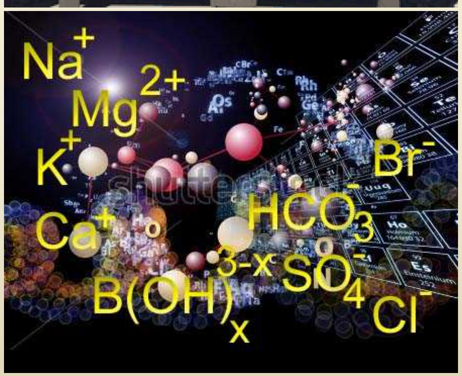
SAND2015-2526C

Exceptional service in the national interest

Sandia National Laboratories



Status of Iron Chemistry Research at Sandia National Laboratories in Support of WIPP

ABC Salt Workshop; April 14- 15, 2015; Heidelberg, Germany

Christi D. Leigh, PhD

Repository Performance Department, 6212

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Acknowledgments

- All iron chemistry work at Sandia Carlsbad has been performed by Dr. Je-Hun Jang with the assistance of Taya Olivas.

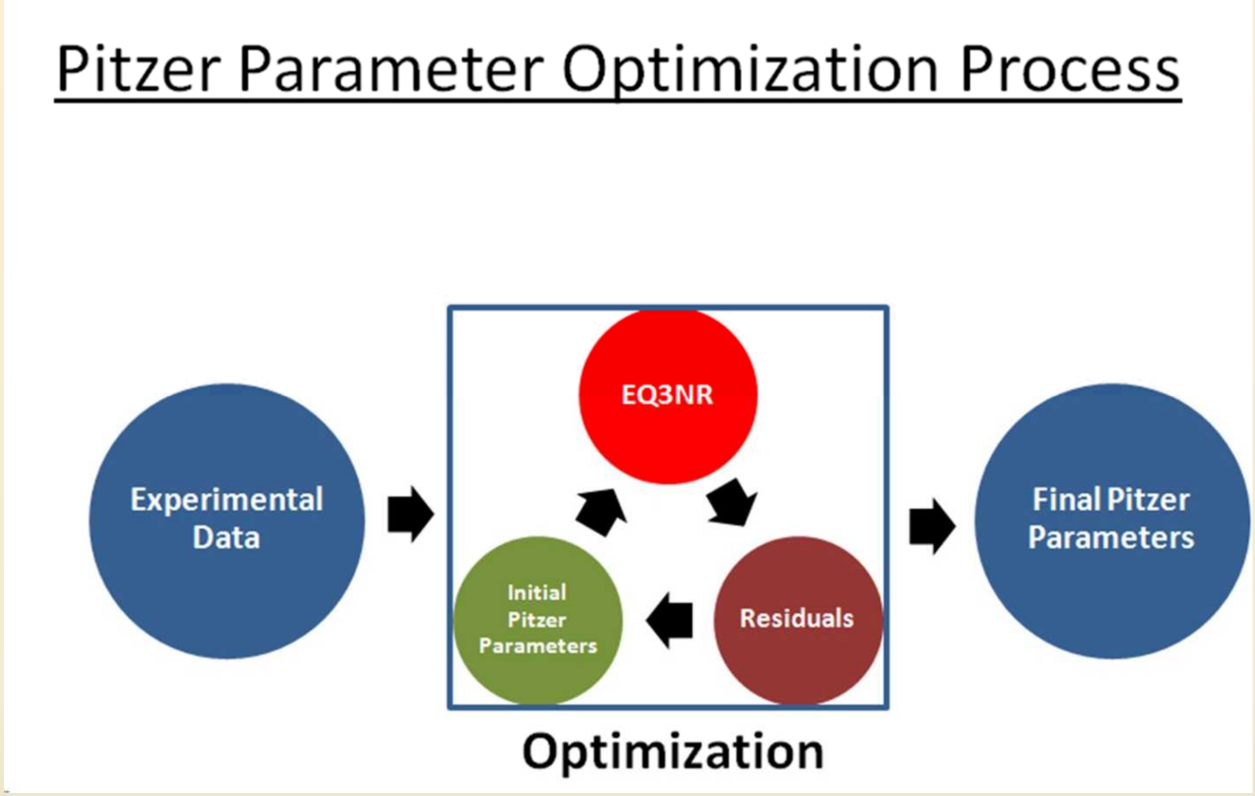
Why do We Care about Fe?

