EXPERIMENTS AND THERMODYNAMIC MODELING IN THE Na+-Cl--Fe2+-SO42- SYSTEM TO HIGH IONIC STRENGTHS

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I. INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) repository uses iron-based waste containers, in which Iron (Fe) is always present. These metals are expected to compete with actinide components for complexation of organic ligands such as citrate, ethylenediaminetetraacetate (EDTA) and oxalate in the repository. To estimate potential radionuclide release from the repository to the environment after closure, it is essential to determine the solubility of the radionuclides in the brine, which is affected by the ligands listed above. The solution chemistry for brines relevant to the WIPP repository is modeled by using the Pitzer model [1,2] to evaluate activity coefficients. To date, the WIPP thermodynamic database does not incorporate iron nor lead species. As part of updating the thermodynamic database, the Pitzer interaction parameters iron and lead aqueous species are being determined. As a result, we present here the experimental data and theoretical derivation of the Pitzer interaction parameters that are relevant to the interaction of sulfate (SO_4^{2-}) with iron (II) species (Fe^{2+} and $FeOH^+$).

II. EXPERIMENTAL WORKS

To mimic an environment consistent with the expected anoxic WIPP conditions, experiments have been performed inside a glovebox, where oxygen levels were maintained below 3 ppm. Under anoxic condition, $Fe_2(OH)_3Cl(s)$ and $Fe(OH)_2(s)$ solids were synthesized by reacting $FeCl_2 \cdot 4H_2O$ with KOH and NaOH, respectively [3]. Phase identification of products were confirmed using an x-ray diffractometer (XRD).

Sample reactors (Xm Na2SO4+0.15NaCl-GR-Kinetics and Ym-SO4-Fe(OH)2-(1,2), where X = 0.01,0.1,0.5,1.0,1.5, and 1.8, Y = 0.05, 0.38, 0.76, 1.14, 1.52, and 1.90, and m = molality) were prepared by adding the synthesized $Fe(OH)_2(s)$ and $Fe_2(OH)_3Cl(s)$. Sample setups of reactors are listed in Table 1.

Table.1. Sample reactors Xm Na2SO4+0.15NaCl-GR-Kinetics and Ym-SO4-Fe(OH)2-(1,2) consisting of distinct amounts of Na2SO4, NaCl, Fe2(OH)3Cl and Fe(OH)2.

Reactors	Na₂SO₄ (m)	NaCl (m)	Fe(OH)₂ (g)	Fe₂(OH)₃Cl (g)
0.01m Na2SO4+0.15NaCl-GR-Kinetics	0.01	0.15	2.05	
0.1m Na2SO4+0.15NaCl-GR-Kinetics	0.1	0.15	2.02	
0.5m Na2SO4+0.15NaCl-GR-Kinetics	0.5	0.15	2.04	
1.0m Na2SO4+0.15NaCl-GR-Kinetics	1.0	0.15	2.02	
1.5m Na2SO4+0.15NaCl-GR-Kinetics	1.5	0.15	2.02	
1.8m Na2SO4+0.15NaCl-GR-Kinetics	1.8	0.15	2.03	
0.05m-SO4-Fe(OH)2-(1,2)	0.05			0.7
0.38m-SO4-Fe(OH)2-(1,2)	0.38			0.7
0.76m-SO4-Fe(OH)2-(1,2)	0.76			0.7
1.14m-SO4-Fe(OH)2-(1,2)	1.14			0.7
1.52m-SO4-Fe(OH)2-(1,2)	1.52			0.7
1.90m-SO4-Fe(OH)2-(1,2)	1.90			0.7

Concentrations of Fe(II) and Na+ were analyzed on an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Perkin Elmer Optima 3300DV), and Cl- and SO42- on an Ion Chromatograph (IC, Dionex IC-3000).

III. RESULTS

SO_4^{2-} and HSO_4^- at current pH ranges

According to the fm1 database, WIPP thermodynamic database, pH appears to control stability of SO_4^{2-} and HSO_4^- ion species by a chemical equilibrium:

$$SO_4^{2-} + H^+ = HSO_4^- \qquad \log K = 1.9786 \text{ at } 25\ °C$$

Under dilute solutions, the Law of Mass Action provides the mole fraction of SO_4^{2-} ion species:

$$f(SO_4^{2-}) = \frac{M_{SO_4^{2-}}}{M_{HSO_4^-} + M_{SO_4^{2-}}} = \frac{1}{1+10^{1.9786-pH}} \sim 1.0 \text{ at pH} > 6$$

In the present sample reactors with pH > 7, sulfate (SO_4^{2-}) is dominant species than hydrogen sulfate (HSO_4^-), resulting in that interaction of hydrogen sulfate with Fe(II) species are excluded.

