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

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Worlds Ahead

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Overview

- Introduction
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  - SPFT
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- Conclusions

Introduction

- DOE Hanford Site groundwater plume is contaminated with **uranium**
- A total of 58,967 kg of uranium was release due to leakages from underground storage tanks
- Injection of **soluble sodium polyphosphate** proved to be effective remediation solution
  - Polyphosphate forms insoluble uranyl-phosphate mineral, **autunite**, $X_{1-2}[(UO_2)(PO_4)]_{2-1} \bullet nH_2O$
  - In Ca- rich environments, Ca replaces Na and the exchange takes place rapidly into Ca-autunite

Introduction

- **Carbonate** is a major ion in the groundwater at Hanford Site (**1.2-2.71mM**)
- **Uranyl ion** (UO_2^{+2}) forms soluble uranyl-carbonate complexes, making uranium **mobile**
- Major uranyl-carbonate complexes are $\mathbf{UO_2(CO_3)_2^{-2}}$ and $\mathbf{UO_2(CO_3)_3^{-4}}$
- Previous research on uranium release from the dissolution of autunite is **limited to pH and temperature**

Objective

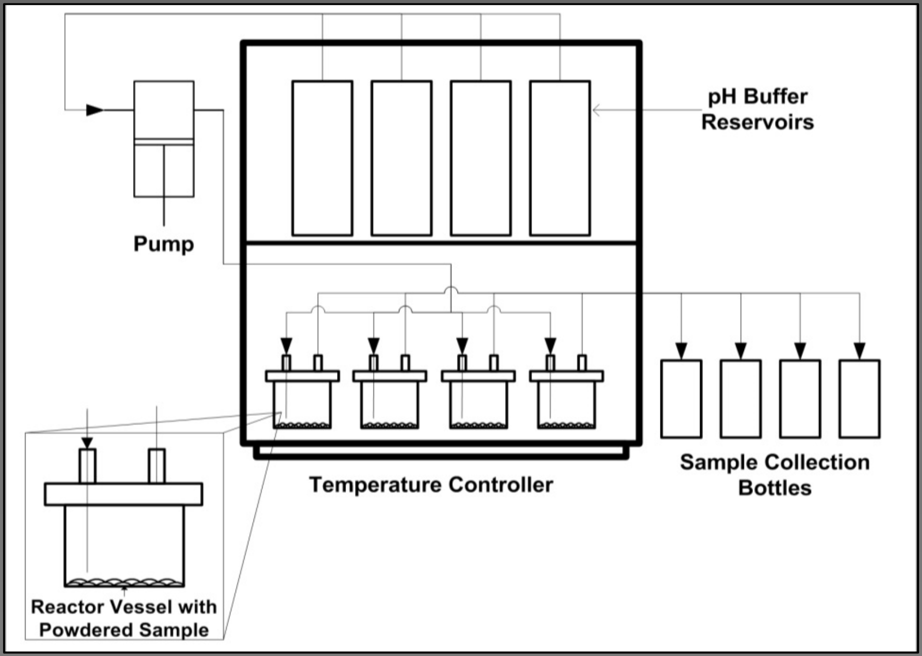
- Quantify the rate of uranium release from autunite in following conditions
  - Bicarbonate: 0.5-3.0 mM
  - pH: 7-11
  - Temperature: 23 - 90^{o}C

Materials and Methods

- **Natural Ca-autunite** was obtained from Excalibur Mineral Corporation
- Characterized via ICO-OES, ICP-MS, XRD, SEM-EDS and confirmed to be **99% pure** (Wellman et al., 2006)
- Sample size: **75 to 150 µm**
- Surface area: **0.88 m^2 g^{-1}**

Single-Pass Flow-Through (SPFT)

- SPFT experiments were designed to measure forward rate under tightly controlled conditions.
- 0.25 grams of autunite
- 0.5-3.0 mM of HCO_3^- and 0.01 M TRIS
- HNO_3 and LiOH
- KPA and ICP-OES



