

Thermodynamic Modeling of Siderite and Chukanovite in the WIPP Relevant Brines

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I. INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) repository uses steel in waste containers and lead in shielded containers. These metals are expected to interact strongly with sulfide, and to compete with the transuranic species in complexation of the organic ligands such as citrate, EDTA and oxalate in brine. To estimate the consequence of potential radionuclide releases from the repository to the environment after decommissioning, it is required to determine the solubilities of the radionuclides in the brine, which are affected by the above interactions. The solution chemistry for brines relevant to the WIPP repository are determined by using the Pitzer model [1,2] to evaluate the activity coefficients for the various components of the brine. To date, the WIPP thermodynamic database does not incorporate iron (II), lead, or sulfide species. As part of updating the thermodynamic database, the parameters necessary for modeling are being determined. As a result, siderite solubility in the WIPP relevant brines were explored at room temperature and high pH (> 10). We present here the experimental findings that are relevant to interaction of carbonate (CO_3^{2-}) and iron species (Fe^{2+} , FeOH^+ , $\text{Fe}(\text{OH})_2^0$ and $\text{Fe}(\text{OH})_3^-$)

synthesized by adding 150 mL of 4.0M NaHCO_3 solution to 200 mL of 2.95M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O} + \text{NaHCO}_3 \rightarrow \text{FeCO}_3(\text{s}) + \text{Na}^+ + 2\text{Cl}^- + \text{H}^+ + 4\text{H}_2\text{O}$), where “m” represents molality. Identification of siderite phase was confirmed using an X-ray diffractometer. Sample reactors ($\text{FeCO}_3\text{-XCO}_3\text{-(3,4,5,6)}$) were prepared by adding the synthesized siderite to Xm $\text{Na}_2\text{CO}_3\text{-Ym NaCl}$ brines (X = 0.01, 0.1, 0.5, 1.0, 1.5, and 2.0, Y = 0.15 and 1.5). Sample setups of reactors are listed in Table 1.

Sample ID	$\text{Na}_2\text{CO}_3(\text{m})$	$\text{NaCl}(\text{m})$	$\text{FeCO}_3(\text{g})$	Sample ID	$\text{Na}_2\text{CO}_3(\text{m})$	$\text{NaCl}(\text{m})$	$\text{FeCO}_3(\text{g})$
$\text{FeCO}_3\text{-0.01CO}_3\text{-3}$	0.0100	1.5001	0.47	$\text{FeCO}_3\text{-0.01CO}_3\text{-5}$	0.0105	0.1501	0.52
$\text{FeCO}_3\text{-0.1CO}_3\text{-3}$	0.1000	1.5001	0.49	$\text{FeCO}_3\text{-0.1CO}_3\text{-5}$	0.1003	0.1503	0.47
$\text{FeCO}_3\text{-0.5CO}_3\text{-3}$	0.4999	1.5003	0.50	$\text{FeCO}_3\text{-0.5CO}_3\text{-5}$	0.4998	0.1504	0.51
$\text{FeCO}_3\text{-1.0CO}_3\text{-3}$	1.0000	1.4999	0.46	$\text{FeCO}_3\text{-1.0CO}_3\text{-5}$	0.9999	0.1499	0.48
$\text{FeCO}_3\text{-1.5CO}_3\text{-3}$	1.5000	1.5000	0.48	$\text{FeCO}_3\text{-1.5CO}_3\text{-5}$	1.4998	0.1500	0.49
$\text{FeCO}_3\text{-2.0CO}_3\text{-3}$	2.0000	1.5001	0.50	$\text{FeCO}_3\text{-2.0CO}_3\text{-5}$	1.9999	0.1500	0.53
$\text{FeCO}_3\text{-0.01CO}_3\text{-4}$	0.0100	1.5001	0.53	$\text{FeCO}_3\text{-0.01CO}_3\text{-6}$	0.0105	0.1501	0.50
$\text{FeCO}_3\text{-0.1CO}_3\text{-4}$	0.1000	1.5001	0.52	$\text{FeCO}_3\text{-0.1CO}_3\text{-6}$	0.1003	0.1503	0.48
$\text{FeCO}_3\text{-0.5CO}_3\text{-4}$	0.4999	1.5003	0.49	$\text{FeCO}_3\text{-0.5CO}_3\text{-6}$	0.4998	0.1504	0.48
$\text{FeCO}_3\text{-1.0CO}_3\text{-4}$	1.0000	1.4999	0.48	$\text{FeCO}_3\text{-1.0CO}_3\text{-6}$	0.9999	0.1499	0.47
$\text{FeCO}_3\text{-1.5CO}_3\text{-4}$	1.5000	1.5000	0.49	$\text{FeCO}_3\text{-1.5CO}_3\text{-6}$	1.4998	0.1500	0.48
$\text{FeCO}_3\text{-2.0CO}_3\text{-4}$	2.0000	1.5001	0.46	$\text{FeCO}_3\text{-2.0CO}_3\text{-6}$	1.9999	0.1500	0.51

