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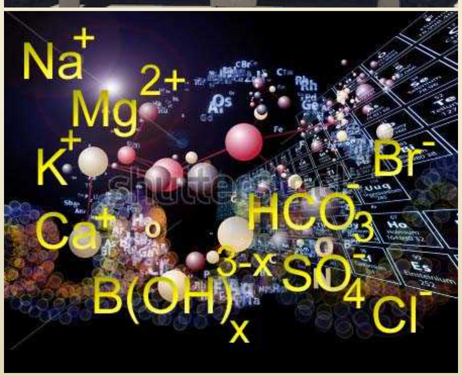

Overview of WIPP Geochemical Modeling[1]

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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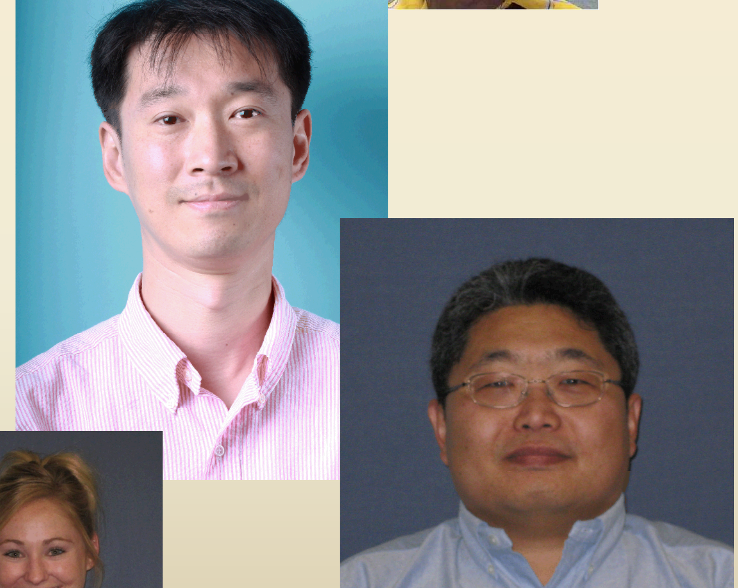
Acknowledgments

- None of this work was performed by me. I have a team of great geochemists and technologists who have done all of the work I discuss today.



Topics to Be Addressed

- Overview of WIPP
- Characteristics of Salado Formation Salt
- Why does solubility matter?
- Near-field Conceptual Models
- Near-field Conceptual Model Predictions
- Thermodynamic Sub-models
- Base Solubilities
- Colloidal Source Term
- Solubility Uncertainty
- How Solubility is Incorporated in PA

Overview of the WIPP Project

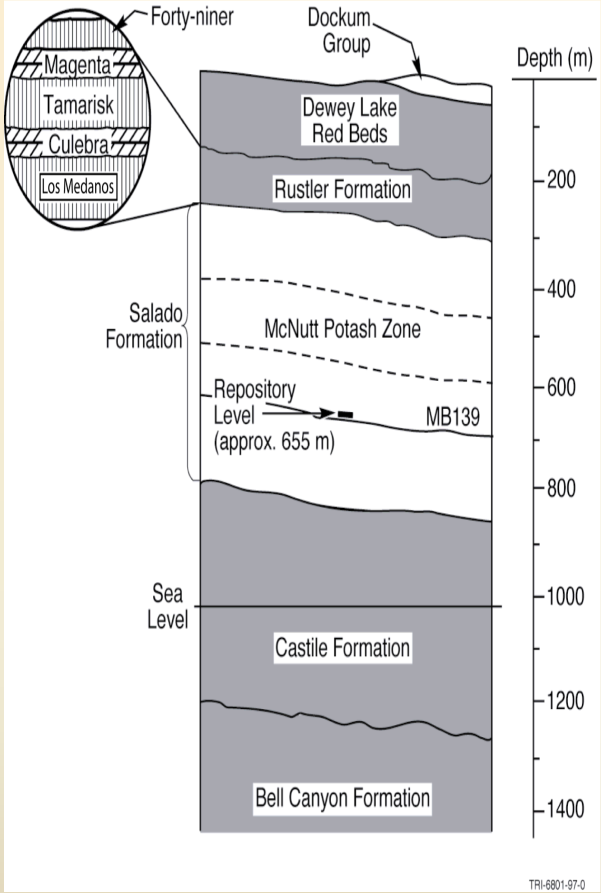
Waste Isolation Pilot Plant (WIPP)

- A U.S. Department of Energy repository in southeast New Mexico for defense-related transuranic waste
- Certified in May 1998
- Opened in March 1999
- First recertification in April 2006

Description

- Located in the Salado Fm., a Permian bedded-salt formation, at a subsurface depth of 655 m (2150 ft)

Characteristics of Salado Fm Salt



Lithology

- Consists mostly of nearly pure halite (NaCl)
- Also includes clay seams and "marker beds" with anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), magnesite ($MgCO_3$), polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$), and clays

Mineralogy

- 90 to 95 wt % halite
- 1 to 2 wt% each anhydrite, gypsum, magnesite, polyhalite and clays

In situ conditions at the repository horizon

- P ~ 150 atm (lithostatic); measured pore pressures close to lithostatic
- T = 28 ° C

Water content

- Contains <u>both</u> intergranular (grain-boundary) brine and intragranular brine (fluid inclusions)
  - Intergranular will flow into disposal rooms after formation of the disturbed rock zone increases Salado permeability
  - Intragranular will not flow into disposal rooms
- Total brine content typically 1-2 wt %, but can be up to 3 wt %

Why does actinide solubility matter?

