy values and slower reactions have higher activation energy values. Zhang et al. (2001) previously reported that pH has a noticeable influence on the activation energy. Also activation energy values help to identify the rate-controlling process of the dissolution of minerals [1, 10]. Reactions with activation energy values less than 20 kJ mol^{-1} are often indicative of surface diffusion rate-controlling reactions. Surface controlled dissolution usually results in higher activation energy.

A modified transition state theory equation describing the rate of reaction as a function of temperature and the activities of the rate enhancing or inhibiting species were used to estimate the activation energy values, described as:

$$r = k \, e^{\frac{-E_a}{RT}} \left[HCO_3^-\right]^{\eta}$$
(Eq. 8)

Where:

   r = dissolution rate (mol m^{-2} s^{-1}) experimentally determined from SPTF tests,

   k = intrinsic rate constant (mol m^{-2} s^{-1}),

   $[HCO_3^-]$ = concentration of bicarbonate solutions (mol L^{-1}),

   η = power law coefficient (dimensionless),

   E_a = activation energy (J mol^{-1}),

   R = universal gas constant (J mol^{-1} K^{-1}), and

   T = temperature (^{o}K).

Fig. 3 depicts normal logarithmic values of the rate of dissolution (ln r) plotted against the values of inverse temperature (T^{-1}) at a constant bicarbonate concentration and at different pH values. The slope of the regression line at each bicarbonate concentration represents activation energy values, which were further averaged at each pH (Table II). The close proximity of regression lines is indicative of the weak effect of HCO_3^- solutions on the rate of uranium release at pH 7 and 8, whereas the separation of curves at pH 9-11 is an indication of rapid uranium release when the concentration of CO_3^{2-} became prominent.

Table II activation energy values of Ca-autunite dissolution at various pH

[HCO_3^-] (M)	Ca-autunite			
	0.0005	0.001	0.002	0.003
pH	E_a (kJ mol^{-1})			
7	21.87	26.39	27.72	26.00
8	22.41	20.72	15.57	13.95
9	2.63	13.07	8.95	7.32
10	8.17	16.68	15.05	15.17
11	11.39	10.19	12.23	11.78

The average activation energy at pH 7 for Ca-autunite was estimated to be 25.50 kJ mol^{-1} and the average activation energy at pH 8 -11 was in the range of 8-18 kJ mol^{-1}. Activation energy at pH 7 is an indication that the dissolution is controlled by the surface bond-breaking of uranyl carbonate and calcium uranyl carbonate ions occurring at the solid/liquid interface by which surface-bound ions move into solution. At pH 8 and above, the reaction is controlled by the rate-limiting mass transfer step of the reaction leading to the crystal sheets cracking or splitting apart.

The pseudo equilibrium constant and the enthalpy of the system were estimated using Eq. 9 and Eq 10. Equation 9 was obtained based on the assumption that the rate limiting factor is the concentration of bicarbonate solutions [8].

$$r = K_g \left[HCO_3^- \right] \qquad \text{(Eq. 9)}$$

$$\Delta H = -RT \ln K_g \qquad \text{(Eq. 10)}$$

Where:

r = dissolution rate (g m^{-2} d^{-1}) experimentally determined from SPTF tests,
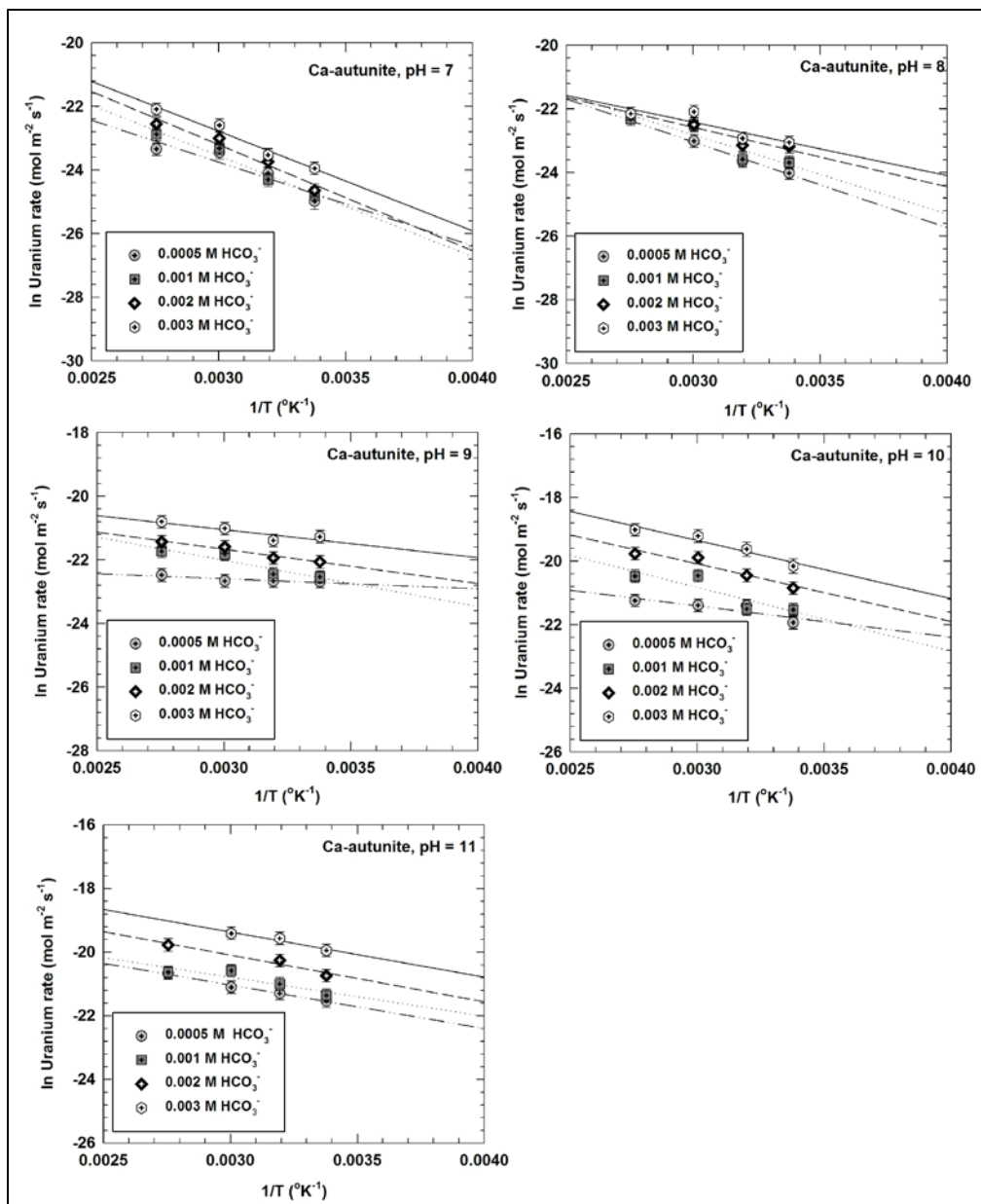
[HCO_3^-] = concentration of bicarbonate solutions (mol L^{-1}),

ΔH = enthalpy (J mol^{-1}),

R = universal gas constant (J mol^{-1} K^{-1}), and

T = temperature (^{o}K).

Fig. 3. Change in the ln of Uranium Release Rate from Ca-Autunite versus Values of Inverse Temperature

The change in the uranium release rate against the change in the bicarbonate concentration were plotted at different pH values and the slope of the regression lines provided the values of the pseudo equilibrium constant (Fig. 4 and TABLE I). This data suggests that the reaction occurred slowly at low pH values and significantly faster at high pH values. A similar trend was shown by the intrinsic rate constant values. A slope of a linear graph with inverse temperature (T^{-1}) on the X-axis and the normal logarithmic values of the pseudo equilibrium constant, ln K_g, on the Y-axis (Fig. 5) were used to estimate the enthalpy of the system at various pH values (TABLE I). This change might not be significant enough to justify any principal differences in the uranium release reaction mechanisms; however, it correlates with the trend shown by the