Dissolution Rate Quantification

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

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

Groundwater Modeling

- Steady state concentrations were used to identify predominant uranium species
- **Visual MINTEQ 3.0** was used for speciation modeling
- Thermodynamic database was updated with
  - Nuclear Energy Agency's thermodynamic database for uranium (Guillaumont et al., 2003)
  - calcium-uranyl-carbonate complexes (Dong and Brooks, 2006)
  - becquerelite (Gorman-Lewis et al. 2008)

Results

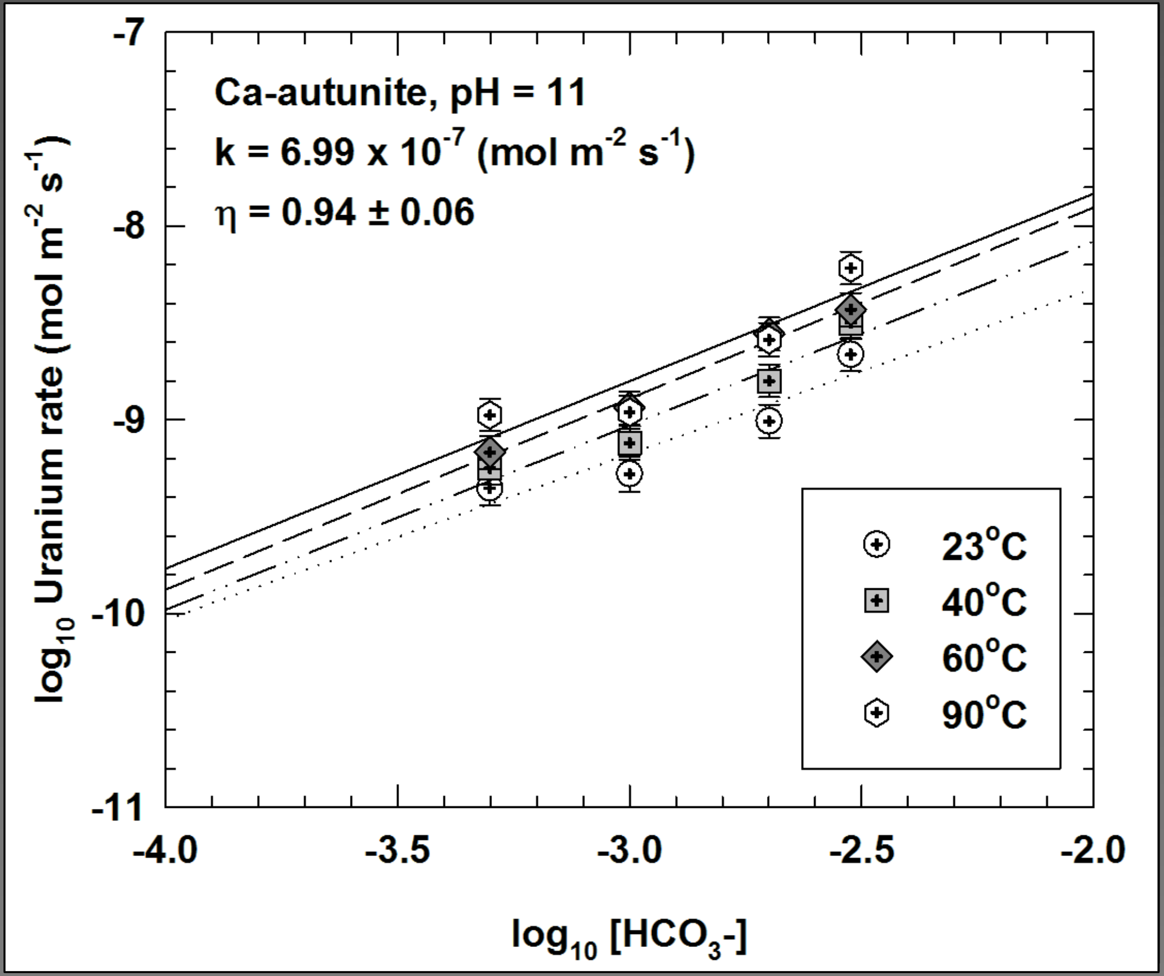
- Influence of bicarbonate on the dissolution of Ca-autunite was experimentally determined using **$\log (r) = \log (k) + \eta \log [HCO_3^-]$**
  - – r is dissolution rate, k is intrinsic rate constant and η is power law coefficient
- Non-linear regression was performed at each temperature, slope of rate vs concentration provided power law coefficient

