



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^+ , $\text{Fe}(\text{OH})_2^\circ$ 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 $\text{Xm Na}_2\text{CO}_3\text{-Ym NaCl}$ brines ($\text{X} = 0.01, 0.1, 0.5, 1.0, 1.5$, and 2.0 , $\text{Y} = 0.15$ 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	$\text{Na}_2\text{CO}_3(\text{m})$	$\text{NaCl}(\text{m})$	$\text{FeCO}_3(\text{g})$
FeCO3-0.01CO3-3	0.0100	1.5001	0.47	FeCO3-0.01CO3-5	0.0105	0.1501	0.52
FeCO3-0.1CO3-3	0.1000	1.5001	0.49	FeCO3-0.1CO3-5	0.1003	0.1503	0.47
FeCO3-0.5CO3-3	0.4999	1.5003	0.50	FeCO3-0.5CO3-5	0.4998	0.1504	0.51
FeCO3-1.0CO3-3	1.0000	1.4999	0.46	FeCO3-1.0CO3-5	0.9999	0.1499	0.48
FeCO3-1.5CO3-3	1.5000	1.5000	0.48	FeCO3-1.5CO3-5	1.4998	0.1500	0.49
FeCO3-2.0CO3-3	2.0000	1.5001	0.50	FeCO3-2.0CO3-5	1.9999	0.1500	0.53
FeCO3-0.01CO3-4	0.0100	1.5001	0.53	FeCO3-0.01CO3-6	0.0105	0.1501	0.50
FeCO3-0.1CO3-4	0.1000	1.5001	0.52	FeCO3-0.1CO3-6	0.1003	0.1503	0.48
FeCO3-0.5CO3-4	0.4999	1.5003	0.49	FeCO3-0.5CO3-6	0.4998	0.1504	0.48
FeCO3-1.0CO3-4	1.0000	1.4999	0.48	FeCO3-1.0CO3-6	0.9999	0.1499	0.47
FeCO3-1.5CO3-4	1.5000	1.5000	0.49	FeCO3-1.5CO3-6	1.4998	0.1500	0.48
FeCO3-2.0CO3-4	2.0000	1.5001	0.46	FeCO3-2.0CO3-6	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 $\text{Fe}(\text{II})$ 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 Carbon Coulometer).

