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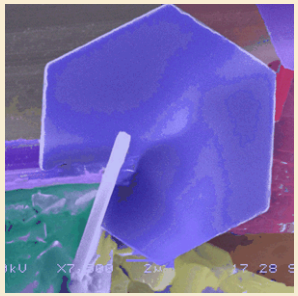



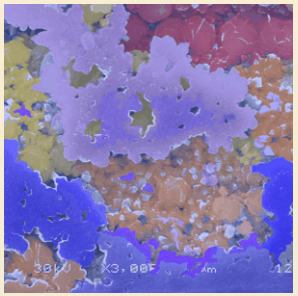

Geochemical Modeling for the WIPP[1]

ABC Salt Workshop; November 7 & 8, 2011; Karlsruhe, Germany

Christi D. Leigh, PhD

Repository Performance Department, 6212

[1]This research is funded by WIPP programs administered by the U.S. Department of Energy (DOE).

U.S. DEPARTMENT OF ENERGY | NNSA

Topics to Be Addressed

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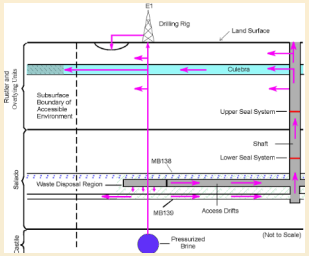
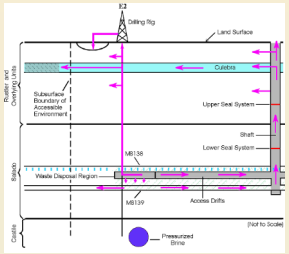
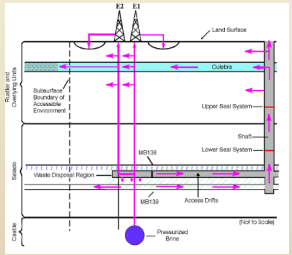
- Why Does Solubility Matter?
- History of Solubility and PA
  - Highlights of upcoming changes
- Base Solubilities
  - Software for Geochemical Modeling
  - Thermodynamic and Pitzer Values
  - New method for derivation of Pitzer Parameters
- Colloidal Source Term
  - What colloidal forms are considered?
- Solubility Uncertainty
  - What is our process for formulating uncertainty?
- How Solubility is Incorporated in PA
  - Solubility in PA Made Simple

Why does actinide solubility matter?