Table 1. Sample reactors $\text{FeCO}_3\text{-XCO}_3\text{-(5,6)}$ consisting of distinct amounts of Na_2CO_3 , NaCl and FeCO_3 .

Concentrations of Fe(II) and Na^+ were analyzed on an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Perkin Elmer Optima 3300DV), Cl^- on an Ion Chromatograph (IC, Dionex IC-3000), and CO_3^{2-} on Coulometer (UIC 5015 ^{JPI3} Carbon Coulometer).

III. RESULTS

Evidence for hydroxyl-bearing phase formation: systematic pH decrease with time.

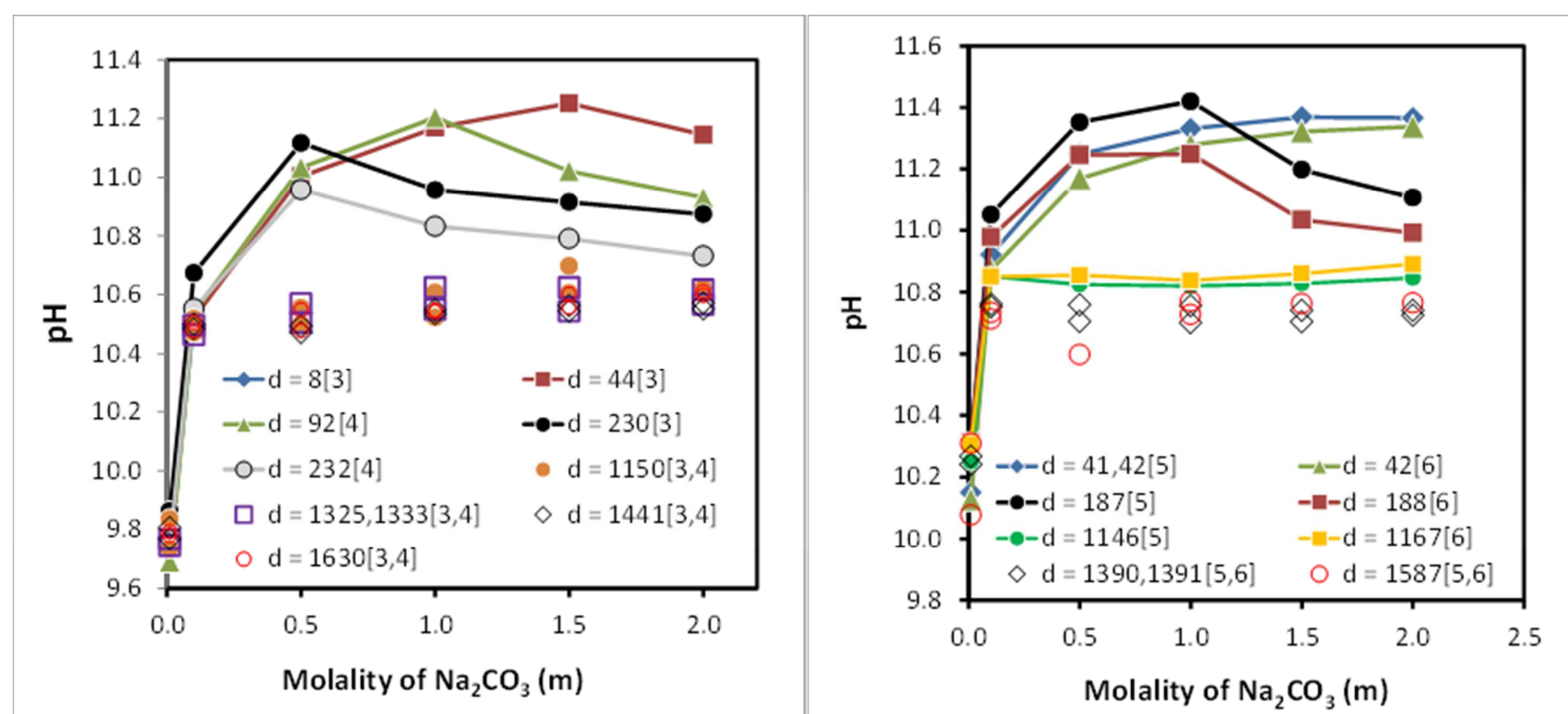


Figure 1. Plot of experimentally measured pH values versus nominal molality of Na_2CO_3 for sample reactors at different aging days. [i] represents replicate number of sample reactors: i = 3,4 is for Xm Na_2CO_3 – 1.5m NaCl, and i = 5,6 is for Xm Na_2CO_3 – 0.15m NaCl, where X = 0.01, 0.1, 0.5, 1.0, 1.5 and 2.0.