III. RESULTS

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

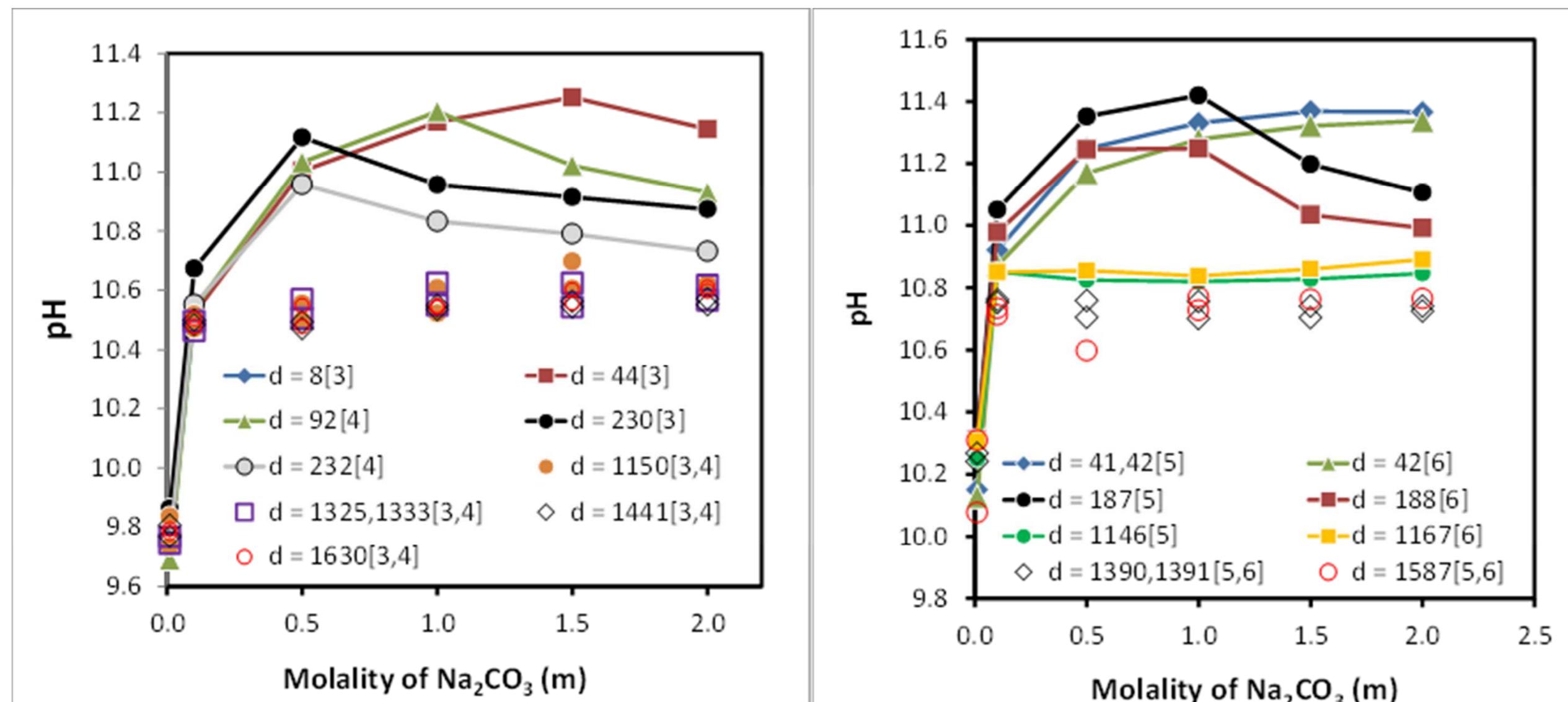


Figure 1. Plot of experimentally measured pH values versus nominal molality of Na_2CO_3 for sample reactors at different aging days. [i] represents replicate number of sample reactors; $i = 3, 4$ is for $\text{Xm Na}_2\text{CO}_3 - 1.5\text{m NaCl}$, and $i = 5, 6$ is for $\text{Xm Na}_2\text{CO}_3 - 0.15\text{m NaCl}$, where $\text{X} = 0.01, 0.1, 0.5, 1.0, 1.5$ and 2.0 .