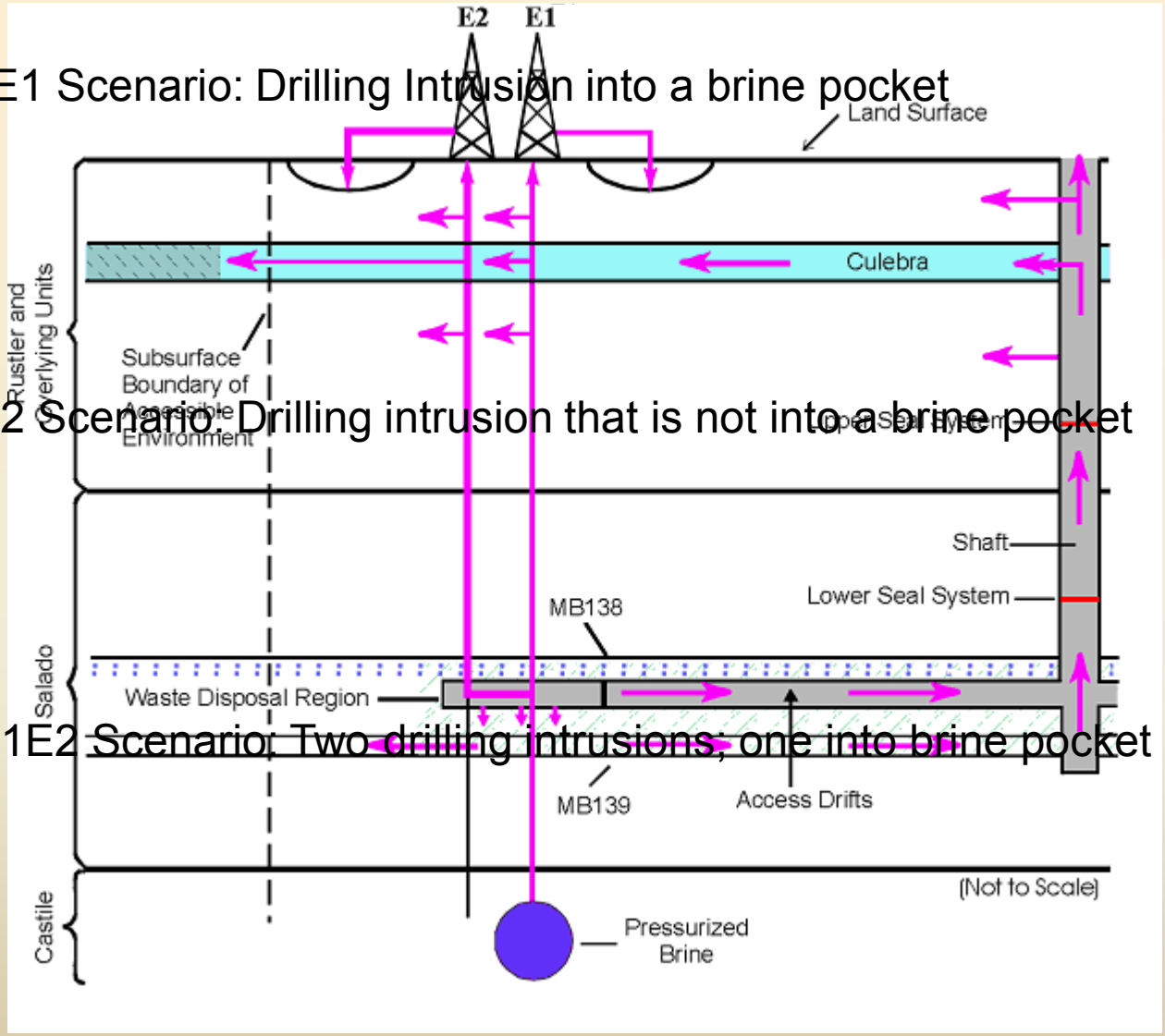




E1 Scenario: Drilling Intrusion into a brine pocket

E2 Scenario: Drilling intrusion that is not into a brine pocket

E1E2 Scenario: Two drilling intrusions; one into brine pocket



History of Solubility and PA

- A set of base solubilities is calculated
  - CRA-2009 the base solubilities used the minimum brine volume to establish concentrations of organics
  - CRA-2014 will use base solubilities interpolated from a table that contains base solubility versus brine volume
- A colloidal source term is calculated
  - This will be updated for CRA-2014
- Uncertainty ranges for actinides in each oxidation state are developed
  - CRA-2009 had revised uncertainty ranges for An(III) and An(IV)
  - CRA-2014 will have revised uncertainty ranges for An(III) and An(IV)
- For Each Vector (100 vectors and 3 replicates)
  - A base solubility is chosen (for CRA-2014 it will be from the brine volume table)
  - An uncertainty is applied
  - The colloidal source term is added

Software for Geochemical Modeling

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The project has been approved by EPA to use EQ3/6 for