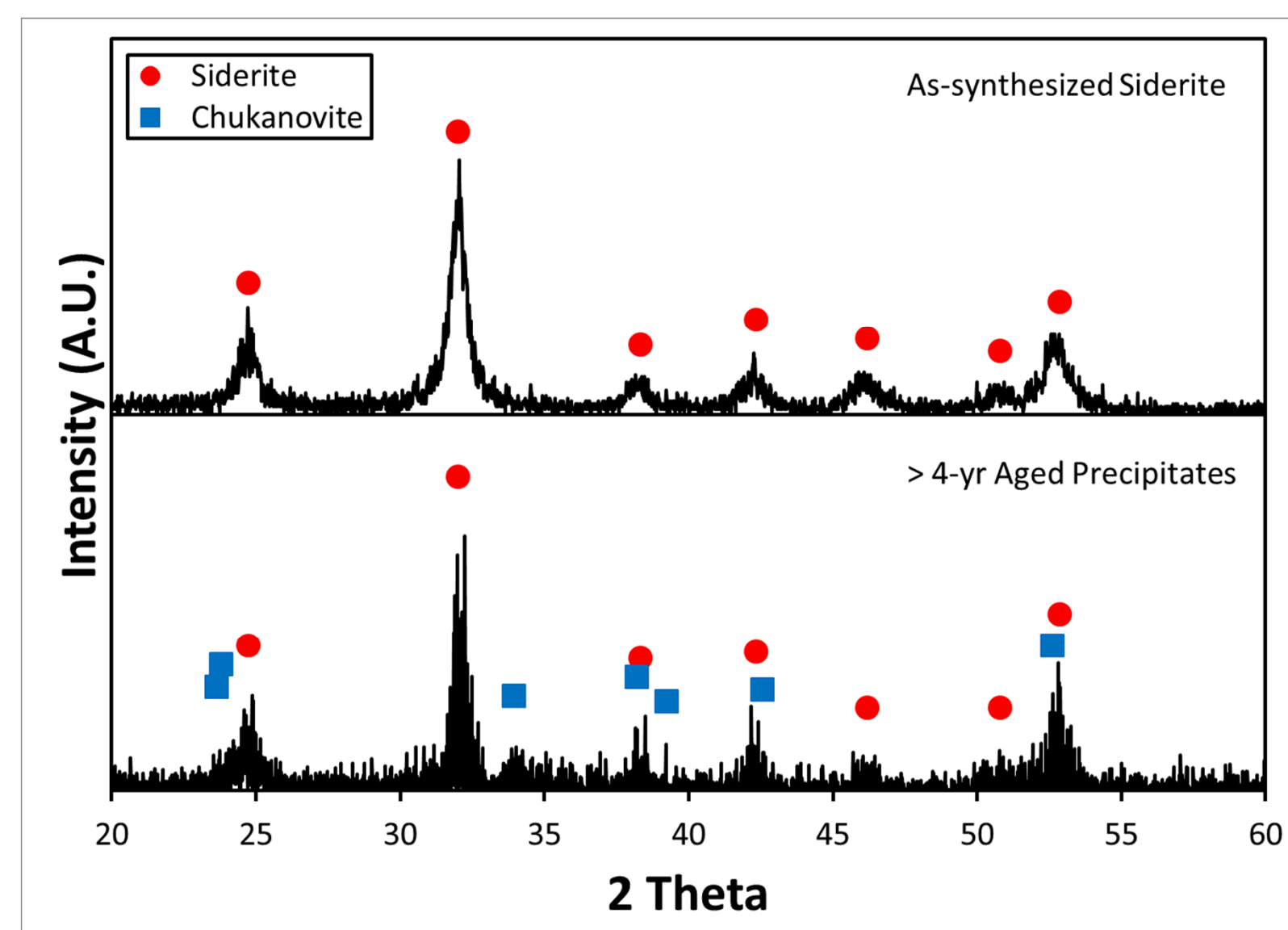


Figure 2. XRD spectra of as-synthesized siderite and the mixture of siderite and chukanovite in > 4-year-aged sample reactors.

The observed decreases of pH values with aging time indicated precipitation of an hydroxyl-bearing phase consistent with chukanovite [$\text{Fe}_2(\text{OH})_2\text{CO}_3$]. X-ray diffraction (XRD) analyses showed as-synthesized siderite evolves into an assemblage of chukanovite and siderite in > 4-year-aged sample reactors (Figure 2).

Thus, the analyzed Fe(II) solubility data from (0.5,1.0,1.5,2.0)m Na_2CO_3 – (0.15,1.5)m NaCl sample reactors were utilized to derive the Pitzer interaction parameters for $\text{Fe}^{2+}/\text{CO}_3^{2-}$ and $\text{FeOH}^+/\text{CO}_3^{2-}$ binary ionic pairs, and log K value of a dissolution reaction of chukanovite.

Thermodynamic Model Parameters

Due to its precipitation, chukanovite is considered the phase controlling Fe(II) speciation for EQ3/6 calculations. Tables 2 and 3 show the chemical reactions and Pitzer interaction parameters that are used in the present study.