Results

- Dissolution showed strong influence on pH

pH	Ca-autunite		
	η	k (mol m^{-2} s^{-1})	Increase compared to pH 7
7	0.50 ± 0.12	1.09 x 10^{-09}	-
8	0.52 ± 0.10	3.15 x 10^{-09}	17
9	0.79 ± 0.08	5.60 x 10^{-08}	65
10	1.09 ± 0.11	1.58 x 10^{-06}	392
11	0.94 ± 0.06	6.99 x 10^{-07}	434

Results


Ca-autunite, pH = 11
k = 6.99 x 10-7 (mol m-2 s-1)
η = 0.94 ± 0.06
23°C
40°C
60°C
90°C
log10 Uranium rate (mol m-2 s-1)
-7
-8
-9
-10
-11
-4.0
-3.5
-3.0
-2.5
-2.0
log10 [HCO3-]

Results - Geochemical Modeling

pH	HCO_3^- (M)	Schoepite	β-$UO_2(OH)_2$	Hydroxyapatite	β-$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$ (am2)	$Ca_3(PO_4)_2$ (am1)	$Ca_4H(PO_4)_3 \cdot 3H_2O(s)$	(UO2)3(PO4)2(s)
7	0.0005	0.057	-0.173						2.904
	0.001	-0.179	-0.409						2.275
	0.002	-0.528	-0.757						1.856
	0.003	-0.758	-0.988						1.587
8	0.0005	0.335	0.106	-0.942					0.98
	0.001	0.011	-0.219	0.575					0.5
	0.002	-0.471	-0.7	2.898					-0.232
	0.003	-0.741	-0.971	3.275					-0.378
9	0.0005	0.586	0.356	6.386	-0.69	-1.526	-4.285	-3.248	-1.078
	0.001	0.361	0.132	6.915	-0.323	-1.16	-3.918	-2.678	-1.261
	0.002	0.034	-0.196	8.487	0.669	-0.168	-2.926	-1.275	-1.757
	0.003	-0.584	-0.814	8.716	0.845	0.008	-2.75	-0.975	-3.227
10	0.0005	0.652	0.422	14.551	3.928	3.091	0.333	2.44	-3.695
	0.001	0.607	0.377	13.598	3.376	2.539	-0.219	1.737	-3.63
	0.002	0.344	0.114	12.11	2.512	1.675	-1.083	0.632	-4.136
	0.003	-0.991	-1.221	11.935	2.393	1.557	-1.202	0.453	-8.272
11	0.0005	0.265	0.035	15.229	3.923	3.087	0.328	1.749	-8.966
	0.001	0.215	-0.015	14.877	3.717	2.88	0.122	1.482	-9.068
	0.002	0.055	-0.175	14.381	3.431	2.594	-0.164	1.118	-9.437
	0.003	-0.333	-0.563	14.155	3.284	2.447	-0.311	0.903	-10.717

Results - Geochemical Modeling

- Predominant species
  - $UO_2(CO_3)_3^{-4}$
  - $H_2PO_4^{-2}$
  - Ca^{2+} (pH 7), $CaUO_2(CO_3)_3^{-2}$ (pH 8-10), $CaPO_4$ (pH 11)

$$Ca[(UO_2)(PO_4)]_2\,xH_2O + HCO_3^- \rightarrow UO_2(CO_3)_3^{-4} + Ca(UO_2)(CO_3)_3^{-2} + HPO_4^{-2} + Ca^{+2} + xH_2O$$

$$Ca[(UO_2)(PO_4)]_2\,xH_2O + CO_3^- \rightarrow UO_2(CO_3)_3^{-4} + HPO_4^{-2} + CaPO_4^- + xH_2O$$