- Brine chemistry calculations
- Actinide solubility calculations

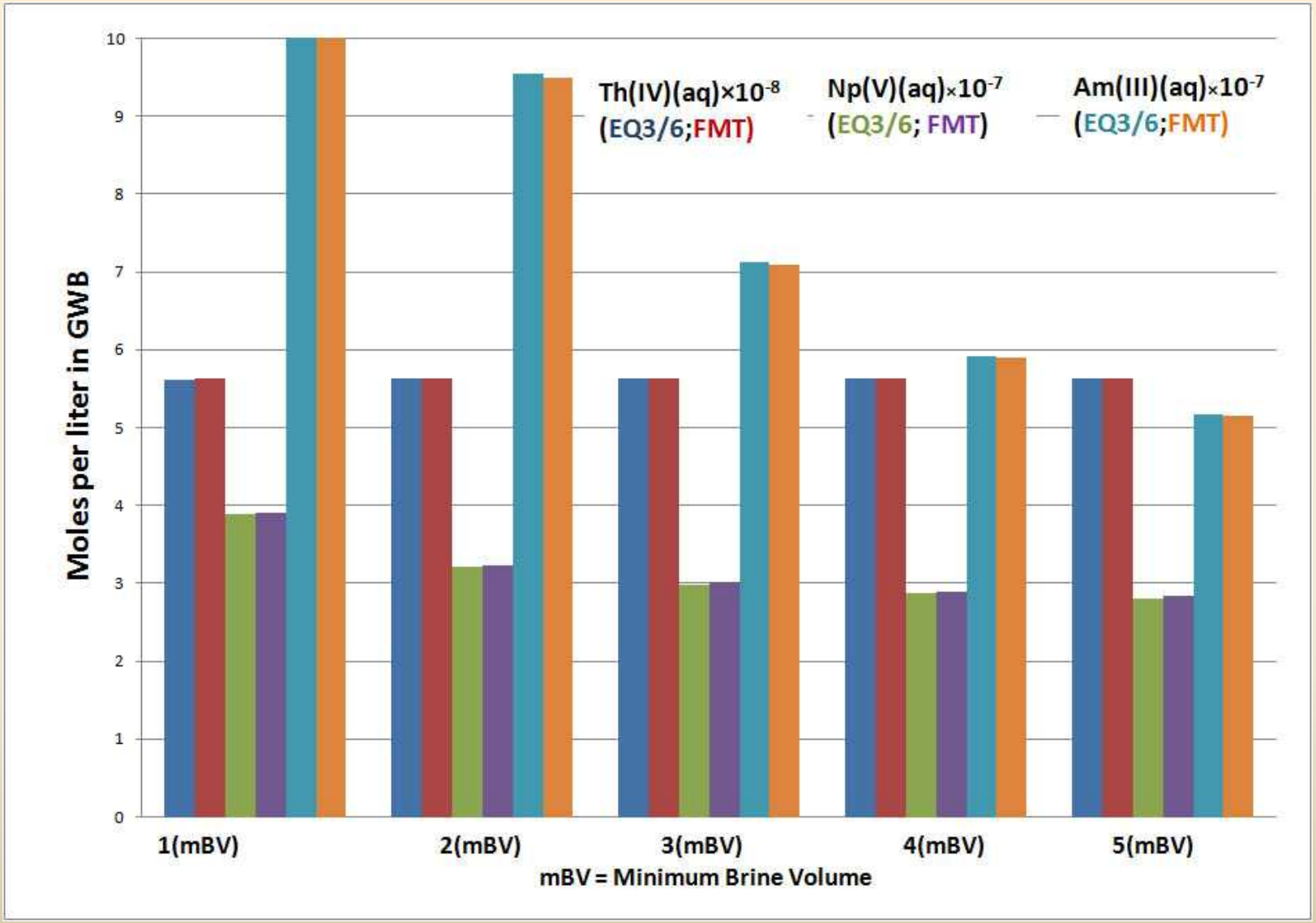
Differences Between FMT and EQ3/6 Version 8.0A

- EQ3/6 uses Harvie Moller Weare Convention for Pitzer Equations
- FMT used Pitzer 1975 Equations
- Corrected Debye-Huckel slope for osmotic coefficient