intrinsic rate constant pertaining to Ca-autunite dissolution suggesting higher U release from this phase.
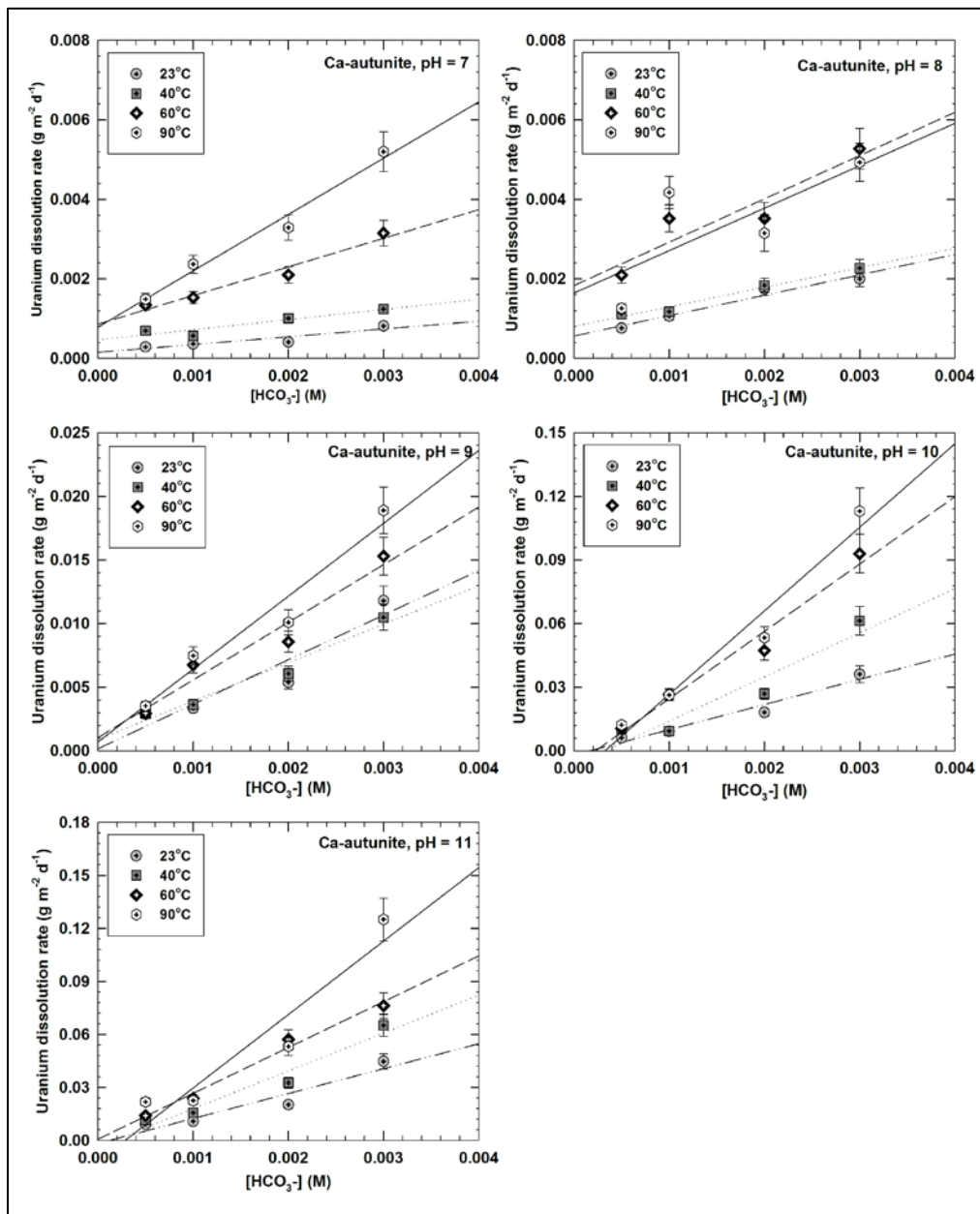