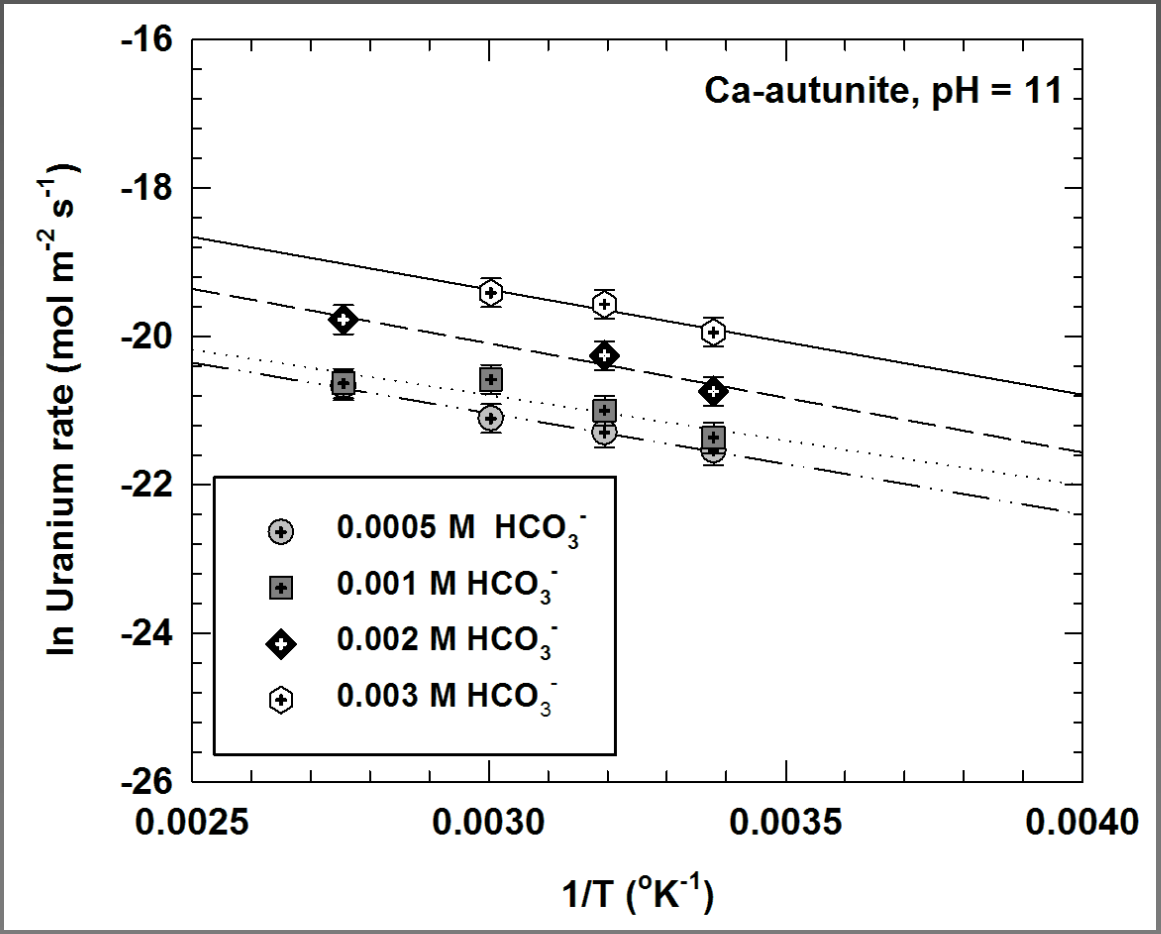
Results - Activation Energy

- Describes the nature of the reaction, < 20 kJ/mol surface dif on
- pH has not
- Modified T

  ln r = l
- Average ac 1)
- Rate contr
  - Surface bond-breaking @ pH 7
  - Rate limiting mass transfer @ pH >=8

pH	$[HCO_3^-]$ (mM)			
	0.5	1.0	2.0	3.0
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

