SAND2019-5591PE

Status of CRA-2019 Geochemistry

PRESENTED BY

Presentation to DOE, May 21, 2019

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.

Outline of Presentation

1. Development of DATA0.FM4
2. Summary Actinide Uncertainty Analysis for CRA-2019
3. Summary Actinide Baseline Solubility Model for CRA-2019
4. Supplemental Information for Actinide Baseline Solubility Model for CRA-2019

Creation of DATA0.FM4

- DATA0.FM4 is based entirely on DATA0.FM1.
- None of the parameters, or parameter updates of DATA0.FM2 are included in FM4.
- The organics EDTA, citrate, and oxalate were updated in DATA0.FM4. The acetate system remains the same as FM1.
- The lead system was added to FM4. The lead system in FM4 does not include Pitzer parameters.
- FM4 includes the iron system, both thermodynamic and Pitzer data.
- The actinide systems are unchanged in FM4.
- No new borate data were added to FM4, the borate system is the same as FM1.

Pertinent Documents

Sisk-Scott, C. 2019 “Analysis Plan to Update the WIPP Geochemical Thermodynamic Database (DATA0.FM1) to Data0.FM4 for CRA-2019”. AP-183, Revision 1. Carlsbad, NM: Sandia National Laboratories. (ERMS#571001).

Jang, J-H. 2019. “Analysis Plan for Derivation and Addition of Equilibrium Constants and Pitzer Interaction rameters to the WIPP Geochemical Thermodynamic Database”. AP-182 (2019). Carlsbad, NM: Sandia National Laboratories. (ERMS# 571074).

Domski, P.S. 2019. “An Update to the EQ3/6 Pitzer Thermodynamic Database DATA0.FM1 with the Creation of DATA0.FM4”. Carlsbad, NM: Sandia National Laboratories. (ERMS#571052).

Domski, P.S. 2019. “Official Release of the Qualified Pitzer Thermodynamic Database, DATA0.FM4, for EQ3/6 under AP-183, Revision 1. Carlsbad, NM: Sandia National Laboratories. (ERMS#571051).

All documents are in WIPP records center

Major Element Chemistry: The Core of the Database

- DATA0.FM1 : All reactions involving Na, K, Ca, Mg, Cl, SO_4, CO_3, B, Br from Harvie et al. (1984).
- DATA0.FM4 : All reactions involving Na, K, Ca, Mg, Cl, SO_4, CO_3, B, Br from Harvie et al. (1984).

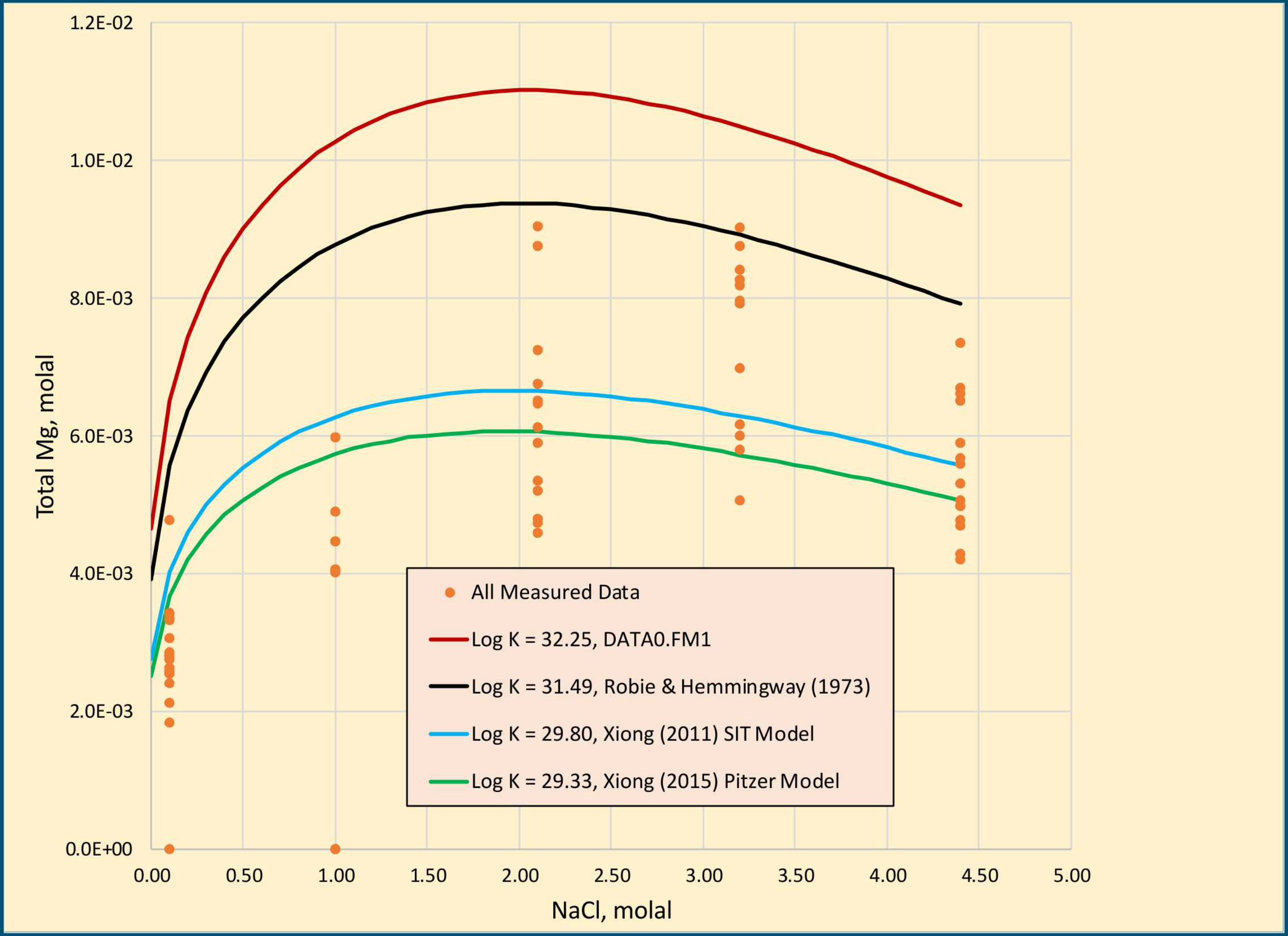
Includes mineral dissolution/precipitation reactions, aqueous speciation reactions, all log K values and associated Pitzer parameters.