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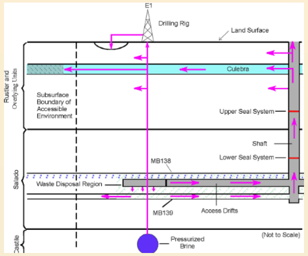
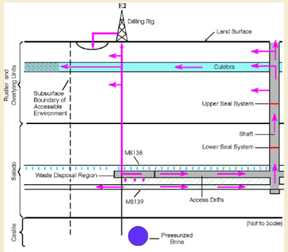
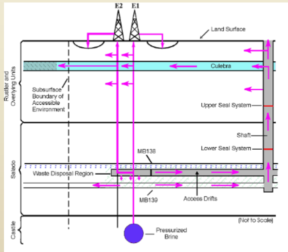


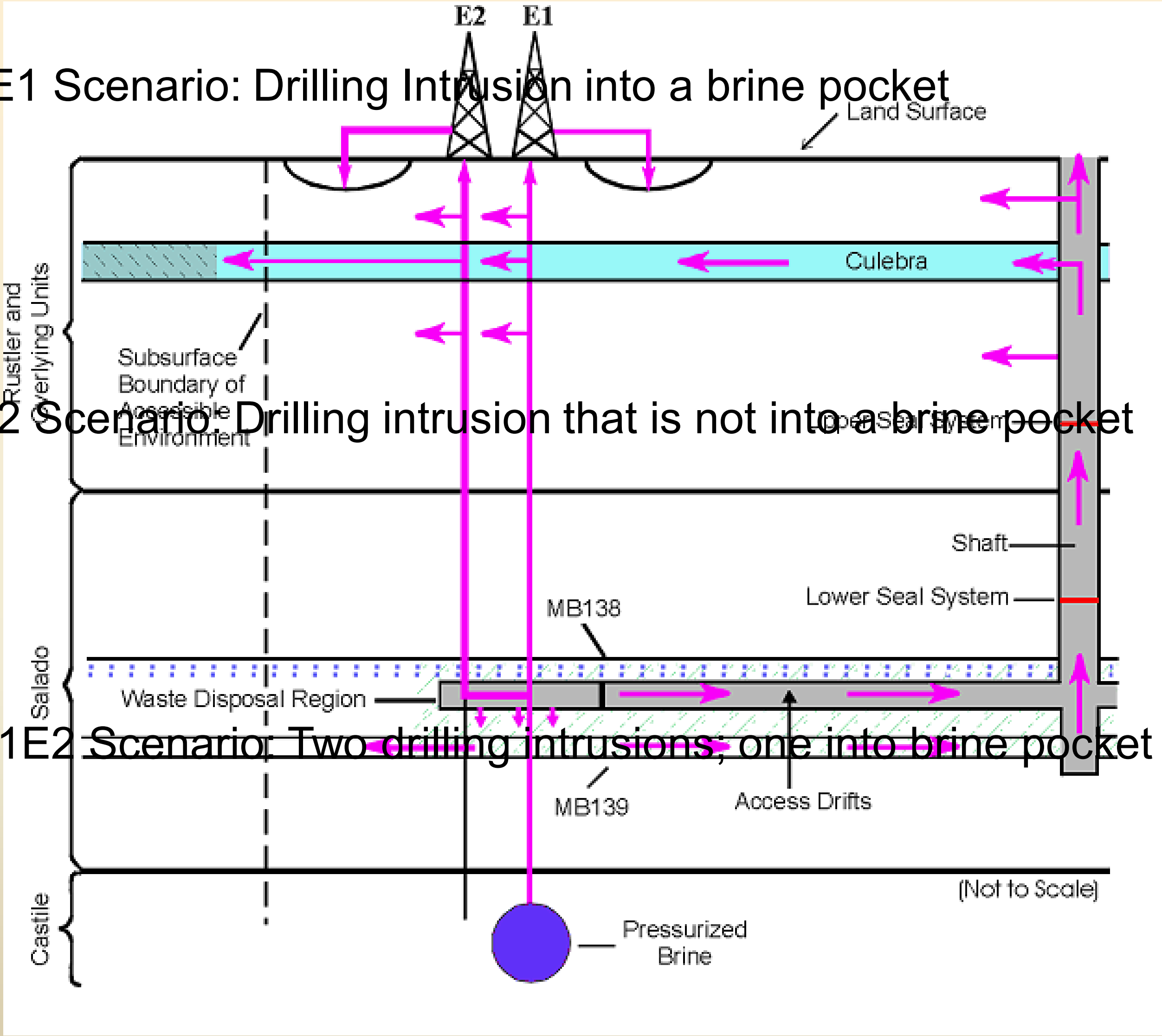
E1 Scenario: Drilling Intrusion into a brine pocket



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



E1E2 Scenario: Two drilling intrusions; one into brine pocket



WIPP Near-Field Conceptual Models

- Instantaneous, reversible equilibria among brines and solids will control chemical conditions
- Equilibration is fast with respect to 10,000-year regulatory period
- MgO added to consume microbial CO_2 and decrease actinide solubilities
  - MgO is the only engineered barrier certified by the EPA
- Two Standard brines
  - Generic Weep Brine (GWB) simulates intergranular Salado brines
  - U.S. Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) simulates Castile brines
- Solids included in modeling
  - Halite and anhydrite (The two most important Salado minerals)
  - Brucite ($Mg(OH)_2$), phase 5 ($Mg_3(OH)_5Cl\cdot 4H_2O$), and the "5424" polymorph of hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$)
- MgO hydration and carbonation products predicted by modeling and observed in lab experiments with GWB
  - Brucite and hydromagnesite
  - Predicted by modeling and observed in lab experiments with ERDA-6

WIPP Near-Field Conceptual Model Predictions

Reaction that will buffer f_{CO_2}, at least initially

- $5Mg(OH)_2 + 4CO_2$(aq or gas) $\rightleftharpoons Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$
  - Hydromagnesite (5424) is metastable with respect to magnesite, but could persist for hundreds to thousands of years
  - The EPA has specified that the brucite-hydromagnesite carbonations reaction be used to calculate f_{CO_2} for actinide- solubility calculations