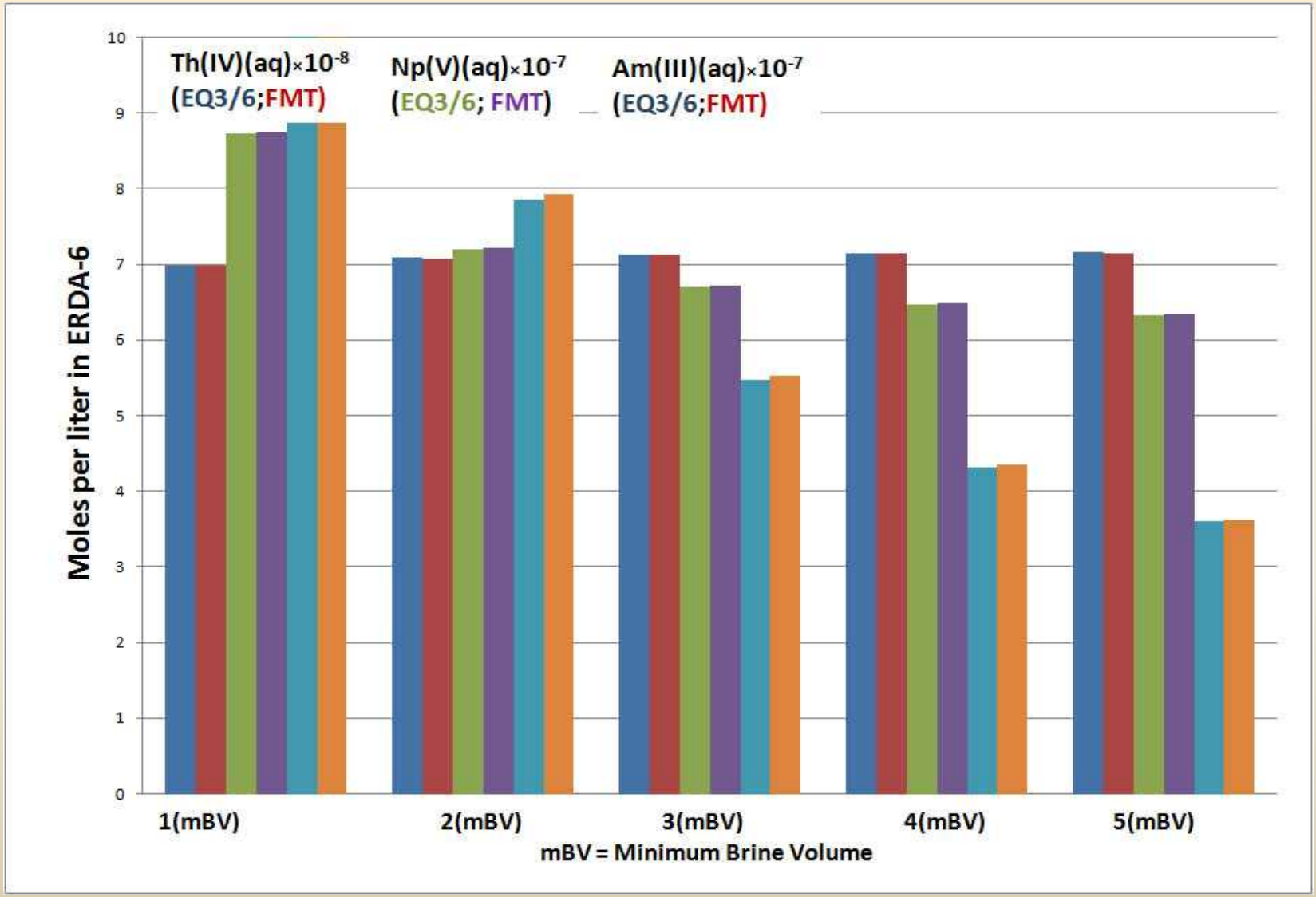
The EQ3/6 Version we are using is EQ3/6 Version 8.0A:

- Incorporates a density model so we can output molarity (moles/liter)
- Can output pH Pitzer – hydrogen ion activity (unitless)
- Can output pcH (hydrogen ion concentration in the moles/liter)
- Can input/output pmH (hydrogen ion concentration in moles/kg water)