Thermodynamic Model Parameters

In sample reactors, FeCO3-YCO3-(5,6) (Y = 0.5, 1.0, 1.5, and 2.0), we consider that thermodynamic interaction of HCO_3^- ion species to other distinct ion species could be ignorable due to its very low concentration. Thermodynamic interactions of Fe(II)/CO_3^{2-} binary ionic pairs in FeCO3-YCO3-(5,6) sample reactors are studied. Tables 2 and 3 show chemical reactions and the Pitzer thermodynamic interaction parameters that are used in the present study.

Table 2. Reactions and 10-based logarithms of their equilibrium constants (logK). "fm1" is the current WIPP thermodynamic database [4]. "ymp" is from References [5].

Aqueous reactions	logK	Source
(1) $H^+ + OH^- = H_2O$	13.9967	fm1
(2) $SO_4^{2-} + H^+ = HSO_4^-$	1.9786	fm1
(3) $FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.3148	ymp
(4) $Fe(OH)_3^- + 3H^+ = Fe^{2+} + 3H_2O$	31.0000	ymp
Dissolution	logK	Source
(5) $NaCl(s) = Na^+ + Cl^-$	1.5704	fm1
(6) $Na_2SO_4 \cdot 10H_2O$ (s) $= 2Na^+ + SO_4^{2-} + 10H_2O$	-1.2278	fm1
(7) $Na_3H(SO_4)_2 = 3Na^+ + H^+ + 2SO_4^{2-}$	-0.8143	fm1
(8) $Na_2SO_4(s) = 2Na^+ + SO_4^{2-}$	-0.2875	fm1
(9) $FeSO_4(s) = Fe^{2+} + SO_4^{2-}$	1.9396	ymp
(10) $Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	12.95	Reference [3]
(11) $Fe_2Cl(OH)_3(s) + 3H^+ = 2Fe^{2+} + Cl^- + 3H_2O$	17.12	Reference [3]

Table 3. Pitzer interaction parameters.

i	j	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	Source
Na⁺	Cl⁻	0.0765	0.2664		0.00127	fm1
Na⁺	OH⁻	0.0864	0.253		0.0044	fm1
Na⁺	HSO₄⁻	0.0454	0.398			fm1
Na⁺	SO₄²⁻	0.01958	1.113		0.00497	fm1
H⁺	Cl⁻	0.1775	0.2945		0.0008	fm1
H⁺	SO₄²⁻	0.0298			0.0438	fm1
H⁺	HSO₄⁻	0.2065	0.5556			fm1
Fe²⁺	SO₄²⁻	0.3359	1.5322		-0.00861	Reference[6]
FeOH⁺	Cl⁻	0.3063	0.29			Reference[7]

i	j	$\theta_{cc'}$ or $\theta_{aa'}$				Source
Na⁺	H⁺	0.036				fm1
Na⁺	Fe²⁺	0.08				Reference[3]
Cl⁻	OH⁻	-0.05				fm1
Cl⁻	SO₄²⁻	0.02				fm1
Cl⁻	HSO₄⁻	-0.006				fm1
SO₄²⁻	OH⁻	-0.013				fm1
Fe(OH)₃⁻	Cl⁻	-0.3553				Reference[7]

i	j	k	$\psi_{cc'a}$ or $\psi_{aa'c}$			Source
Na⁺	H⁺	HSO₄⁻	-0.0129			fm1
Na⁺	H⁺	Cl⁻	-0.004			fm1
Cl⁻	OH⁻	Na⁺	-0.006			fm1
Cl⁻	SO₄²⁻	Na⁺	0.0014			fm1
Cl⁻	HSO₄⁻	Na⁺	-0.006			fm1
Cl⁻	HSO₄⁻	H⁺	0.013			fm1
SO₄²⁻	HSO₄⁻	Na⁺	-0.0094			fm1
SO₄²⁻	OH⁻		-0.009			fm1

