Derivation of Pitzer Interaction Parameters for an Aqueous Species Pair of $FeEDTA^{2-}$ and Na^{+}

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NNSA National Nuclear Security Administration

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Introduction

- **$EDTA^{4-}$**
  - Present in the waste
  - Capable of solubilizing actinides via aqueous complexation
- **Fe**
  - Present in the waste and containers
  - Competes with actinides for complexation with EDTA
- **Pitzer formulation**
  - Ideal for the activity coefficients for solutions of medium to high ionic strength

Objectives

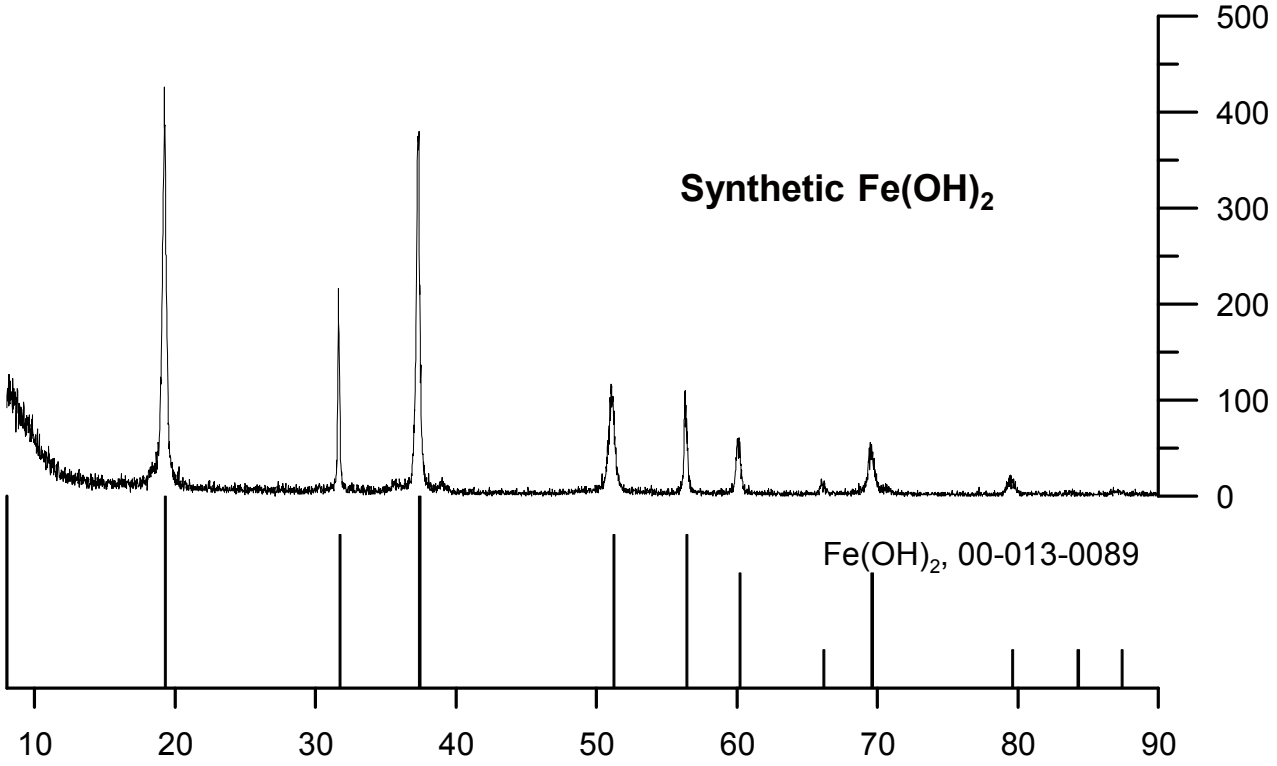
- To determine the Pitzer interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}) for the pair of $FeEDTA^{2-}$ and Na^{+}

Material and Methods (1/3)

- Iron(II) hydroxide was synthesized: $Fe(OH)_2(s)$
- Na_2H_2EDTA, NaCl purchased
- Reactors were prepared in the glovebox
  - Po_2 less than 10 ppm
  - Serum bottles with rubber seals and aluminum crimps
  - Room temperature
  - $Fe(OH)_2(s)$ in mixed Na_2H_2EDTA and NaCl solutions
  - Powder reagents degassed in the glovebox for at least overnight
  - Solutions prepared using deoxygenated deionized water
  - For most conditions, more than two replicates prepared
- Aged for more than 1000 days

Material and Methods (2/3)

XRD of $Fe(OH)_2(s)$



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Material and Methods (3/3)

- ICP-AES for Na and Fe
- IC for Cl
- Total Carbon Coulometer for EDTA
- pH: glass combination electrode calibrated using commercial pH buffers
- XRD: characterization of solid

Aqueous speciation model used for this fitting

Table 1: Reactions and 10-based logarithms of their equilibrium constants (logK's) used in this model fitting.