Reactions	logK	Source	I	J	β^0	β^1	β^2	C^0	Source
Aqueous reactions									
(1) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	13.9967	[5]	Na^+	Cl^-	0.0765	0.2664	0.00127	[5]	
(2) $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	10.3392	[5]	Na^+	OH^-	0.0864	0.253	0.0044	[5]	
(3) $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	-6.3374	[5]	Na^+	HCO_3^-	0.0277	0.0411		[5]	
(4) $\text{FeOH}^+ + \text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O}$	9.3148	[6]	Na^+	CO_3^{2-}	0.0399	1.389	0.0044	[5]	
(5) $\text{Fe}(\text{OH})_2(\text{aq}) + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	20.94	Present study	H^+	Cl^-	0.1775	0.2945	0.0008	[5]	
(6) $\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	31.0	[6]	Fe^{2+}	Cl^-	0.3359	1.5322	-0.00861	[7]	
			Fe^{2+}	CO_3^{2-}	TBD	TBD	TBD	Present study	
			FeOH^+	CO_3^{2-}	TBD	TBD	TBD	Present study	
Dissolution									
(7) $\text{Fe}_2(\text{OH})_2\text{CO}_3(\text{s}) + 3\text{H}^+ = 2\text{Fe}^{2+} + \text{HCO}_3^- + 2\text{H}_2\text{O}$	TBD	Present study	Na^+	H^+	β_{NaH} or β_{NaH}			[5]	
(8) $\text{FeCO}_3(\text{s}) + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$	-0.192	[6]	Na^+	Fe^{2+}	0.08			[8]	
(9) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}(\text{s}) + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + \text{H}_2\text{O}$	10.8211	[5]	Cl^-	OH^-	-0.05			[5]	
(10) $\text{Na}_2\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s}) + \text{H}^+ = 3\text{Na}^+ + 2\text{HCO}_3^- + 2\text{H}_2\text{O}$	9.2948	[5]	Cl^-	HCO_3^-	0.03			[5]	
(11) $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}(\text{s}) + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + 7\text{H}_2\text{O}$	9.8791	[5]	Cl^-	CO_3^{2-}	-0.02			[5]	
(12) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s}) + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + 10\text{H}_2\text{O}$	9.5145	[5]	OH^-	CO_3^{2-}	0.1			[5]	
(13) $\text{NaHCO}_3(\text{s}) = \text{Na}^+ + \text{HCO}_3^-$	-0.4030	[5]	HCO_3^-	CO_3^{2-}	-0.04			[5]	
(14) $\text{NaCl}(\text{s}) = \text{Na}^+ + \text{Cl}^-$	1.5704	[5]							

Table 2. Reactions and 10-based logarithms of their equilibrium constants (logK).

Table 3. Pitzer interaction parameters.

EQ3/6 [3,4] used data in Tables 2 and 3 and experimentally measured pH and concentrations of ion species to derive the Pitzer interaction parameters for $\text{Fe}^{2+}/\text{CO}_3^{2-}$ and $\text{FeOH}^+/\text{CO}_3^{2-}$ binary ionic pairs. Figure 3 and 4 show that the total Fe(II) solubility estimated with the optimized Pitzer parameters for $\text{Fe}^{2+}/\text{CO}_3^{2-}$ and $\text{FeOH}^+/\text{CO}_3^{2-}$ binary ionic pairs are comparable to those experimentally measured (open diamond in figures).