EQ3NR [8,9] used data in Tables 2 and 3 and experimentally measured pH and concentrations of ion species to derive the Pitzer interaction parameters for Fe(II)/SO42- binary ion pairs. Figures 1 and 2 show that the total Fe(II) solubilities estimated with the optimized Pitzer parameters for Fe(II)/SO42- binary ionic pairs are comparable to those experimentally measured.
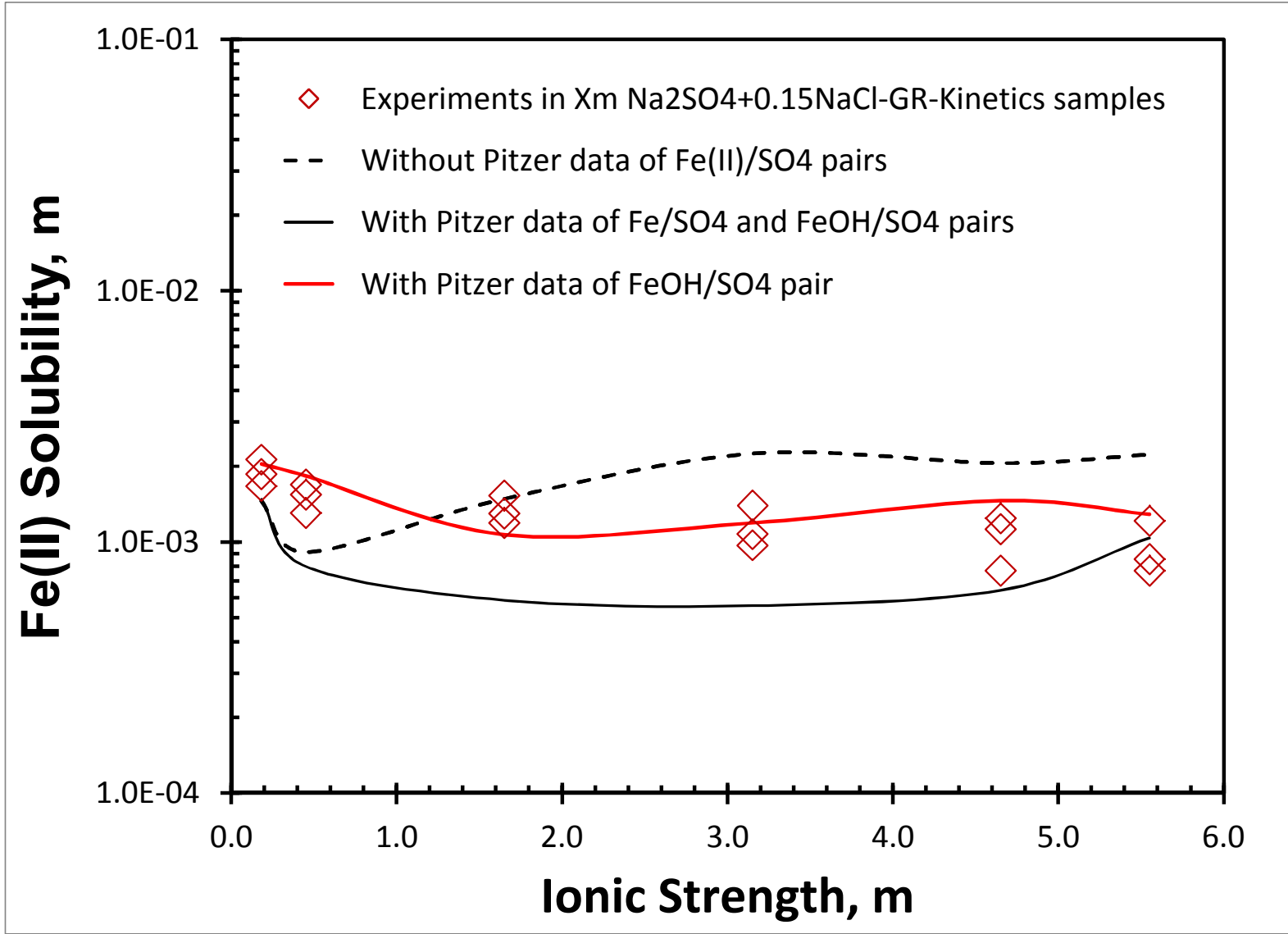