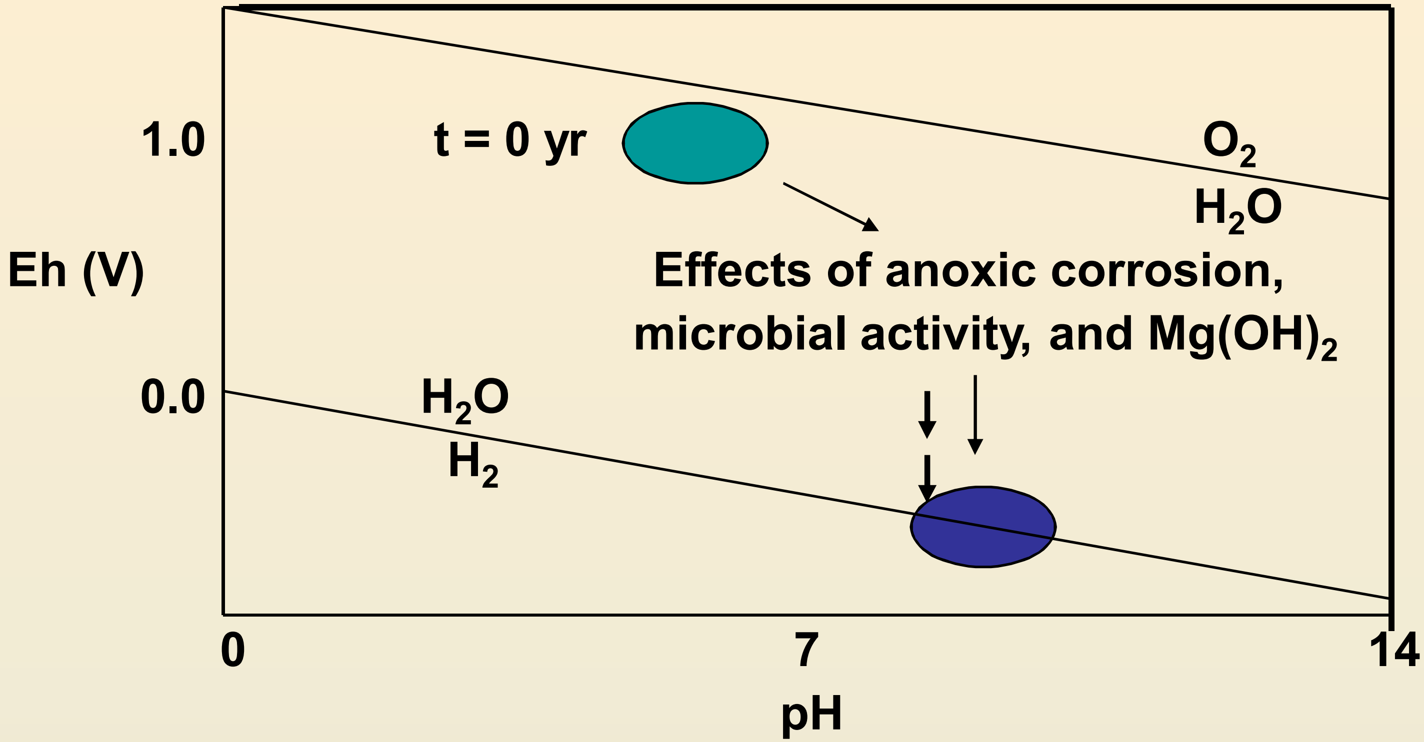
Possible long-term f_{CO_2} buffer reaction

- $Mg(OH)_2 + CO_2$(aq or gas) $\rightleftharpoons MgCO_3 + H_2O$(aq or gas)
  - Magnesite is stable with respect to hydromagnesite (5424), and is present in the Salado