- Waste Isolation Pilot Plant (WIPP)
  - Permanent disposal of TRU wastes
  - Located within the bedded salt formation (NaCl, $CaSO_4$)
- Iron
  - Present in the waste; waste packages, and infrastructure
  - Competes with actinides for complexation with organic ligands
  - May be sequestered by sulfide
  - Total iron concentrations in solution will be low – trace

Pitzer Activity Coefficient Model

- We have high ionic strength brines
  - Ideal for the activity coefficients for solutions of zero to higher ionic strengths (~10 mol/kg)
  - Other activity coefficient models (SIT) cover lower ionic strength
- We use solubility experiments
  - Both over saturation and under saturation
  - Because we are interested in trace elements
  - Osmotic coefficients cannot be measured for the aqueous species of interest

Software for Geochemical Modeling



1. We have the solubility data (*molal*) that are experimentally measured.
2. Initial estimates of Pitzer parameters and logKs are inserted into the EQ3NR database
3. Based on Pitzer estimates, the EQ3NR calculates the equilibrium solubility (molality) of basis species.
4. Residual difference between the experimentally obtained and the calculated concentration of basis species is estimated. Values of the Pitzer parameters and logKs are modified and re-inserted into the EQ3NR database. This is repeated until the residual is minimized.
5. At minimum residual the above optimization process stops. Last input values of Pitzer parameters and logKs become the final set of parameters we seek.

Iron Chemistry Experiments at Sandia Carlsbad

Solids	Brines	Ion-Pairs
$Fe_2(OH)_3Cl(s)$; $Fe(OH)_2(s)$	$NaCl$; Na_2SO_4	$FeOH^+—SO_4^{2-}$
$FeCO_3(s)$	Na_2CO_3 ; $NaCl$	$FeOH^+—CO_3^{2-}$
FeS	NaHS ; Na_2S	$FeOH^+—HS^–$
FeS	Na_2S	$Fe^{2+}—HS$
$Fe_2(OH)_3Cl(s)$; $Fe(OH)_2(s)$	NaCl	$Na^+—Fe(OH)^{3–}$
$Fe_2(OH)_3Cl(s)$; $Fe(OH)_2(s)$	$CaCl_2$	$Ca^{2+}—Fe(OH)^{3–}$
$Fe_2(OH)_3Cl(s)$	$MgCl_2$	$Mg^{2+}—Fe(OH)^{3–}$
$FeC_2O_4•2H_2O(s)$	NaCl	$FeOx(aq)—Na^+$
$FeC_2O_4•2H_2O(s)$	$MgCl_2$	$FeOx(aq)—Mg^{2+}$
$Fe(OH)_2(s)$	H_2Na_2EDTA	$Na^+—FeEDTA^{2–}$
$Fe(OH)_2(s)$	$C_{10}H_{12}MgN_2Na_2O_8•4H_2O$; $MgNa_2EDTA•4H_2O$	$Mg^{2+}—FeEDTA^{2–}$
$Fe(OH)_2(s)$	$Na_3C_6H_5O_7•2H_2O$ ($Na_3Citrate•2H_2O$)	$Na^+—FeCit^–$
$Fe(OH)_2(s)$	MgHCitrate and NaCl	$Mg^{2+}—FeCit^–$

Systems in Black Have Completed Sampling; Systems in red are being sampled and analyzed

Thermodynamic Sub-model with Iron Species

Complexation (all items in red are not approved for public distribution; still under review)

(IV-1) $FeOH^{+} + H^{+} = Fe^{2+} + H_2O$ (Log K = 9.3148; data0.ymp.R2)

(IV-2) $Fe(OH)_3^{-} + 3H^{+} = Fe^{2+} + 3H_2O$ (Log K = 31.0000; data0.ymp.R2)

(IV-3) FeOxalate(aq) = Fe^{2+} + Oxalate^{2-}

(LV Log K = -4.05; Harrison and Thyme (1992)) -4.78 (Jang 2015)

(IV-4) FeEDTA^{2-} = Fe^{2+} + EDTA^{4-} (Log K = -16.1; Morel and Hering (1993))