Figure 1. Total Fe(II) solubilities in Xm Na2SO4+0.15NaCl-GR-Kinetics sample reactors (aging days: 55, 85, 1135), that are evaluated using the Pitzer interaction parameters for Fe(II)/SO42- binary ionic pairs.
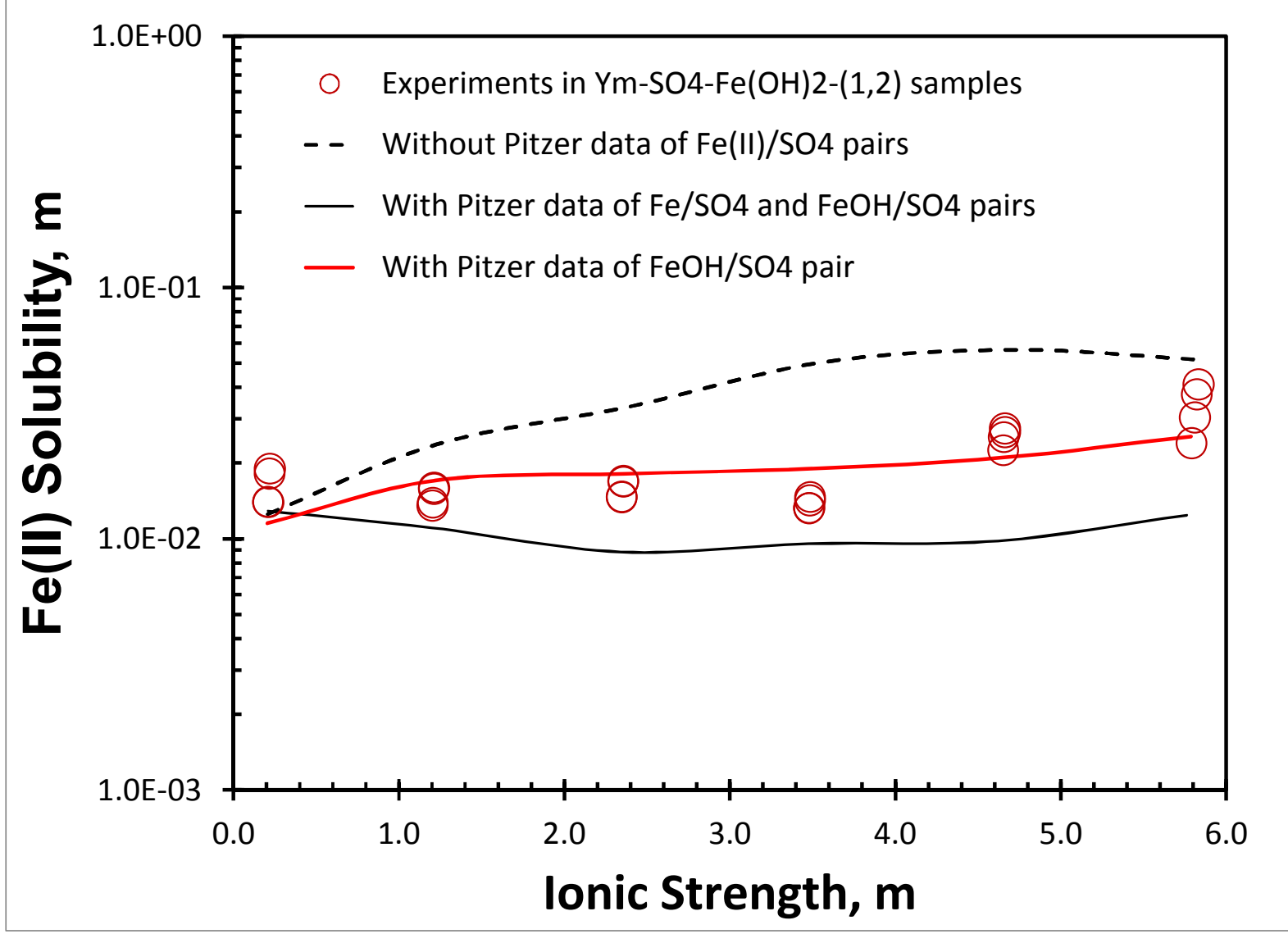
Figure 2. Total Fe(II) solubilities in Ym-SO4-Fe(OH)2-(1,2) sample reactors (aging days: 1374, 2065), that are evaluated using the Pitzer interaction parameters for Fe(II)/SO42- binary ionic pairs.

Solid and dashed lines connect data points for molality data that are computed using the Pitzer interaction parameters of ionic pairs in Table 3 and the Fe(II)/SO42- pairs. Open symbols are the experimentally analyzed total Fe(II) solubility data of sample reactors.

1. Dashed line was obtained using thermodynamic data listed in Tables 2 and 3. No Pitzer interaction parameters of Fe(II)/SO42- pairs are included.
2. Black solid line was obtained using thermodynamic data listed in Tables 2 and 3, and the Pitzer interaction parameters of Fe2+/SO42-, and FeOH+/SO42- pairs derived using all experimentally analyzed total Fe(II) solubility data. Aging days of the sample reactors are less than 7 months for Xm Na2SO4+0.15NaCl-GR-Kinetics, and less than 4 years for Ym-SO4-Fe(OH)2-(1,2). For Ym-SO4-Fe(OH)2-(1,2), total Fe(II) solubility at high ionic strength has molality range in more than 1 order of magnitude, indicating sample reactors with aging days less than 1 year may not reach equilibrium.
3. Addition of newly analyzed total Fe(II) solubility data. Exclusion of total Fe(II) solubility data from Ym-SO4-Fe(OH)2-(1,2) with aging days less than 1 year. Addition of literature data of the Pitzer interaction parameters of Fe2+/SO42- pair [10]. Based on these activities, the Pitzer interaction parameters of FeOH+/SO42- pair was re-derived. Red solid line was obtained using these updates and the re-derived Pitzer parameters.

Collaboration with other institute is still on-going, resulting in that Figures 1 and 2 present preliminary results.

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