Reaction that will increase pH to mildly basic values

- $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

WIPP Near-Field Conceptual Model Predictions

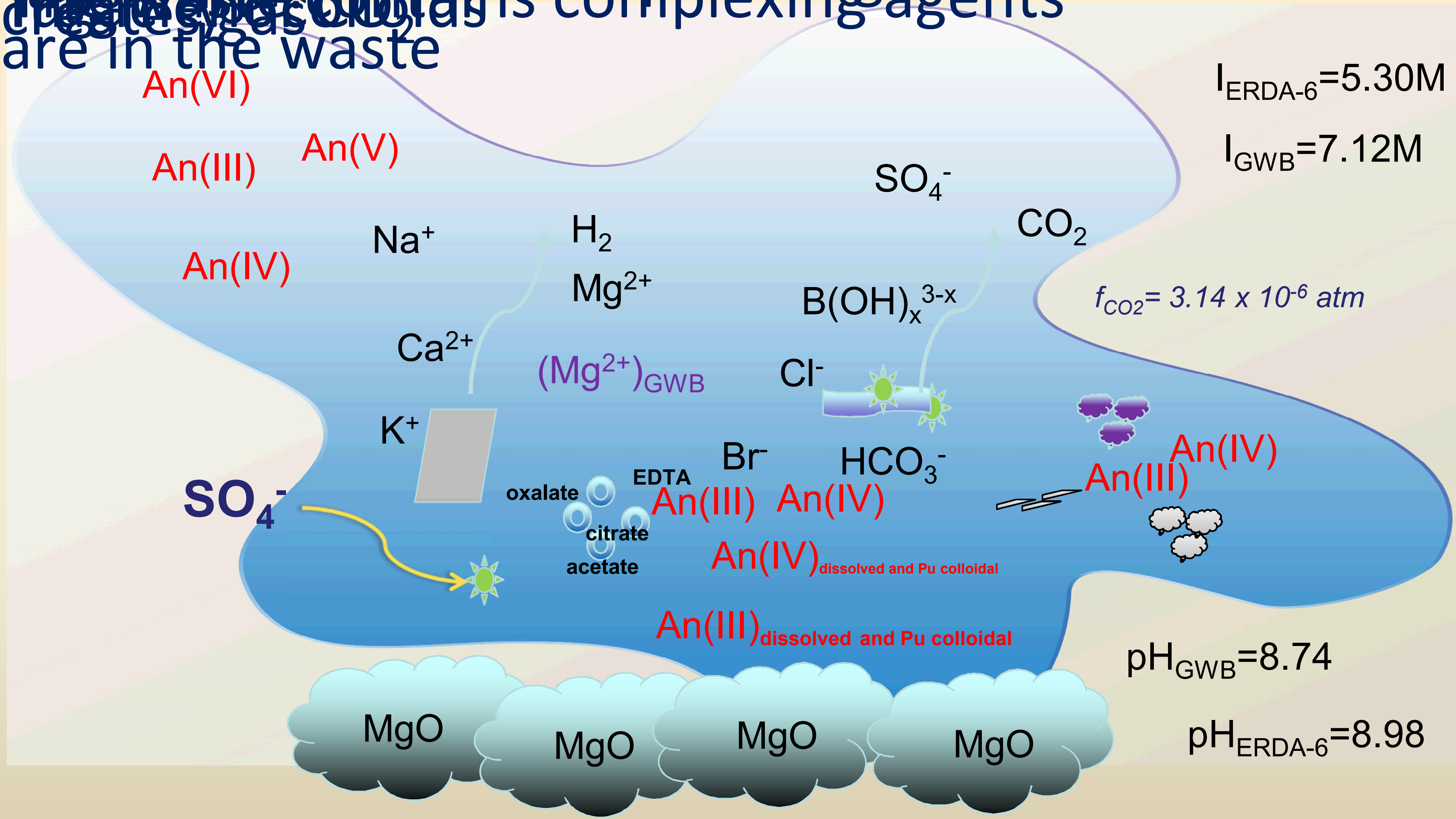


- $f_{CO_2} \cong 3 \times 10^{-6}$ possibly decreasing to 1×10^{-7} atm
- TIC $\cong 3 \times 10^{-4}$ M (GWB) or 4×10^{-4} M (ERDA-6), possibly decreasing to 1×10^{-5} M (GWB) or 2×10^{-5} M (ERDA-6)
- Very low f_{O_2} (at or even below the lower stability limit of H_2O on an Eh-pH diagram)
- H_2O unstable in the WIPP (reduced to H_2 by steels and other metals)
- pH $\cong$ 9; Relative humidity (RH) $\cong$ 73 to 75%

Put this altogether and this is the geochemical ... Model

... contact with ... that ... complexing agents

... are in the waste



Basic Thermodynamic Model Major Ions and Minerals

(I-1) $H_2O = OH^- + H^+$
(I-2) $Ca^{2+} + 2H_2O = Ca(OH)_2$(portlandite) $+ 2H^+$
(I-3) $Na^+ + Cl^- = NaCl$(halite)
(I-4) $K^+ + Cl^- = KCl$(sylvite)
(I-5) $Ca^{2+} + 2Cl^- + 4H_2O = CaCl_2{\bullet}4H_2O$(cr)
(I-6) $4Ca^{2+} + 2Cl^- + 19H_2O = Ca_4Cl_2(OH)_6{\bullet}13H_2O$(CaOxychloride_A) $+ 6H^+$
(I-7) $2Ca^{2+} + 2Cl^- + 3H_2O = Ca_2Cl_2(OH)_2{\bullet}H_2O$(CaOxychloride_B) $+ 2H^+$
(I-8) $K^+ + Mg^{2+} + 3Cl^- + 6H_2O = KMgCl_3{\bullet}6H_2O$(carnallite)
(I-9) $H^+ + HCO_3^- = CO_2(aq) + H_2O$
(I-10) $HCO_3^- = CO_3^{2-} + H^+$
(I-11) $Na^+ + HCO_3^- = NaHCO_3$(nahcolite)
(I-12) $3Na^+ + 2HCO_3^- + 2H_2O = Na_3H(CO_3)_2{\bullet}2H_2O$(trona) $+ H^+$
(I-13) $2Na^+ + HCO_3^- + 10H_2O = Na_2CO_3{\bullet}10H_2O$(natron) $+ H^+$
(I-14) $2Na^+ + HCO_3^- + 7H_2O = Na_2CO_3{\bullet}7H_2O$(cr) $+ H^+$
(I-15) $2Na^+ + HCO_3^- + H_2O = Na_2CO_3{\bullet}H_2O$(thermonatrite) $+ H^+$
(I-16) $K^+ + HCO_3^- = KHCO_3$(kalicinite)
(I-17) $2K^+ + HCO_3^- + 1.5H_2O = K_2CO_3{\bullet}3/2H_2O$(cr) $+ H^+$
(I-18) $8K^+ + 6HCO_3^- + 3H_2O = K_8H_4(CO_3)_6{\bullet}3H_2O$(cr) $+ 2H^+$
(I-19) $K^+ + Na^+ + HCO_3^- + 6H_2O = KNaCO_3{\bullet}6H_2O$(cr) $+ H^+$
(I-20) $2K^+ + Na^+ + 2HCO_3^- + 2H_2O = K_2NaH(CO_3)_2{\bullet}2H_2O$(K-trona) $+ H^+$
(I-21) $Ca^{2+} + HCO_3^- = CaCO_3$(aragonite) $+ H^+$
(I-22) $Ca^{2+} + HCO_3^- = CaCO_3$(calcite) $+ H^+$
(I-23) $Ca^{2+} + 2Na^+ + 2HCO_3^- + 5H_2O = CaNa_2(CO_3)_2{\bullet}5H_2O$(gaylussite) $+ 2H^+$
(I-24) $2Na^+ + Ca^{2+} + 2HCO_3^- + 2H_2O = Na_2Ca(CO_3)_2{\bullet}2H_2O$(pirssonite) $+ 2H^+$
(I-25) $SO_4^{2-} + H^+ = HSO_4^- + H^+$
(I-26) $Ca^{2+} + SO_4^{2-} = CaSO_4$(anhydrite)
(I-27) $Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4{\bullet}2H_2O$(gypsum)
(I-28) $2K^+ + SO_4^{2-} = K_2SO_4$(arcanite)

Basic Thermodynamic Model Major Ions and Minerals

- (I-29) $8K^+ + 6H^+ + 7SO_4^{2-} = K_8H_6(SO_4)_7$(misenite)
- (I-30) $3K^+ + H^+ + 2SO_4^{2-} = K_3H(SO_4)_2$(cr)
- (I-31) $K^+ + Ca^{2+} + 2SO_4^{2-} + H_2O = K_2Ca(SO_4)_2 \bullet H_2O$(syngenite)
- (I-32) $2Na^+ + SO_4^{2-} + 10H_2O = Na_2SO_4 \bullet 10H_2O$(mirabilite)
- (I-33) $2Na^+ + SO_4^{2-} = Na_2SO_4$(thenardite)
- (I-34) $Na^+ + H^+ + 2SO_4^{2-} = Na_3H(SO_4)_2$(cr)
- (I-35) $Na^+ + 3K^+ + 2SO_4^{2-} = NaK_3(SO_4)_2$(aphthitalite, galerite)
- (I-36) $2Na^+ + Ca^{2+} + 2SO_4^{2-} = Na_2Ca(SO_4)_2$(glauberite)
- (I-37) $4Na^+ + Ca^{2+} + 3SO_4^{2-} + 2H_2O = Na_4Ca(SO_4)_3 \bullet 2H_2O$(labile salt)
- (I-38) $HPO_4^{2-} + 2H^+ = H_3PO_4$(aq)
- (I-39) $HPO_4^{2-} + H^+ = H_2PO_4^- + H^+$
- (I-40) $HPO_4^{2-} = PO_4^{3-} + H$