Software for Geochemical Modeling



Software for Geochemical Modeling



Software for Geochemical Modeling

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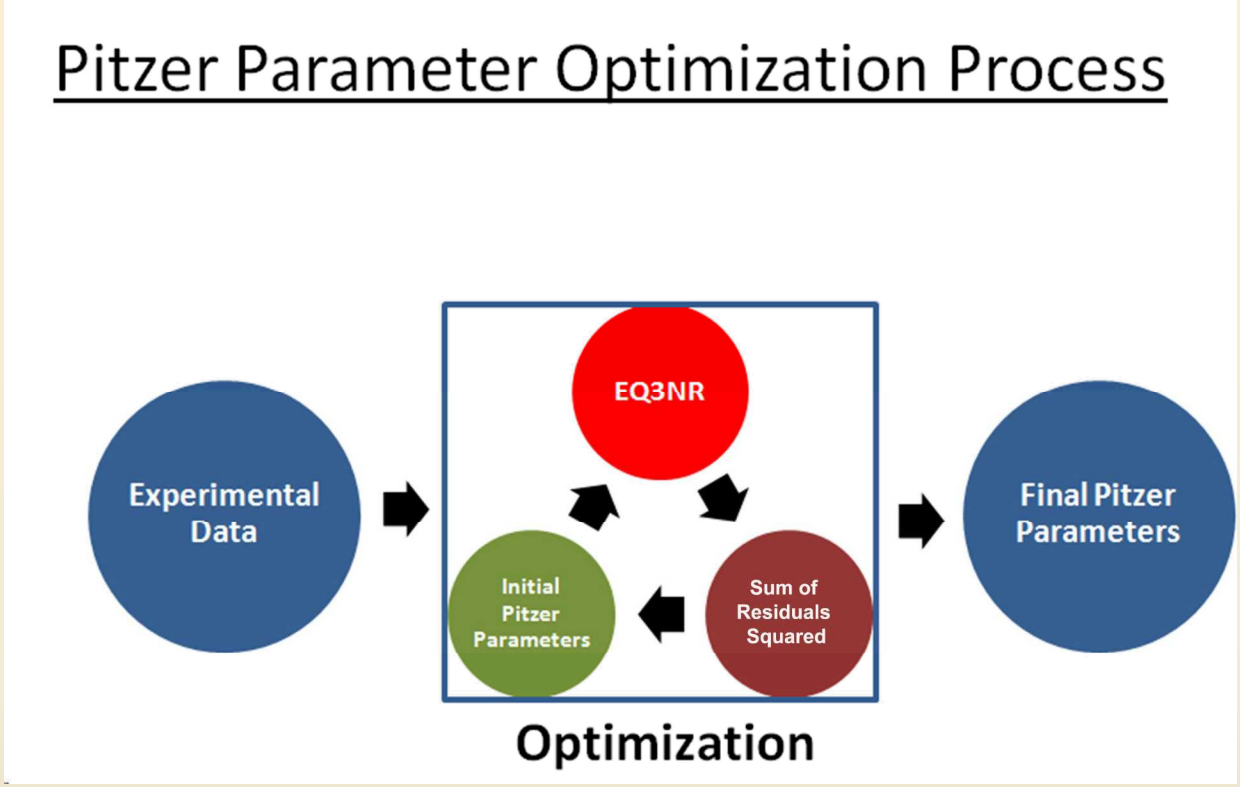
1. We have the solubility data (*molal)* that are experimentally analyzed.
2. Based on experimental data, the equilibrium constant (*log* $K_{experiments}$) is calculated.
3. Initial estimates of Pitzer parameters are inserted into the EQ3NR database
4. Based on Pitzer estimates, the EQ3NR calculates the equilibrium solubility (molality) of basis species which is used to estimate the calculated equilibrium constant (*log* $K_{calculation}$).