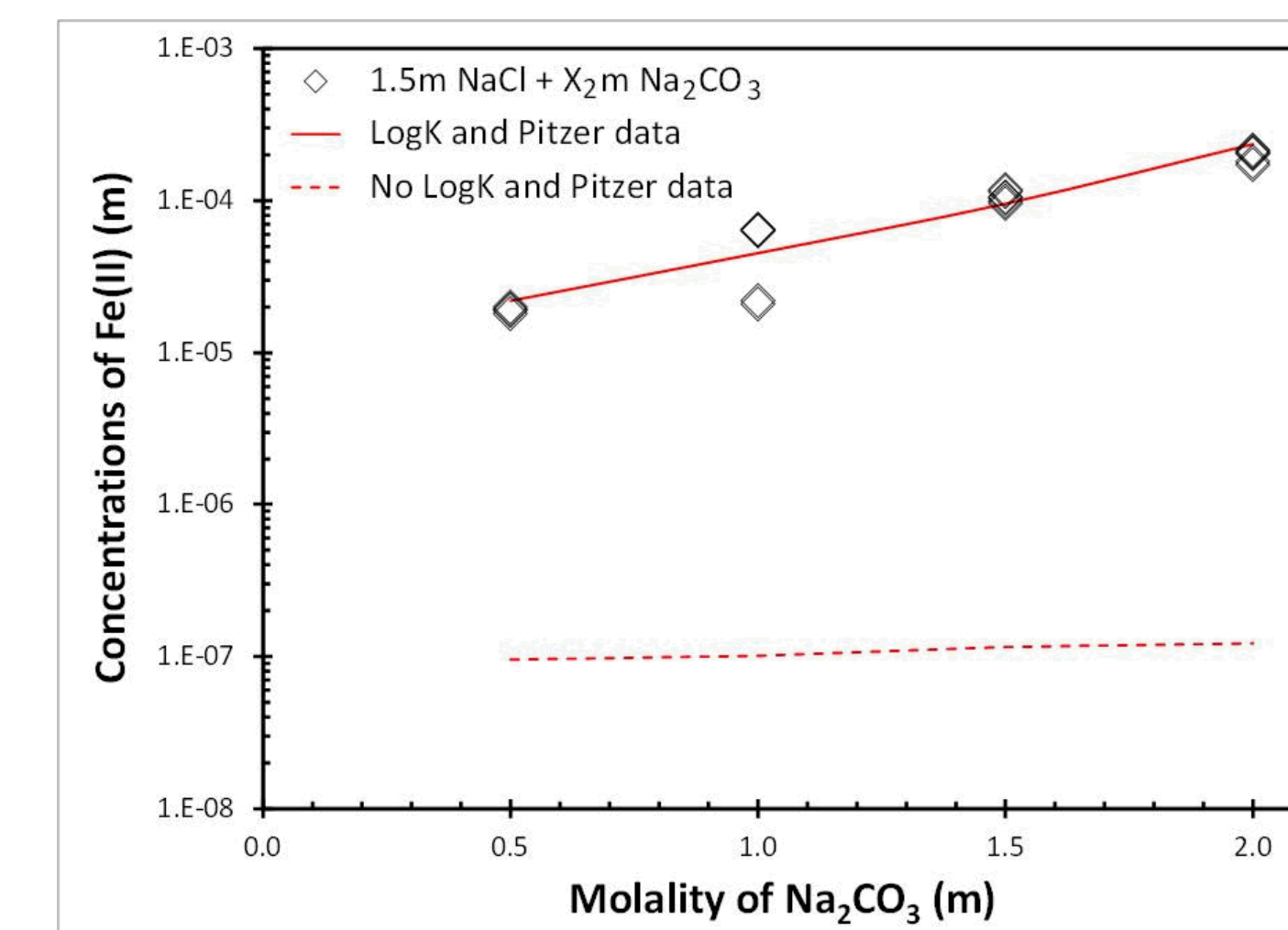


Figure 3. Total Fe(II) solubility in $\text{FeCO}_3\text{-XCO}_3\text{-(3,4)}$ sample reactors, where $X_2 = 0.5, 1.0, 1.5$ and 2.0.