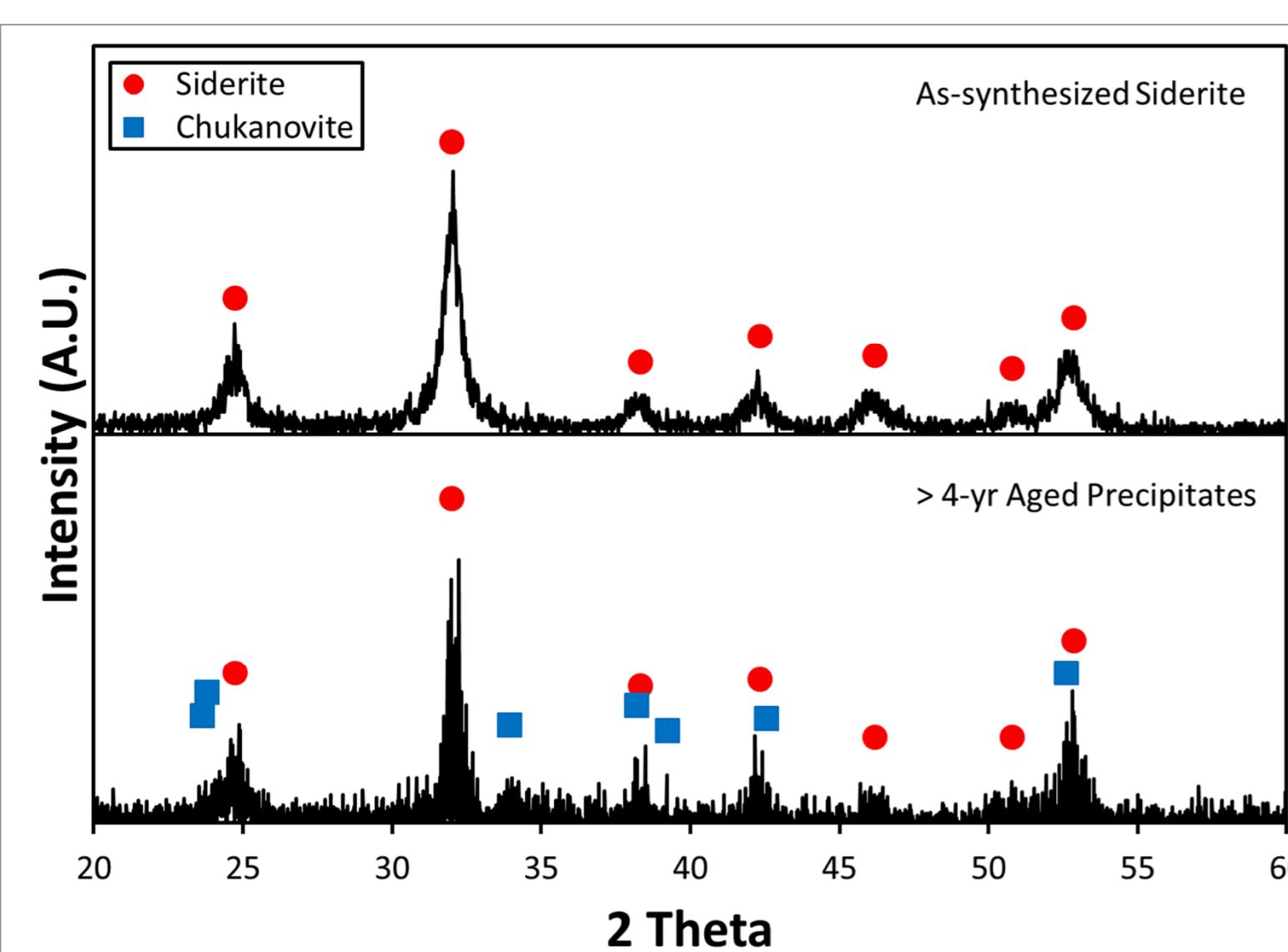


Figure 2. XRD spectra of as-synthesized siderite and the mixture of siderite and chukanovite in >4-year-aged sample reactors.

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 $\text{Fe}(\text{II})$ solubility data from $(0.5, 1.0, 1.5, 2.0)\text{m Na}_2\text{CO}_3 - (0.15, 1.5)\text{m NaCl}$ 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 $\text{Fe}(\text{II})$ 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	β^3	Source
(1) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	13.9967	[5]	Na^+	Cl^-	0.0765	0.2664	0.00127	0.0044	[5]
(2) $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	10.3392	[5]	Na^+	HCO_3^-	0.0277	0.1111	0.00044	0.0044	[5]
(3) $\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	-6.3374	[5]	Na^+	H^+	0.0399	0.389	0.00088	0.00088	[5]
(4) $\text{Fe}^{2+} + \text{H}^+ = \text{Fe}^{2+} \cdot \text{H}_2\text{O}$	9.3148	[6]	Fe^{2+}	Cl^-	0.1775	1.5222	0.00061	0.00061	[7]
(5) $\text{Fe}(\text{OH})_2(\text{aq}) + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	20.94	Present study	Fe^{2+}	CO_3^{2-}	TBD	TBD	TBD	TBD	Present study
(6) $\text{Fe}(\text{OH})_2(\text{aq}) + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	31.0	[6]	$\text{Fe}(\text{OH})_2$	CO_3^{2-}	TBD	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^+	0.036				[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) $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_2 + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + \text{H}_2\text{O}$	10.8211	[5]	Cl^-	OH^-	-0.05				[5]
(10) $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_2 + 2\text{H}^+ = 3\text{Na}^+ + 2\text{HCO}_3^- + 2\text{H}_2\text{O}$	9.2948	[5]	Cl^-	HCO_3^-	0.03				[5]
(11) $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_2 + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + 7\text{H}_2\text{O}$	9.8791	[5]	OH^-	CO_3^{2-}	-0.02				[5]
(12) $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_2 + \text{H}^+ = 2\text{Na}^+ + \text{HCO}_3^- + 10\text{H}_2\text{O}$	9.5145	[5]	HCO_3^-	CO_3^{2-}	0.1				[5]
(13) $\text{NaHCO}_3(\text{s}) = \text{Na}^+ + \text{HCO}_3^-$	-0.4030	[5]	Na^+	HCO_3^-	-0.04				[5]
(14) $\text{NaCl}(\text{s}) = \text{Na}^+ + \text{Cl}^-$	1.5704	[5]	Na^+	Cl^-	0.002				[5]

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

I	J	$\beta_{\text{a}} \text{ or } \beta_{\text{as}}$	Source
Na^+	H^+	0.036	[5]
Na^+	Fe^{2+}	0.08	[8]
Cl^-	OH^-	-0.05	[5]
Cl^-	HCO_3^-	0.03	[5]
Cl^-	CO_3^{2-}	-0.02	[5]
OH^-	CO_3^{2-}	0.1	[5]
HCO_3^-	CO_3^{2-}	-0.04	[5]

Table 3. Pitzer interaction parameters.