5. Residual difference between the experimentally obtained and the calculated equilibrium constants is estimated. Based on residual value, values of the Pitzer parameters are modified and re-inserted into the EQ3NR database. This is repeated until the residual is minimized.
6. At minimum residual the above optimization process stops. Last input values of Pitzer parameters become the final Pitzer parameters we seek.

Thermodynamic and Pitzer Values

Thermodynamic and Pitzer Values Related to Iron

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	$Ca^{2+}—Fe(OH)^{3-}$
$Fe_2(OH)_3Cl(s)$	$MgCl_2$	$Mg^{2+}—Fe(OH)^{3-}$
$FeC_2O_4•2H_2O(s)$	NaCl	$FeOx(aq)—Na^+$
$FeC_2O_4•2H_2O(s)$	$MgCl_2$	$FeOx(aq)—Mg^{2+}$
$FeC_2O_4•2H_2O(s)$	$MgCl_2$	$FeOx(aq)—Cl^-$
$Fe(OH)_2(s)$	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	$Mg^{2+}—FeCit^-$

We have posters here on these systems; Systems in Black Have Come to Equilibrium; Systems in blue have been initiated but are not at equilibrium yet; Systems in purple have not been initiated.

Thermodynamic and Pitzer Values

Thermodynamic and Pitzer Values Related to Lead

Solids	Brines	Ion-Pairs
$PbCO_3(s)$	$NaHCO_3$	$PbCl^+—HCO^{3-}$
$PbCO_3(s)$	$Na2CO_3$	$PbCl^+—CO_3^{2-}$
$PbSO_4(s)$	Na_2SO_4	$PbCl^+—SO_4^{2-}$
PbS(s)	NaHS	$PbCl^+—HS^-$
PbO(s)	NaCl Mg_2EDTA	$Na^+—PbEDTA_2$
PbO(s)	$MgCl_2$ Na_2H_2EDTA	$Mg^{2+}—PbEDTA_2$
PbO(s)	NaCl and MgHCitrate	$Na^+—PbCit^-$
PbO(s)	$MgCl_2$ and MgHCitrate	$Mg^{2+}—PbCit^-$
$PbC_2O_4(s)$	NaCl	$PbOx(aq)—Na^+$
$PbC_2O_4(s)$	$MgCl_2$	$PbOx(aq)—Mg^{2+}$
$PbC_2O_4(s)$	NaCl and $MgCl_2$	$PbOx(aq)—Cl^-$

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Thermodynamic and Pitzer Values

Thermodynamic and Pitzer Values Related to Borate

Solids	Brines	Ion-Pairs
$Na_2B_4O_7 \bullet 10H_2O(s)$	NaCl	$NaB(OH)_4(aq)—Na^+$ and log K for dissolution of $Na_2B_4O_7 \bullet 10H_2O(s)$
$Na_2B_4O_7 \bullet 10H_2O(s)$	$MgCl_2$	$NaB(OH)_4(aq)—Mg^{2+}$
$Na_2B_4O_7 \bullet 10H_2O(s)$	$NaCl + MgCl_2$	$NaB(OH)_4(aq)—Na^+—Mg^{2+}$
$Mg(OH)_2(s)$	$Na_2SO_4 + H_3BO_3$	$MgB(OH)_4^+—SO_4^{2-}$
$Ca(OH)_2(s)$	$Na_2SO_4 + H_3BO_3$	$CaB(OH)_4^+—SO_4^{2-}$
PbO(s)	$NaCl + H_3BO_3$	$PbB(OH)_4^+—Cl^-$
PbO(s)	$Na_2SO_4 + H_3BO_3$	$PbB(OH)_4^+—SO_4^{2-}$
PbO(s)	$NaCl + H_3BO_3$	$Na^+—Pb[B(OH)_4]_3^-$
PbO(s)	$MgCl_2 + H_3BO_3$	$Mg^{2+}—Pb[B(OH)_4]_3^-$
PbO(s)	$NaCl + H_3BO_3$	$PbB_4O_7(aq)—Na^+$
PbO(s)	$MgCl_2 + H_3BO_3$	$PbB_4O_7(aq)—Mg^{2+}$
PbO(s)	$NaCl + MgCl_2 + H_3BO_3$	$PbB_4O_7(aq)—Na^+—Mg^{2+}$

We have posters here on these systems; Systems in Black Have Come to Equilibrium; Systems in blue have been initiated but are not at equilibrium yet.