Results - Activation Energy



Results - Pseudo Equilibrium and Enthalpy

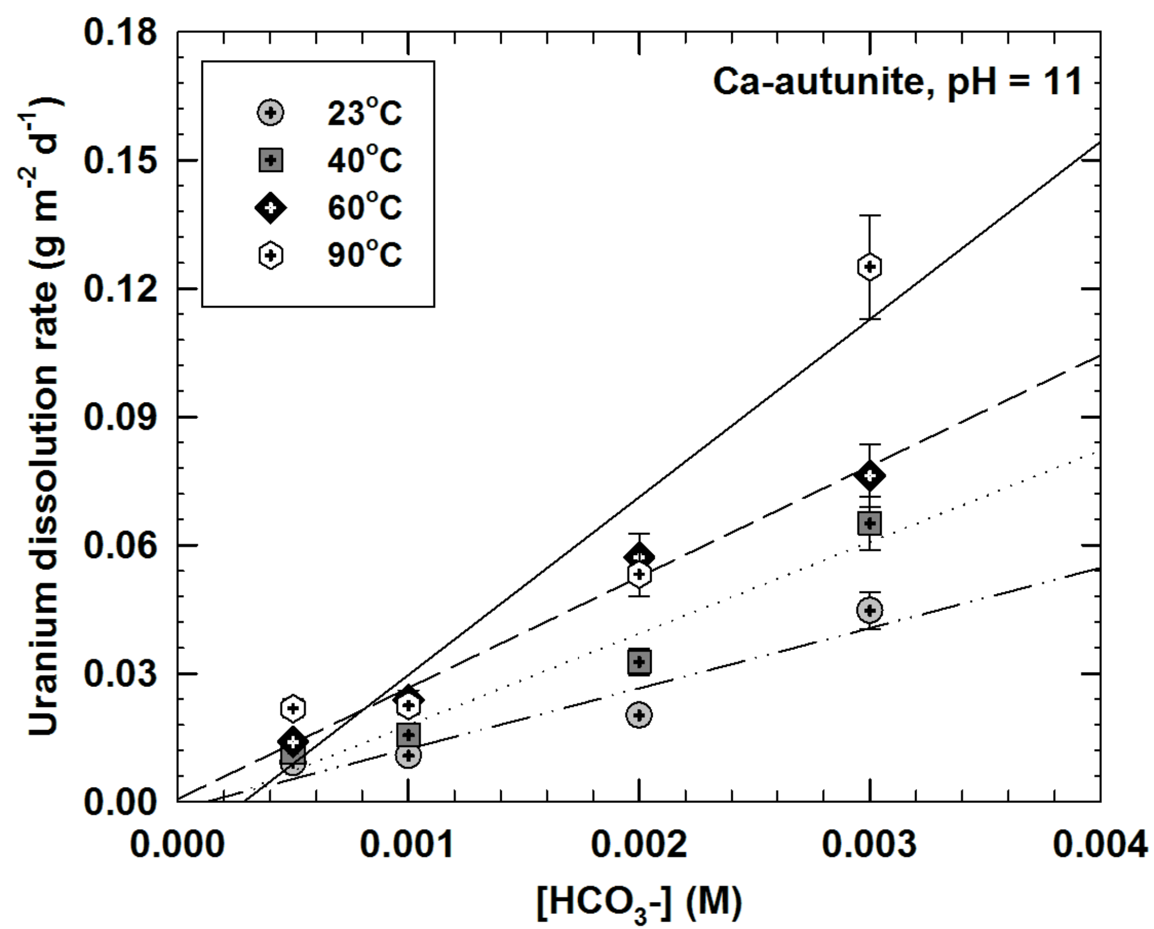
$$r = K_g \left[HCO_3^- \right]$$

$$\Delta H = -RT \ln K_g$$

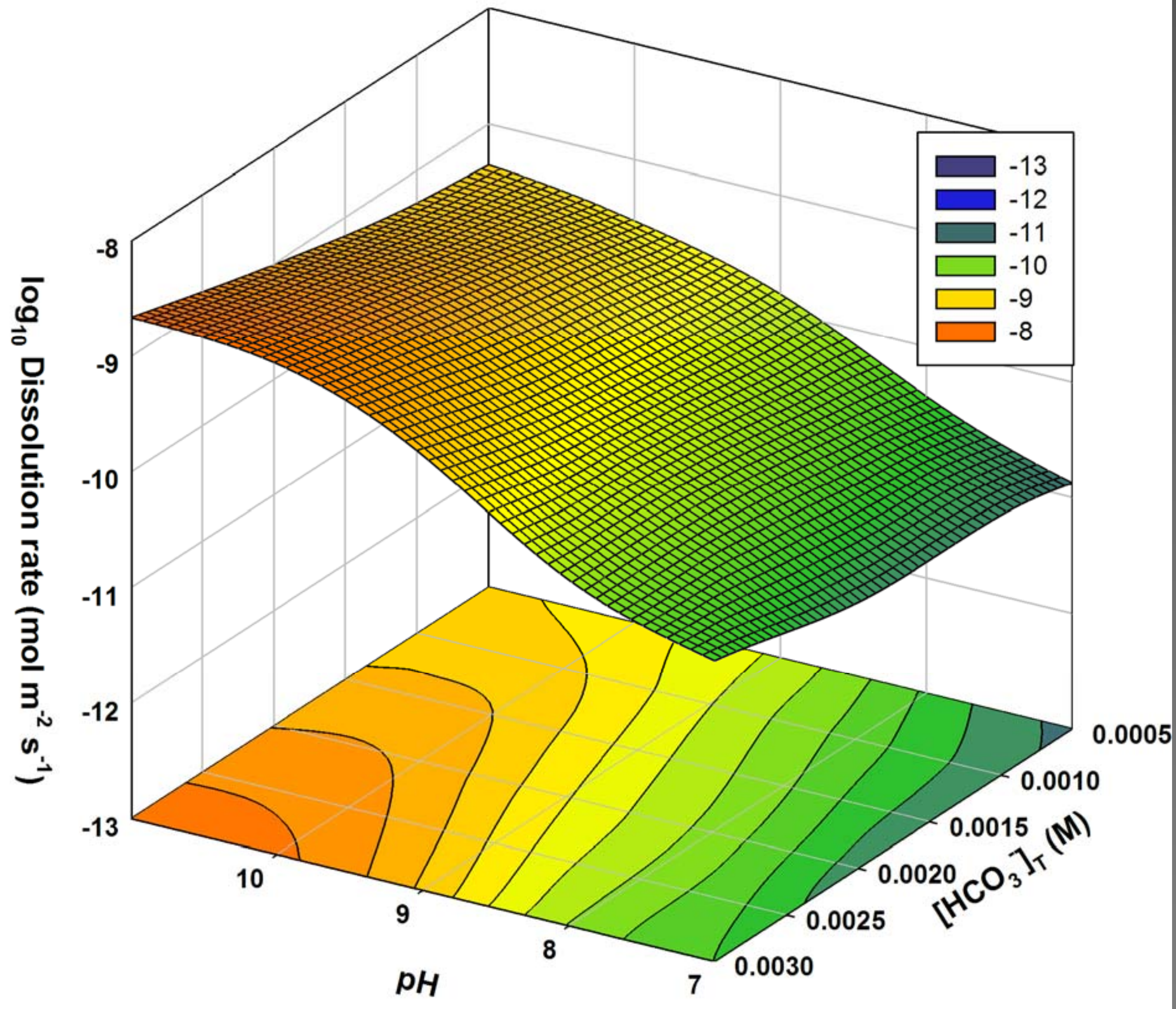
pH	Ca-autunite	
	K_g	ΔH
7	0.65	28.58
8	0.79	11.83
9	4.20	11.90
10	25.97	15.88
11	27.75	13.84

- Reaction is slow at low pH and significantly fast at high pH
- Enthalpy data is not significant to justify the uranium release mechanism but correlates to the intrinsic rate (k)

Results - Pseudo Equilibrium and Enthalpy



Results - 3D


-13
-12
-11
-10
-9
-8
log10 Dissolution rate (mol m-2 s-1)
-8
-9
-10
-11
-12
-13
10
9
8
7
pH
0.0005
0.0010
0.0015
0.0020
0.0025
0.0030
[HCO3]T (M)

Conclusions

- Power law coefficient is 0.5-1.0, no finite dependency on temperature
- Dissolution is slower at pH 7 and faster at pH 8 and beyond
- Dissolution data indicate **low concentration** of bicarbonate can **impact the stability** of autunite
- Data is being incorporated into modeling at Hanford Site

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