MgO System: Hydromagnesite (5424)

Reaction	log K	Source
Solid Dissolution Reactions		
$Mg_5(CO_3)_4(OH)_2\bullet 4H_2O + 6H^+ \leftrightarrow 5Mg^{2+} + 4HCO_3^- + 6H_2O$	31.49	Robie and Hemingway (1973)

The solubility product (log K) of Hydromagnesite(5424) used in FM4 was that of Robie and Hemingway (1973) in accordance with EPA’s wishes. However, the experimental data does not support this decision, and it should be re-evaluated for CRA-2024.

Log K for hydromagnesite – 31.49 based on Robie and Hemingway (1973)



MgO System: Phase 5

- Has been in the WIPP geochemical model since at least CRA-2009 PA, and the log K has not been changed, i.e., the converted FMT value is included in DATA0.FM1, and it is the same as that in DATA0.FM4.

$$3Mg^{2+} + Cl^- + 9H_2O \leftrightarrow Mg_3Cl(OH)_5 \bullet 4H_2O + 5H^+$$

Borate System

- The borate system in DATA0.FM1 is that of Felmy and Weare (1986).
- The borate system in DATA0.FM4 is exactly the same as DATA0.FM1 (Felmy and Weare, 1986) with no changes or additions.

Organics

EDTA:

- DATA0.FM1 all log K and Pitzer parameters from Giambalvo (2002).
- DATA0.FM4 all log K values from Hummel et al., (2005), Pitzer parameters from Giambalvo (2002) Felmy & Mason (2003), and Domski (2018).

Citrate:

- DATA0.FM1 all log K and Pitzer parameters from Giambalvo (2002).
- DATA0.FM4 all log K values from Hummel et al., (2005), Pitzer parameters same as FM1 (Giambalvo, 2002).

Organics (continued)

Oxalate:

- DATA0.FM1 all log K and Pitzer parameters from Giambalvo (2002), and Xiong (2004) (whewellite).
- DATA0.FM4 all log K values from Hummel et al., (2005) Xiong (2004) (whewellite), Jang & Kim (2016), and AP-182 (glushinskite). Pitzer parameters from Giambalvo (2002f).

Acetate:

- No changes, FM4 same as FM1.

EDTA Updated Thermodynamic Data

Reaction	log K	Source	DATA0.FM1
Solid Dissolution Reactions			
$Ca_2EDTA \bullet 7H_2O(s) \leftrightarrow 2Ca^{2+} + EDTA^{4-} + 7H_2O$	-16.81	Domski (2018)	N/A
Aqueous Dissociation Reactions			
$H_4EDTA(aq) \leftrightarrow EDTA^{4-} + 4H^+$	-23.42	Hummel et al. (2005)	-23.04
$H_3EDTA^- \leftrightarrow EDTA^{4-} + 3H^+$	-21.19	Hummel et al. (2005)	-20.54
$H_2EDTA^{2-} \leftrightarrow EDTA^{4-} + 2H^+$	-18.04	Hummel et al. (2005)	-17.45
$HEDTA^{3-} \leftrightarrow EDTA^{4-} + H^+$	-11.24	Hummel et al. (2005)	-10.57
$NaEDTA^{3-} \leftrightarrow Na^+ + EDTA^{4-}$	-2.80	Hummel et al. (2005)^A	N/A
$MgEDTA^{2-} \leftrightarrow Mg^{2+} + EDTA^{4-}$	-10.90	Hummel et al. (2005)	-10.13
$MgHEDTA^{1-} \leftrightarrow H^+ + Mg^{2+} + EDTA^{4-}$	-15.40	Hummel et al. (2005)^A	N/A
$CaEDTA^{2-} \leftrightarrow Ca^{2+} + EDTA^{4-}$	-12.69	Hummel et al. (2005)	-10.13
$CaHEDTA^{1-} \leftrightarrow H^+ + Ca^{2+} + EDTA^{4-}$	-16.23	Hummel et al. (2005)^A	N/A
A – New to DATA0.FM4			