Thermodynamic and Pitzer Values

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Thermodynamic and Pitzer Values Related to Organic Acids

Solids	Brines	Ion-Pairs
$Ca_3[Citrate]_2 \bullet 4H_2O(s)$	NaCl	$Na^+—CaCit^-$
$Ca_2EDTA(s)$	NaCl	$Na^+—HEDTA^{3-}$
$Ca_2EDTA(s)$	$MgCl_2$	$Mg^{2+}—HEDTA^{3-}$
$FeC_2O_4 \bullet 2H_2O(s)$	$MgCl_2$ and NaCl	$FeOx(aq)—Mg^{2+}—Na^+$
$Ca_3[Citrate]_2 \bullet 4H_2O(s)$	NaCl	$Na^+—CaCit^-$

Thermodynamic and Pitzer Values Related to Sulfide

Solids	Brines	Ion-Pairs
FeS	NaHS ; Na_2S	$FeOH^+—HS^-$
FeS	Na_2S	$Fe^{2+}—HS$
$Na_2B_4O_7 \bullet 10H_2O(s)$	NaHS	$Na^+—HS^-$
$Mg(OH)_2(s)$	NaHS/Na_2S	$Mg^{2+}–HS^-$
PbS(s)	NaCl	$Cl^-—HS^-$

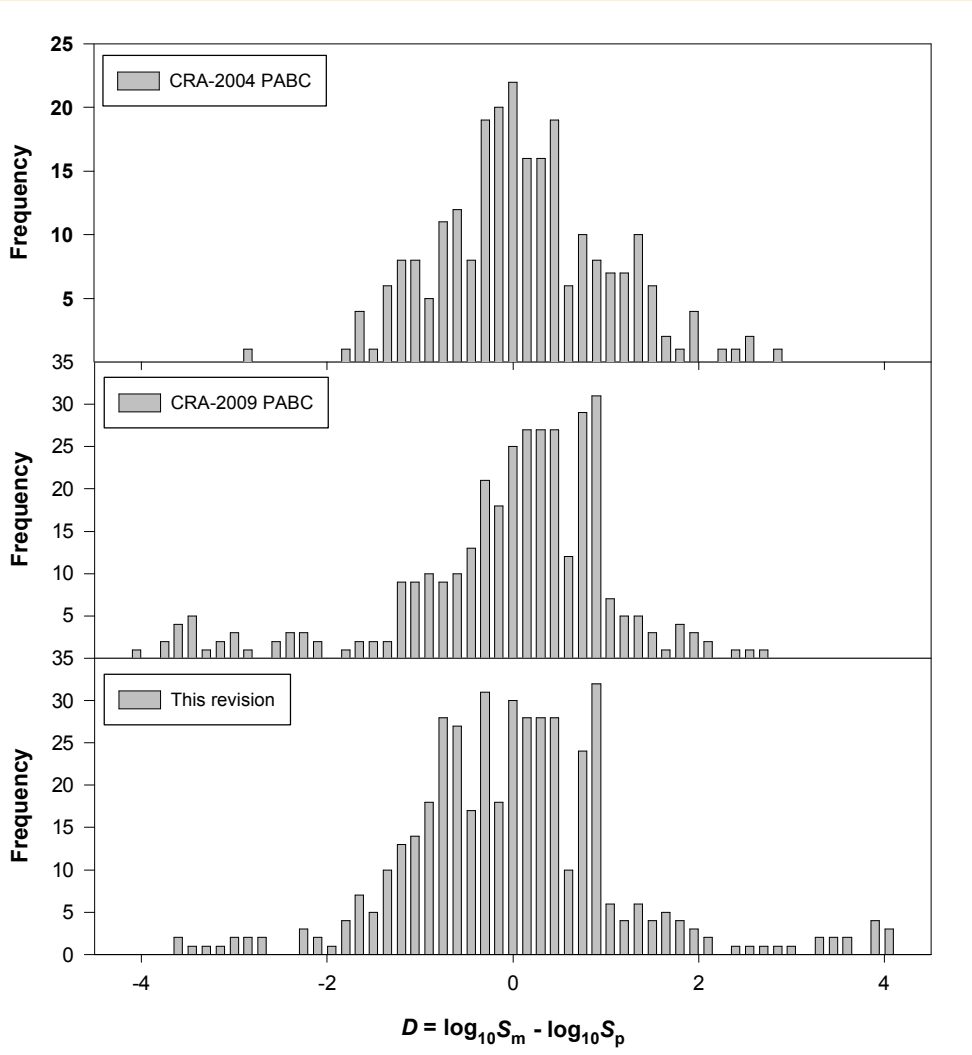
Systems in purple have not been initiated; Systems in Black Have Come to Equilibrium; Systems in blue have been initiated but are not at equilibrium yet.