Reactions	logK
Aqueous reactions	
(1) $H^+ + OH^- = H_2O$	13.99
(2) $H_4EDTA(aq) = 4H^+ + EDTA^{4-}$ [a]	-23.03
(3) $H_3EDTA^- = 3H^+ + EDTA^{4-}$	-20.53
(4) $H_2EDTA^{2-} = 2H^+ + EDTA^{4-}$	-17.45
(5) $HEDTA^{3-} = H^+ + EDTA^{4-}$	-10.57
(6) $FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.31
(7) $FeEDTA^{2-} = Fe^{2+} + EDTA^{4-}$	-16.1
Dissolution	
(8) $Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	12.95
(9) $NaCl(s) = Na^+ + Cl^-$	1.57

[a] $EDTA^{4-}$: $C_{10}H_{12}O_8N_2^{4-}$

Table 2: Pitzer interaction parameters used in this model fitting. Three Pitzer parameters for $FeEDTA^{2-}/Na^+$ pair ($\beta^{(0)}$, $\beta^{(1)}$, and C^φ) were fitted to the experimental data.

i	*j*	$\beta^{(0)}$	$\beta^{(1)}$	C^φ
Na^+	Cl^-	0.0765	0.2664	0.00127
Na^+	OH^-	0.0864	0.253	0.0044
Na^+	H_3EDTA^-	-0.2345	0.29	0.059
Na^+	H_2EDTA^{2-}	-0.1262	1.74	0.054
Na^+	$HEDTA^{3-}$	0.5458	5.22	-0.048
Na^+	$EDTA^{4-}$ [a]	1.016	11.6	0.001
H^+	Cl^-	0.1775	0.2945	0.0008
Fe^{2+}	Cl^-	0.3359	1.5322	-0.00861
Na^+	$FeEDTA^{2-}$	TBD[b]	TBD[b]	TBD[b]

i	*j*	$\theta_{cc'}$ or $\theta_{aa'}$
Na^+	H^+	0.036
Na^+	Fe^{2+}	0.08
Cl-	OH^-	-0.05

i	*j*	*k*	$\psi_{cc'a}$ or $\psi_{aa'c}$
Na^+	H^+	Cl^-	-0.004
Cl^-	OH^-	Na^+	-0.006

[a] $EDTA^{4-}$: $C_{10}H_{12}O_8N_2^{4-}$

[b] TBD: To Be Determined

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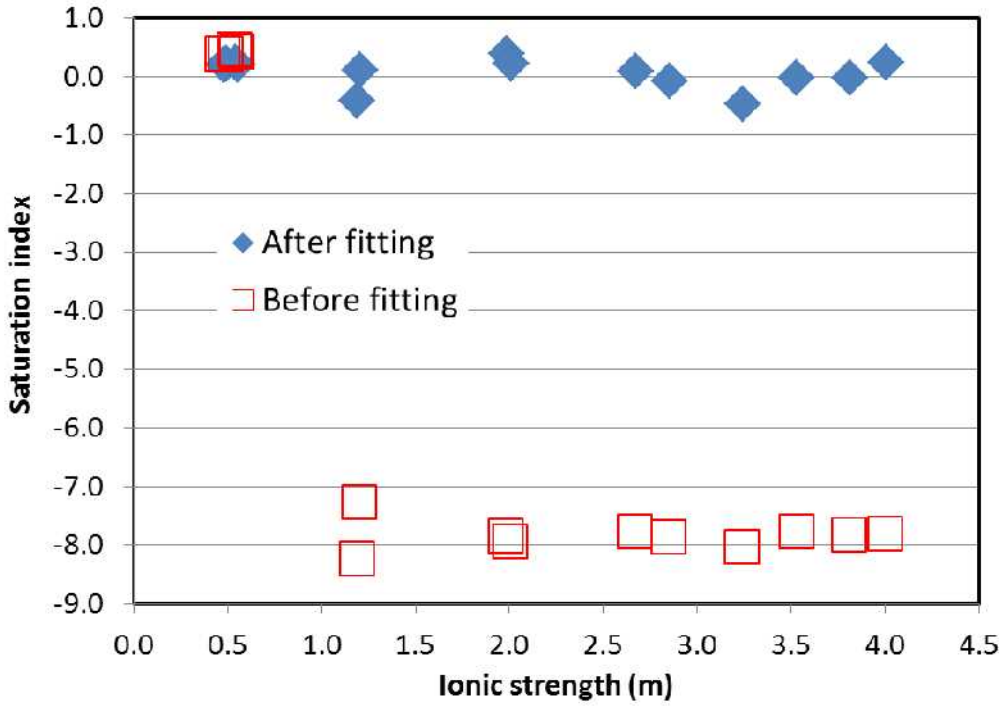
Fitting process

- **Saturation index:**
  - How far the system is from equilibrium with respect to the solid of interest
  - Can be calculated from the aqueous speciation (EQ3/6)
  - Can be positive, “ZERO”, and negative
- **Minimization of the sum of squared saturation indices:**

$$\text{Sum} = \Sigma[\text{Log}\,(Q/K)]^2$$

- **The repetition driven by a script written in Python programming language.**

Fitting Results



Plot of saturation indices over ionic strength. Blue solid diamonds aligned around 0.0 (within a range of -0.463 to 0.390) represent the saturation indices calculated with fitting of the Pitzer interaction parameters for $Na^+/FeEDTA^{2-}$ pair to the experimental data. Red open squares represent the saturation indices calculated without considering Pitzer interaction for $Na^+/FeEDTA^{2-}$ pair.

Table 3: Fitting results for the $FeEDTA^{2-}/Na^+$ pair.

Pitzer parameters	value	Residual
$\beta^{(0)}$	-8.43	
$\beta^{(1)}$	52.49	0.854
C^{φ}	3.41	

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Conclusions

- Current model without the parameters predicted significant undersaturation.
- Model fit greatly improved as the new parameters were considered in the model.
- Now, the newer model with the parameters would predict lower total dissolved Fe, impacting the prediction of total dissolved actinide concentration in the presence of Fe and $EDTA^{4-}$.