Thermodynamic Sub-model for MgO

- (II-1) $Mg^{2+} + H_2O = MgOH^+ + H^+$
- (II-2) $Mg^{2+} + 2H_2O = Mg(OH)_2$(brucite) $+ 2H^+$
- (II-3) $Mg^{2+} + 2Cl^- + 6H_2O = MgCl_2{\bullet}6H_2O$(bischofite)
- (II-4) $2Mg^{2+} + Cl^- + 7H_2O = Mg_2Cl(OH)_3{\bullet}4H_2O$(phase 3) $+ 3H^+$
- (II-5) $3Mg^{2+} + Cl^- + 9H_2O = Mg_3Cl(OH)_5{\bullet}4H_2O$(phase 5) $+ 5H^+$
- (II-6) $2Mg^{2+} + Ca^{2+} + 6Cl^- + 12H_2O = Mg_2CaCl_6{\bullet}12H_2O$(tachyhydrite)
- (II-7) $K^+ + Mg^{2+} + 3Cl^- + 6H_2O = KMgCl_3{\bullet}6H_2O$(carnallite)
- (II-8) $Mg^{2+} + HCO_3^- = MgCO_3$(magnesite) $+ H^+$
- (II-9) $Mg^{2+} + HCO_3^- + 3H_2O = MgCO_3{\bullet}3H_2O$(nesquehonite) $+ H^+$
- (II-10) $4Mg^{2+} + 3HCO_3^- + 5H_2O = Mg_4(CO_3)_3(OH)_2{\bullet}3H_2O$(hydromagnesite4323) $+ 5H^+$
- (II-11) $5Mg^{2+} + 4HCO_3^- + 6H_2O = Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$(hydromagnesite5424) $+ 6H^+$
- (II-12) $2K^+ + Mg^{2+} + 2SO_4^{2-} + 4H_2O = K_2Mg(SO_4)_2{\bullet}4H_2O$(leonite)
- (II-14) $2Na^+ + Mg^{2+} + 2SO_4^{2-} + 2H_2O = Na_2Mg(SO_4)_2{\bullet}4H_2O$(boedite)
- (II-15) $Mg^{2+} + SO_4^{2-} + 7H_2O = MgSO_4{\bullet}7H_2O$(epsomite)
- (II-16) $Mg^{2+} + SO_4^{2-} + 6H_2O = MgSO_4{\bullet}6H_2O$(hexahydrite)
- (II-17) $Mg^{2+} + SO_4^{2-} + H_2O = MgSO_4{\bullet}H_2O$(kieserite)
- (II-18) $K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + 3H_2O = KMgClSO_4{\bullet}3H_2O$(kainite)

Thermodynamic Sub-model for Organic Ligands

- (III-1) $Mg^{2+} + Acetate^{-} = MgAcetate^{+}$
- (III-2) $Ca^{2+} + Acetate^{-} = CaAcetate^{+}$
- (III-3) $Citrate^{3-} + 3H^{+} = H_3Citrate\ (aq)$
- (III-4) $Citrate^{3-} + 2H^{+} = H_2Citrate^{-}$
- (III-5) $Citrate^{3-} + H^{+} = HCitrate^{2-}$
- (III-6) $Mg^{2+} + Citrate^{3-} = MgCitrate^{-}$
- (III-7) $Ca^{2+} + Citrate^{3-} = CaCitrate^{-}$
- (III-8) $Ca_3(Citrate)_2{\bullet}4H_2O$ (earlandite) $= 3Ca^{2+} + 2Citrate^{3-} + 4H_2O$
- (III-9) $EDTA^{4-} + 4H^{+} = H_4EDTA(aq)$
- (III-10) $EDTA^{4-} + 3H^{+} = H_3EDTA^{-}$
- (III-11) $EDTA^{4-} + 2H^{+} = H_2EDTA^{2-}$
- (III-12) $EDTA^{4-} + H^{+} = HEDTA^{3-}$
- (III-13) $Mg^{2+} + EDTA^{4-} = MgEDTA^{2-}$
- (III-14) $Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$
- (III-15) $Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-}$
- (III-16) $Oxalate^{2-} + 2H^{+} = H_2Oxalate(aq)$
- (III-17) $Oxalate^{2-} + H^{+} = HOxalate^{-}$
- (III-18) $Mg^{2+} + Oxalate^{2-} = MgOxalate(aq)$
- (III-19) $Ca^{2+} + Oxalate^{2-} = CaOxalate(aq)$
- (III-20) $Oxalate^{2-} + 2H^{+} + 2H_2O = H_2Oxalate{\bullet}2H_2O$
- (III-21) $Na^{+} + H^{+} + Oxalate^{2-} + H_2O = NaHOxalate{\bullet}H_2O$
- (III-22) $2Na^{+} + Oxalate^{2-} = Na_2Oxalate$
- (III-23) $Ca^{2+} + Oxalate^{2-} + H_2O = CaOxalate{\bullet}H_2O$
- (III-24) $Lactate^{-} + H^{+} = HLactate(aq)$

Thermodynamic Sub-model for An(III)