The Colloidal Source Term

- Actinide intrinsic colloids are
  - macromolecules of actinides
  - may mature into a mineral fragment type colloidal particles (Immature = hydrophilic; mature = hydrophobic).
- Mineral fragments colloids are
  - hydrophobic, hard-sphere particles
  - kinetically stabilized/destabilized by electrostatic forces
  - crystalline or amorphous solids
  - sorptive substrates and/or co-precipitated
- Humic substance colloids are
  - hydrophilic, soft-sphere particles
  - stabilized by solvation forces
  - relatively small (less than 100,000 atomic mass units)
  - sorptive substrates
- Microbial colloids are
  - relatively large colloidal particles
  - stabilized by hydrophilic coatings on their surfaces
  - sorptive substrates or bioaccumulation

Solubility Uncertainty

- We look in the literature for
  - Publications that are relevant to expected WIPP conditions
  - Publications that give original, not derived, data
- We model the experimental data
  - Previously with FMT; now with EQ3/6
  - We derive solubilities from each data set
- We compare
  - Each result from the published data sets
  - To the calculated result using EQ3/6 (FMT)
- We calculate
  - The differences for each data set
  - Derive a probability distribution on the differences
  - Sample that distribution to obtain an uncertainty factor for each vector



How Solubility is Incorporated in PA

A maximum concentration S_T(Br, Ox, El) (mol/liter [M]) is calculated for each brine type (Br : {Salado, Castile}), oxidation state (Ox : {III, IV, V, VI}), and element (El :{Am, Pu, U, Th}).

$$S_T(Br, Ox, El) = S_D(Br, Ox) - S_C(Br, Ox, El)$$

$$S_D(Br, Ox) = S_{FMT}(Br, Ox) \times 10^{UF(Ox)}$$

$$S_C(Br, Ox, El) = S_{Hum}(Br, Ox, El) + S_{Mic}(Br, Ox, El) + S_{Act}(El) + S_{Mn}$$

$$S_{Hum}(Br, Ox, El) \quad \min\left\{SF_{Hum}(Br, Ox, El) \times S_D(Br, Ox), UB_{Hum}\right\}$$

$$S_{Mic}(Br, Ox, El) \quad \min\left\{SF_{Mic}(Ox, El) \times S_D(Br, Ox), UB_{Mic}(Ox, El)\right\}$$

$$S_{Act}(El) \quad \begin{cases} 1 \times 10^{-9}\ \text{mol/L} & \text{if } El = \text{Pu} \\ 0\ \text{mol/L} & \text{otherwise} \end{cases}$$

S_{Mn} = 2.6 X 10^{-8} mol/liter

Dankeschön

- Ich hoffe, dass Sie diese Geochemical-Tour von WIPP genossen haben