(IV-5) FeCitrate^{-} = Fe^{2+} + Citrate^{3-}

(LV = -5.7 Morel and Hering (1993); Log K = -12.98(NaCl)/-14.31(MgCl); Jang (2014))

Dissolution (all items in red are not approved for public distribution; still under review)

(IV-6) $FeSO_4(s) = Fe^{2+} + SO_4^{2-}$ (Log K_{sp} = 1.9396; data0.ymp.R2)

(IV-7) $FeCO_3$(siderite) + $H^{+} = Fe^{2+} + HCO_3^{-}$ (Log K_{sp} = -0.192; data0.ymp.R2)

(IV-8) $Fe(OH)_2(s) + 2H^{+} = Fe^{2+} + 2H_2O$ (Log K_{sp} = 12.95; Nemer et. al. (2011))

(IV-9) $Fe_2Cl(OH)_3$(hibbingite) + $3H^{+} = 2Fe^{2+} + Cl^{-} + 3H_2O$ (Log K_{sp} = 17.12; Nemer et al. (2011))

(IV-10) Fe**Oxalate•2**H_2O(s) = Fe^{2+} + Oxalate^{2-} + $2H_2O$

(Log K_{sp} = -8.26; Jang 2014)

(all items in red are not approved for public distribution; still under review

Pitzer Interaction Coefficients – Binary Charged Species

i	*j*	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Source
Fe^{2+}	Cl^-	0.3359	1.5322	-	-0.00861	Pitzer and Mayorga (1973)
$FeOH^+$	Cl^-	0.3063	0.29	0.0	0.0	Jang & Kim (2014)
Fe^{2+}	SO_4^{2-}	0.3022	3.27	-45.74	0.0	Jang & Kim (2014)
$FeOH^+$	SO_4^{2-}	-1.1826	1.74	0.0	0.0	Jang & Kim (2014)
Fe^{2+}	CO_3^{2-}	2.8409	3.27	-45.74	0.0	Jang & Kim (2014)
$FeOH^+$	CO_3^{2-}	-1.9839	1.74	0.0	0.0	Jang & Kim (2014)
Ca^{2+}	$Fe(OH)_3^-$	0.5926	1.74	0.0	-0.5209	Jang & Kim (2014)
Na^+	$Fe(OH)_3^-$	0.0	0.0	0.0	0.0	Jang & Kim (2014)
Na^+	$FeEDTA^{2-}$	2.33	1.74	0.0	0.0	Jang & Kim (2014)
Mg^{2+}	$FeEDTA^{2-}$	0.0	3.27	-45.74	0.0	Jang & Kim (2014)
Na^+	$FeCitrate^-$	-0.4406 -0.0657	0.29	0.0	0.0	Jang & Kim (2014) Jang (2015
Mg^{2+}	$FeCitrate^-$	-0.01205 0	1.74 0	0.0	0.0	Jang & Kim (2014) Jang (2015)

(all items in red are not approved for public distribution; still under review

Pitzer Interaction Coefficients – Same Charge

i	j		$\theta_{aa'}$			Source
$Fe(OH)_3^-$	CO_3^{2-}		-1.2858			Jang & Kim (2014)
$Fe(OH)_3^-$	Cl^-		-0.3553			Jang & Kim (2014)
$Fe(OH)_3^-$	SO_4^{2-}		0.0			Jang & Kim (2014)

(all items in red are not approved for public distribution; still under review

Pitzer Interaction Coefficients – Neutral Species

i	j		λ_{nc}			Source
FeOxalate(aq)	Na^+		-0.0589 -0.0549(under review)			Jang & Kim (2014)
FeOxalate(aq)	Mg^{2+}		0.1104 -1.28 (under review)			Jang & Kim (2014)

But what about Sulfide?

- WIPP Brines Contain Sulfide
  - Sulfide and Iron are happy bed fellows $FeS = Fe^{2+} + S^{2-}$
  - Iron sulfide experimental work is under way and parameters are estimated to be calculated within the next year
- Initiated Experiments
  - To determine total iron and lead in WIPP brines
  - Developing a reliable and safe sampling and analysis process
  - Currently synthesizing equilibrated WIPP brines
  - Preparing test reactors