Fig. 4. Uranium Release Rate as a Function of Bicarbonate Solution Concentrations at Various pH Values
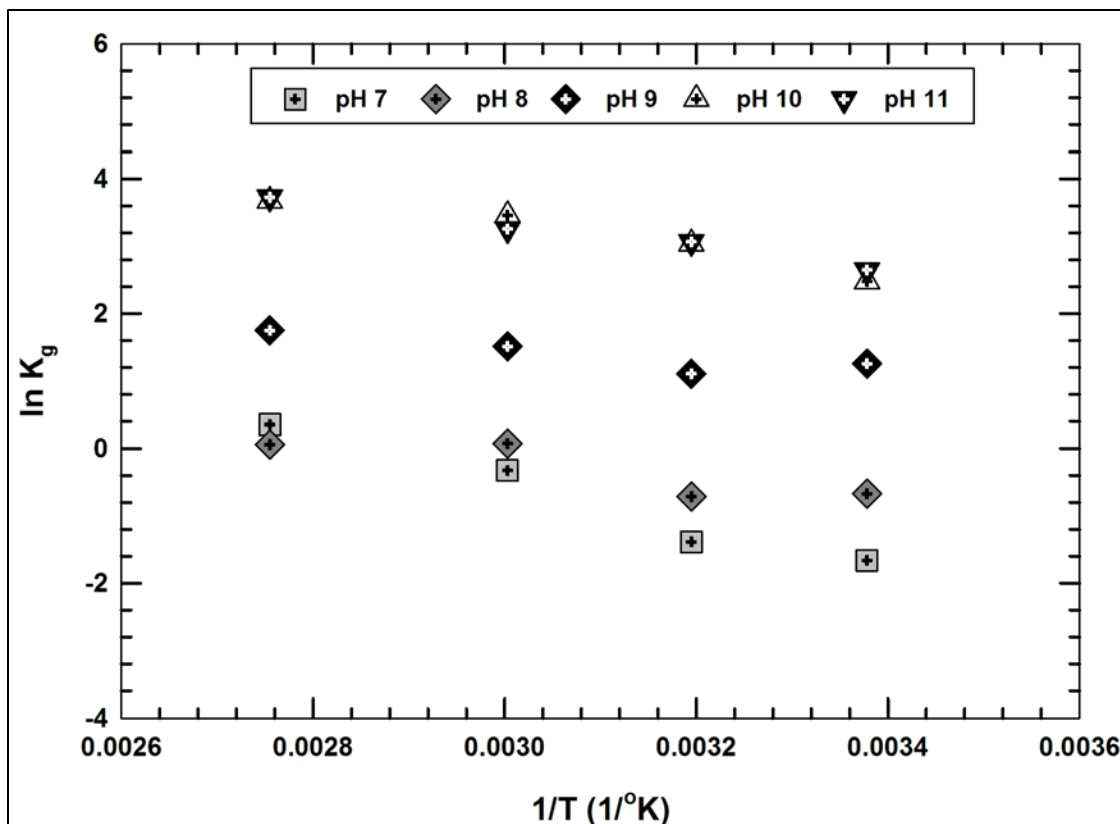
Fig. 5. Changes in the Pseudo Equilibrium Constant as a Function of Inverse Temperature

CONCLUSIONS

The rate of uranium release from the Ca-autunite under the bicarbonate concentration ranging from 0.5 - 3.0 mM, and at pH 7-11 and temperature of 23 - 90 ^{o}C was investigated via single-pass flow-through apparatus. The power law coefficient, η, was found to be between 0.5 and 1.0, with no finite temperature dependency on the uranium release. Pseudo equilibrium and enthalpy data showed that the dissolution process is slower at pH 7; at pH 8 and beyond the speed of dissolution increased. A similar observation was made based on the activation energy values; at pH 7, elevated activation energy suggested that the reaction is deliberate and at pH values 8-11, activation was low, suggesting a faster reaction. The dissolution rate data indicates that low concentrations of bicarbonate in the subsurface environment can impact the stability of the uranyl phosphate minerals. The information presented here provides critical fundamental aspects to refine the bulk kinetic parameters currently being used to predict the stability of autunite minerals and the fate of uranium in the subsurface.

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