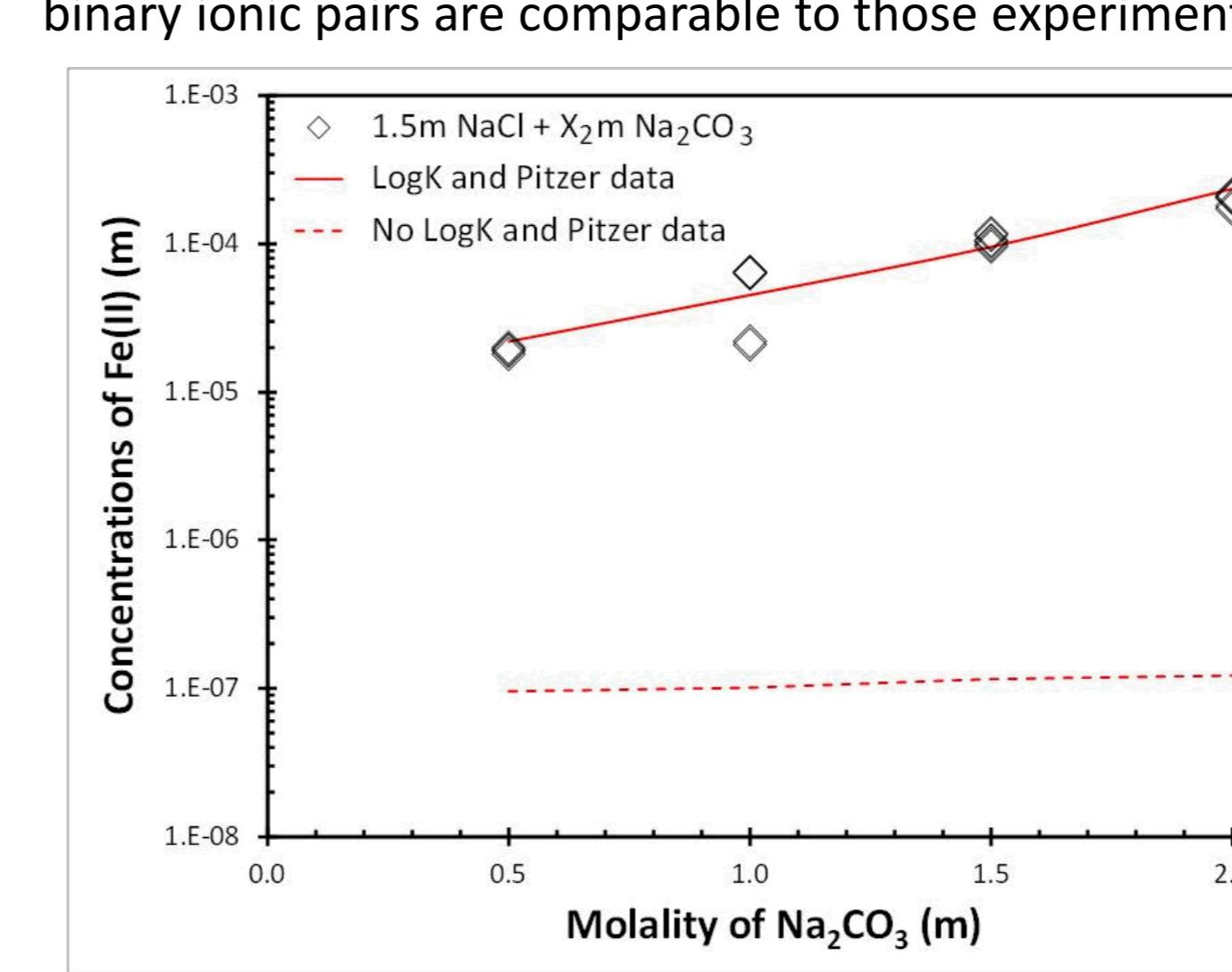


Figure 3. Total $\text{Fe}(\text{II})$ solubility in $\text{FeCO}_3\text{-XCO}_3\text{-}(3,4)$ sample reactors, where