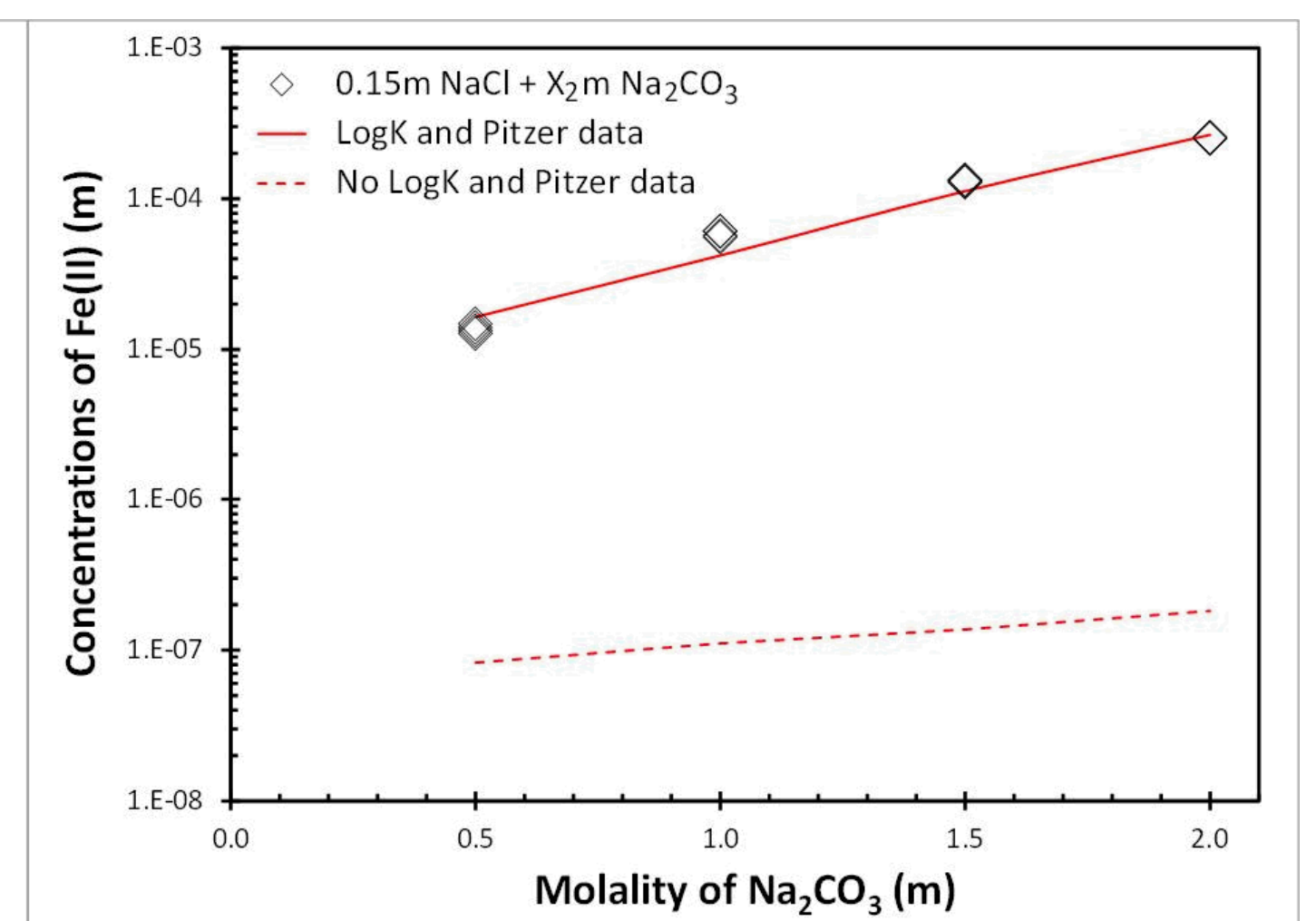


Figure 4. Total Fe(II) solubility in $\text{FeCO}_3\text{-XCO}_3\text{-(5,6)}$ sample reactors, where $X_2 = 0.5, 1.0, 1.5$ and 2.0.

Parameter	Fit Value
$\text{Fe}^{2+} - \text{CO}_3^{2-} \beta^{(0)}$	-1.20940
$\text{Fe}^{2+} - \text{CO}_3^{2-} \beta^{(1)}$	3.27
$\text{Fe}^{2+} - \text{CO}_3^{2-} \beta^{(2)}$	-45.74
$\text{FeOH}^+ - \text{CO}_3^{2-} \beta^{(0)}$	-0.74874
$\text{FeOH}^+ - \text{CO}_3^{2-} \beta^{(1)}$	1.74
log K (chukanovite)	16.2527

Table 4. The derived Pitzer parameters and log K value of chukanovite

Table 4 shows the derived Pitzer interaction parameters for $\text{Fe}^{2+}/\text{CO}_3^{2-}$ and $\text{FeOH}^+/\text{CO}_3^{2-}$ binary ionic pairs, and log K value of chukanovite (Reaction (7) in Table 2). From this log K value, the formation energy of chukanovite was estimated.

$$\Delta G_f^\circ (\text{chukanovite}) = -1149.6 \text{ kJ/mol.}$$

The estimated formation energy of chukanovite is compared to the literature data in Table 5, where the log K value is computed for a reaction of $\text{Fe}_2(\text{OH})_2\text{CO}_3(\text{s}) + 2\text{H}^+ = 2\text{Fe}^{2+} + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$.