- (IV-1) $AmCO_3^+ + H^+ = Am^{3+} + HCO_3^-$
- (IV-2) $Am(CO_3)_2^- + 2H^+ = Am^{3+} + 2HCO_3^-$
- (IV-3) $Am(CO_3)_3^{3-} + 3H^+ = Am^{3+} + 3HCO_3^-$
- (IV-4) $Am(CO_3)_4^{5-} + 4H^+ = Am^{3+} + 4HCO_3^-$
- (IV-5) $Am(OH)^{2+} + H^+ = Am^{3+} + H_2O$
- (IV-6) $Am(OH)_2^+ + 2H^+ = Am^{3+} + 2H_2O$
- (IV-7) $Am(OH)_3(aq) + 3H^+ = Am^{3+} + 3H_2O$
- (IV-8) $AmCl^{2+} = Am^{3+} + Cl^-$
- (IV-9) $AmCl_2^+ = Am^{3+} + 2Cl^-$
- (IV-10) $AmSO_4^+ = Am^{3+} + SO_4^{2-}$
- (IV-11) $Am(SO_4)_2^- = Am^{3+} + 2SO_4^{2-}$
- (IV-12) $AmAcetate^{2+} = Am^{3+} + Acetate^-$
- (IV-13) $AmCitrate(aq) = Am^{3+} + Citrate^{3-}$
- (IV-14) $AmEDTA^- = Am^{3+} + EDTA^{4-}$
- (IV-15) $AmLactate^{2+} = Am^{3+} + Lactate^-$
- (IV-16) $AmOxalate^+ = Am^{3+} + Oxalate^{2-}$
- (IV-17) $AmOHCO_3(s) + 2H^+ = Am^{3+} + H_2O + HCO_3^-$
- (IV-18) $Am(OH)_3(s) + 3H^+ = Am^{3+} + 3H_2O$
- (IV-19) $NaAm(CO_3)_2 \bullet 6H_2O(s) + 2H^+ = Na^+ + Am^{3+} + 2HCO_3^- + 6H_2O$
- (IV-20) $AmPO_4(cr) + H^+ = Am^{3+} + HPO_4^{2-}$
- (IV-21) $AmHB_4O_7^{2+} + 9H_2O = Am^{3+} + 4B(OH)_4^- + H^+$
- (IV-22) $Am_2S_3(s) + 3H^+ = 2Am^{3+} + 3HS^-$

Thermodynamic Sub-model for An(IV)

- (VI-1) $Th(CO_3)_5^{6-} + 5H^+ = Th^{4+} + 5HCO_3^-$
- (VI-2) $Th(OH)_3(CO_3)^- + 4H^+ = Th^{4+} + 3H_2O + HCO_3^-$
- (VI-3) $Th(OH)_4(aq) + 4H^+ = Th^{4+} + 4H_2O$
- (VI-4) $Th(SO_4)_2(aq) = Th^{4+} + 2SO_4^{2-}$
- (VI-5) $Th(SO_4)_3^{2-} = Th^{4+} + 3SO_4^{2-}$
- (VI-6) $ThAcetate^{3+} = Th^{4+} + Acetate^-$
- (VI-7) $Th(Acetate)_2^{2+} = Th^{4+} + 2Acetate^-$
- (VI-8) $ThCitrate^+ = Th^{4+} + Citrate^{3-}$
- (VI-9) $ThEDTA(aq) = Th^{4+} + EDTA^{4-}$
- (VI-10) $ThLactate^{3+} = Th^{4+} + Lactate^-$
- (VI-11) $Th(Lactate)_2^{2+} = Th^{4+} + 2Lactate^-$
- (VI-12) $ThOxalate^{2+} = Th^{4+} + Oxalate^{2-}$
- (VI-13) $ThO_2(am) + 4H^+ = Th^{4+} + 2H_2O$
- (VI-14) $Th(SO_4)_2{\bullet}9H_2O(s) = Th^{4+} + 2SO_4^{2-} + 9H_2O$
- (VI-15) $Th(SO_4)_2{\bullet}8H_2O(s) = Th^{4+} + 2SO_4^{2-} + 8H_2O$
- (VI-16) $Th(SO_4)_2{\bullet}Na_2SO_4{\bullet}6H_2O(s) = Th^{4+} + 3SO_4^{2-} + 2Na^+ + 6H_2O$
- (VI-17) $Th(SO_4)_2{\bullet}K_2SO_4{\bullet}4H_2O(s) = Th^{4+} + 3SO_4^{2-} + 2K^+ + 4H_2O$
- (VI-18) $Th(SO_4)_2{\bullet}2K_2SO_4{\bullet}2H_2O(s) = Th^{4+} + 4SO_4^{2-} + 4K^+ + 2H_2O$
- (VI-19) $2[Th(SO_4)_2{\bullet}7/2K_2SO_4(s)] = 2Th^{4+} + 11SO_4^{2-} + 14K^+$
- (VI-20) $ThS_2(s) + 2H^+ = Th^{4+} + 2HS^-$

Thermodynamic Sub-model for An(V)

- (VII-1) $NpO_2CO_3^- + H^+ = NpO_2^+ + HCO_3^-$
- (VII-2) $NpO_2(CO_3)_2^{3-} + 2H^+ = NpO_2^+ + 2HCO_3^-$
- (VII-3) $NpO_2(CO_3)_3^{5-} + 3H^+ = NpO_2^+ + 3HCO_3^-$
- (VII-4) $NpO_2(OH)(aq) + H^+ = NpO_2^+ + H_2O$
- (VII-5) $NpO_2(OH)_2^- + 2H^+ = NpO_2^+ + 2H_2O$
- (VII-6) $NpO_2Acetate(aq) = NpO_2^+ + Acetate^-$
- (VII-7) $NpO_2Citrate^{2-} = NpO_2^+ + Citrate^{3-}$
- (VII-8) $NpO_2H_2EDTA^- = NpO_2^+ + EDTA^{4-} + 2H^+$
- (VII-9) $NpO_2HEDTA^{2-} = NpO_2^+ + EDTA^{4-} + H^+$
- (VII-10) $NpO_2EDTA^{3-} = NpO_2^+ + EDTA^{4-}$
- (VII-11) $NpO_2Lactate(aq) = NpO_2^+ + Lactate^-$
- (VII-12) $NpO_2Oxalate^- = NpO_2^+ + Oxalate^{2-}$
- (VII-13) $NpO_2OH(aged) + H^+ = NpO_2^+ + H_2O$
- (VII-14) $NpO_2OH(am) + H^+ = NpO_2^+ + H_2O$
- (VII-15) $2[NaNpO_2CO_3 \bullet 7/2H_2O](s) + 2H^+ = 2NpO_2^+ + 2HCO_3^- + 2Na^+ + 7H_2O$
- (VII-16) $Na_3NpO_2(CO_3)_2(s) + 2H^+ = NpO_2^+ + 2HCO_3^- + 3Na^+$
- (VII-17) $KNpO_2CO_3(s) + H^+ = NpO_2^+ + HCO_3^- + K^+$
- (VII-18) $K_3NpO_2(CO_3)_2(s) + 2H^+ = NpO_2^+ + 2HCO_3^- + 3K^+$
- (VII-19) $Np_2S_5(s) + 4H_2O = 2NpO_2^+ + 5HS^- + 3H^+$