pH	Standard formation energy (kJ/mol)				log K at 25°C
	$\text{Fe}_2(\text{OH})_2\text{CO}_3(\text{s})$	Fe^{2+}	CO_3^{2-}	H_2O	
10.4 – 10.9	-1149.6				5.91
~ 8.3[10]	-1169.3[10]				2.46
8.2 – 9.1[11]	-1174.4[11]	-90.53	-527.90	-237.18	1.56
10.26 – 10.91[12]	-1171.5[12]				2.07

Table 5. Comparison of the estimated Standard formation energy of chukanovite and the log K value of $\text{Fe}_2(\text{OH})_2\text{CO}_3(\text{s}) + 2\text{H}^+ = 2\text{Fe}^{2+} + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$ at 25°C to the literature data.

IV. SUMMARY

The range of pH values of the sample reactors used for the current modeling was 10.4 – 10.9. The estimated standard formation energy of chukanovite was -1149.6 kJ/mol, which embodies a 1.7 – 2.1% difference from literature values [10-12]. However, the log K value reported here is appreciably different from those calculated from the literature. The current study investigated the formation of chukanovite in siderite-added NaCl + Na_2CO_3 brines. In an extension of this study, the stability of chukanovite will be investigated by adding chukanovite to NaCl + Na_2CO_3 brines. In this way, the formation energy of chukanovite is subject to update.

REFERENCES

- [1] Pitzer, K.S., “Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations.” Journal of Physical Chemistry, vol. 77 p. 268 (1973).
- [2] Pitzer, K.S., “Thermodynamics of Electrolytes. V. Effects of Higher-Order Electrostatic Terms.” Journal of Solution Chemistry, vol. 4 p. 249 (1975).
- [3] Wolery, T.J., Y.-L. Xiong, and J.J. Long, Verification and validation plan/validation document for EQ3/6 version 8.0a for actinide chemistry, document version 8.10, 2010: Carlsbad, NM: Sandia National Laboratories, ERMS 550239.
- [4] Xiong, Y.-L., WIPP verification and validation plan/validation document for EQ3/6 version 8.0a for actinide chemistry, Revision 1, 2011: Carlsbad, NM: Sandia National Laboratories: ERMS 555358.
- [5] Xiong, Y.-L., Release of EQ3/6 Database data0.fm1, 2011, Sandia National Laboratories: ERMS 548926: Carlsbad, NM.
- [6] Wolery, T.J. and R.L. Jarek, data0.ymf.R2 dataset included in the aqueous speciation code EQ3/6 v.8.0a package, 2008.
- [7] Pitzer, K.S., Ion Interaction Approach: Theory and Data Correlation, in Activity Coefficients in Electrolyte Solutions, K.S. Pitzer, Editor. 1991, CRC Press: Boca Raton, FL p. 75-153.
- [8] Nemer, M.B., et al., Solubility of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ (pure-iron end member of hibbingite) in NaCl and Na_2SO_4 brines. Chemical Geology, 2011. 280: p. 26-32.
- [9] Ptacek, C.J., Experimental Determination of Siderite Solubility in High Ionic-Strength Aqueous Solutions, in Earth Sciences1992, University of Waterloo.
- [10] Nishimura, T. and J. Dong, Corrosion Behavior of Carbon Steel for Overpack in Groundwater Containing Bicarbonate Ions. Journal of Power and Energy Systems, 2009. 3(1): p. 23-30.
- [11] Lee, T.R. and R.T. Wilkin, Iron hydroxy carbonate formation in zerovalent iron permeable reactive barriers: Characterization and evaluation of phase stability. Journal of Contaminant Hydrology, 2010. 116: p. 47-57.
- [12] Azoulay, I., C. Remazeilles, and P. Refait, Determination of standard Gibbs free energy of formation of chukanovite and Pourbaix diagrams of iron in carbonated media. Corrosion Science, 2012. 58: p. 229-36.

Strictly speaking, ICP-AES measures total iron. Fe(II) can, of course, be determined by spectrophotometry.

How do you know that chuckanovite is present in enough mass to control the concentrations (activities) of all the species in your reactor?
Izenhower, Jonathan Paul, 6/10/2016