Sub-model for Borate Species

- (VIII-1) $B(OH)_4^- + H^+ = B(OH)_3(aq) + H_2O$
- (VIII-2) $CaB(OH)_4^+ = Ca^{2+} + B(OH)_4^-$
- (VIII-3) $MgB(OH)_4^+ = Mg^{2+} + B(OH)_4^-$
- (VIII-4) $B_3O_3(OH)_4^- + 5H_2O = 3B(OH)_4^- + 2H^+$
- (VIII-5) $B_4O_5(OH)_4^{2-} + 7H_2O = 4B(OH)_4^- + 2H^+$
- (VIII-6) $NaB(OH)_4(aq) = Na^+ + B(OH)_4^-$
- (VIII-7) $Na_2B_4O_7 \bullet 10H_2O$(Na-tetraborate) $= 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$
- (VIII-8) $B(OH)_3(cr) + H_2O = B(OH)_4^- + H^+$
- (VIII-9) $KB_5O_8 \bullet 4H_2O$(K-pentaborate) $+ 8H_2O = K^+ + 5B(OH)_4^- + 4H^+$
- (VIII-10) $K_2B_4O_7 \bullet 4H_2O$(K-tetraborate) $+ 5H_2O = 2K^+ + 4B(OH)_4^- + 2H^+$
- (VIII-11) $NaBO_2 \bullet 4H_2O$(Na-metaborate) $= Na^+ + B(OH)_4^- + 2H_2O$
- (VIII-12) $NaB_5O_8 \bullet 5H_2O$(Na-pentaborate) $+ 7H_2O = Na^+ + 5B(OH)_4^- + 4H^+$
- (VIII-13) $NaBO_2 \bullet NaCl \bullet 2H_2O$(teepleite) $= 2Na^+ + B(OH)_4^- + Cl^-$

Sub-model for Iron Species

- (IX-1) $FeOH^+ + H^+ = Fe^{2+} + H_2O$
- (IX-2) $Fe(OH)_3^- + 3H^+ = Fe^{2+} + 3H_2O$
- (IX-3) FeOxalate(aq) = Fe^{2+} + Oxalate^{2-}
- (IX-4) $FeEDTA^{2-} = Fe^{2+} + EDTA^{4-}$
- (IX-5) FeCitrate$^-$ = Fe^{2+} + Citrate^{3-}
- (IX-6) $FeSO_4(s) = Fe^{2+} + SO_4^{2-}$
- (IX-7) $FeCO_3$(siderite) + $H^+ = Fe^{2+} + HCO_3^-$
- (IX-8) $Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$
- (IX-9) $Fe_2Cl(OH)_3$(hibbingite) + $3H^+ = 2Fe^{2+} + Cl^- + 3H_2O$
- (IX-10) FeOxalate•$2H_2O(s)$ = Fe^{2+} + Oxalate^{2-} + $2H_2O$

Sub-model for Lead Species

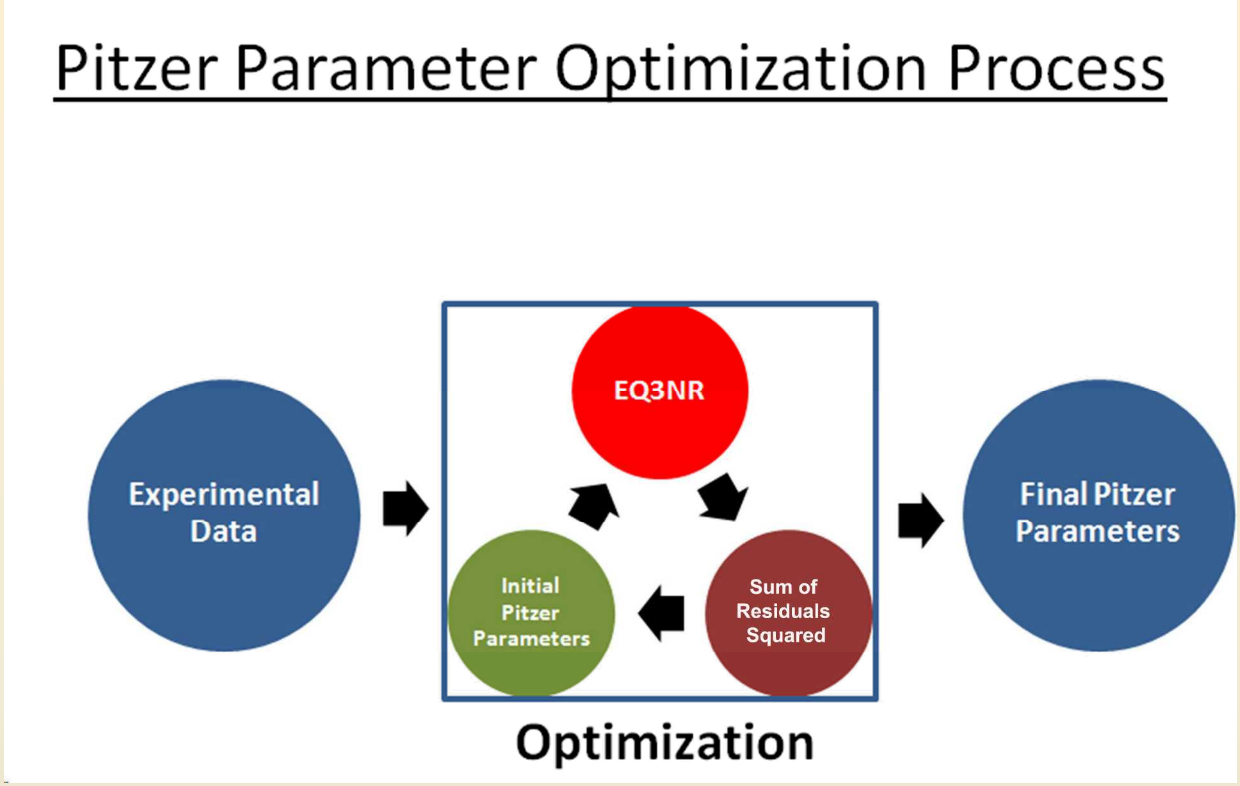
- (X-1) $Pb^{2+} + Cl^{-} = PbCl^{+}$
- (X-2) $Pb^{2+} + 2Cl^{-} = PbCl_2(aq)$
- (X-3) $Pb^{2+} + 3Cl^{-} = PbCl_3^{-}$
- (X-4) $Pb^{2+} + Oxalate^{2-} = PbOxalate(aq)$
- (X-5) $Pb^{2+} + 2Oxalate^{2-} = Pb(Oxalate)_2^{2-}$
- (X-6) $Pb^{2+} + CO_3^{2-} = PbCO_3(aq)$
- (X-7) $Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$
- (X-8) $Pb^{2+} + CO_3^{2-} + Cl^{-} = Pb(CO_3)Cl^{-}$
- (X-9) $Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$
- (X-10) $Pb^{2+} + Citrate^{3-} = PbCitrate^{-}$
- (X-11) $PbOxalate(cr) = Pb^{2+} + Oxalate^{2-}$
- (X-12) $PbCO_3(cerussite) = Pb^{2+} + CO_3^{2-}$
- (X-13) $PbO(litharge) + 2H^{+} = Pb^{2+} + H_2O$
- (X-14) $PbSO4(anglesite) = Pb^{2+} + SO_4^{2-}$
- (X-15) $PbClOH(cr) + H^{+} = Pb^{2+} + Cl^{-} + H_2O$
- (X-16) $Pb5(PO_4)_3Cl(pyromorphite) + 3H^{+} = 5Pb^{2+} + Cl^{-} + 3HPO_4^{2-}$

Sub-model for Sulfide Species

- (XI-1) $PbS(galena) + H^+ = Pb^{2+} + HS^-$
- (XI-2) $Pb^{2+} + HS^- = Pb(HS)^+$
- (XI-3) $Pb^{2+} + 2HS^- = Pb(HS)_2(aq)$
- (XI-4) $FeS(mackinawite) + H^+ = Fe^{2+} + HS^-$
- (XI-5) $Fe^{2+} + HS^- = Fe(HS)^+$
- (XI-6) $Fe^{2+} + 2HS^- = Fe(HS)_2(aq)$
- (XI-7) $SO_4^{2-} + 4H_2(g) + H^+ = HS^- + 4H_2O(l)$

Software for Geochemical Modeling

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 ($log\ K_{calculation}$).



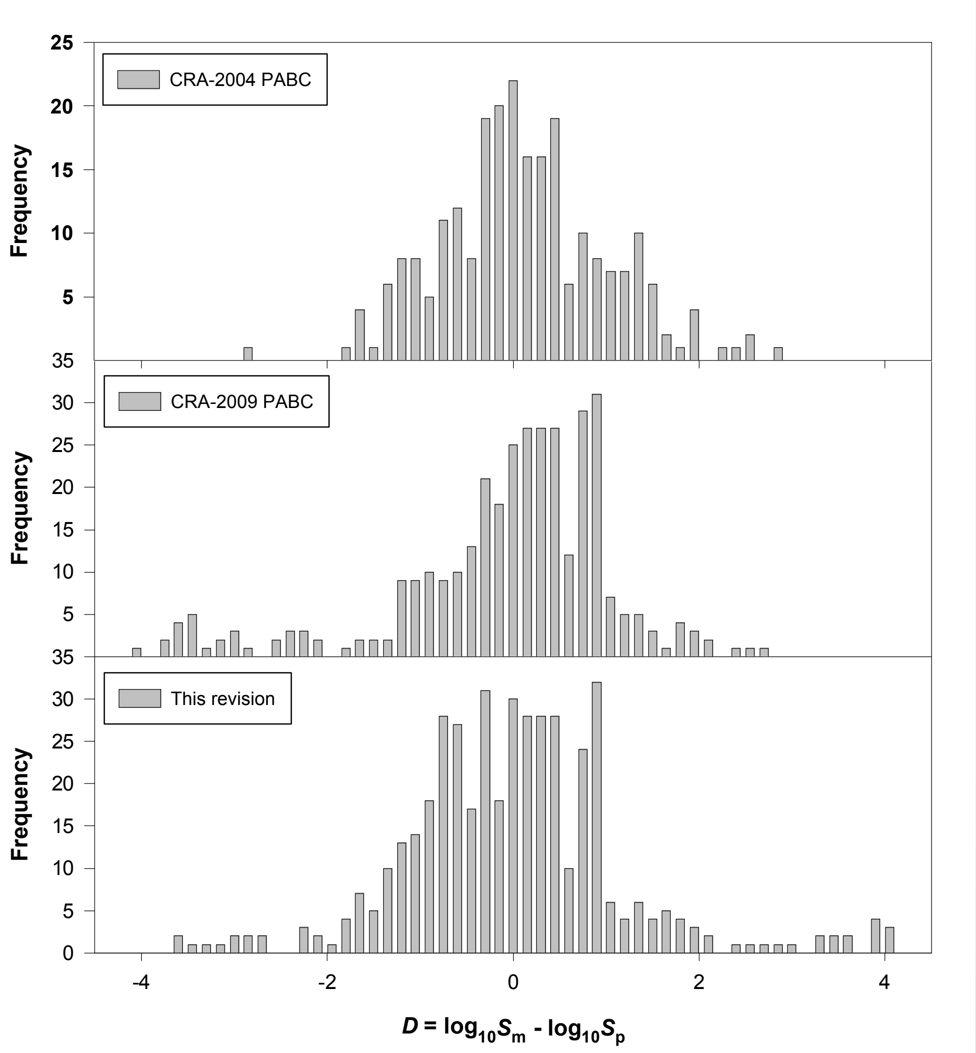
5. Residual difference between the experimentally obtained and the calculated equilibrium constants is estimated. Based on residual value, values of the Pitzer parameters are modified and re-inserted into the EQ3NR database. This is repeated until the residual is minimized.
6. At minimum residual the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

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}).

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

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

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

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

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

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

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