EDTA Updated Pitzer parameters

I	j	α_1/α_2^A	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	Source
Cation-Anion Interactions						
$EDTA^{4-}$	Na^+	2.0/12.0	1.10	15.6	0.001	Felmy and Mason (2003)
$EDTA^{4-}$	K^+	2.0/12.0	1.10	15.6	0.001	Felmy and Mason (2003)
$NaEDTA^{3-}$	Na^+	2.0/12.0	0.59	5.39	0	Felmy and Mason (2003)
$CaEDTA^{2-}$	Na^+	2.0/12.0	0.185	2.405	0	Domski (2018a)^A
A – New to FM4						

Citrate Updated Thermodynamic Data

Reaction	log K	Source	DATA0.FM1
Solid Dissociation Reactions			
$Ca_3(Citrate)_2 \bullet 4H_2O(s) \leftrightarrow 3Ca^+ + 2Citrate^{3-} + 4H_2O$	-17.90	Hummel et al. (2005)[A]	N/A
Aqueous Dissociation Reactions			
$H_3Citrate\ (aq) \leftrightarrow Citrate^{3-} + 3H^+$	-14.27	Hummel et al. (2005)	-14.51
$H_2Citrate^- \leftrightarrow Citrate^{3-} + 2H^+$	-11.14	Hummel et al. (2005)	-11.26
$HCitrate^{2-} \leftrightarrow Citrate^{3-} + H^+$	-6.36	Hummel et al. (2005)	-6.42
$MgHCitrate\ (aq) \leftrightarrow Mg^{2+} + H^+ + Citrate^{3-}$	-8.96	Hummel et al. (2005)[A]	N/A
$Mg(H_2Citrate)^+ \leftrightarrow Mg^{2+} + 2H^+ + Citrate^{3-}$	-12.45	Hummel et al. (2005)[A]	N/A
$MgCitrate^- \leftrightarrow Mg^{2+} + Citrate^{3-}$	-4.81	Hummel et al. (2005)	-5.30
$CaCitrate^- \leftrightarrow Ca^{2+} + Citrate^{3-}$	-4.80	Hummel et al. (2005)	-5.30
$CaHCitrate(aq) \leftrightarrow Ca^{2+} + H^+ + Citrate^{3-}$	-9.28	Hummel et al. (2005)[A]	N/A
$Ca(H_2Citrate)^+ \leftrightarrow Ca^{2+} + 2H^+ + Citrate^{3-}$	-12.67	Hummel et al. (2005)[A]	N/A
A - New to FM4			

Oxalate Updated Thermodynamic Data

Reaction	log K	Source
Solid Dissolution Reactions		
MgOxalate•$2H_2O(s)$ (glushinskite) ↔ Mg^{2+} + $Oxalate^{2-}$ + $2H_2O$	-6.41	AP-182[A]
Aqueous Dissociation Reactions		
$Mg(Oxalate)_2^{2-}$ ↔ Mg^{2+} + $2Oxalate^{2-}$	-5.24	AP-182[A]
A – new to FM4		

Oxalate Updated Pitzer Data

I	j	α_1/α_2	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Source
Cation-Anion Interactions							
$Mg(Oxalate)_2^{2-}$	Na^+	2.0/12.0	0.07	0	0	0	AP-182

i	j	$\lambda_{nc'}$ or $\lambda_{na'}$	Source
Neutral-Cation Interactions			
MgOxalate(aq)	Na^+	0.08	AP-182
MgOxalate(aq)	Mg^{2+}	-0.20	AP-182

Oxalate data that was originally sourced from Domski (2018) in early drafts of APP GEOCHEM was changed to AP-182 value(s) due to issues found during the creation of DATA0.FM4.

Acetate

The acetate data in DATA0.FM4 is identical to that in DATA0.FM1, there were no changes or additions.

The Actinides: Am(III), Th(IV), and Np(V) Systems

There were no changes in the Am(III), Th(IV), and Np(V) systems, i.e., the Am(III), Th(IV), and Np(V) systems in DATA0.FM4 is identical to those in DATA0.FM1.

Lead System: Included Thermodynamic Data

Reaction	log K	Source
Solid Dissolution Reactions		
α-PbO(litharge) + $2H^+ \leftrightarrow Pb^{2+} + H_2O(l)$	12.62	Powell et al. (2009)
$PbCO_3$(cerussite) + $H^+ \leftrightarrow Pb^{2+} + HCO_3^-$	-2.84	Powell et al. (2009)
$Pb_2CO_3Cl_2(s) + H^+ \leftrightarrow 2Pb^{2+} + HCO_3^{1-} + 2Cl^-$	0.41	Powell et al. (2009)
$PbSO_4(s) \leftrightarrow Pb^{2+} + SO_4^{2-}$	-7.80	Powell et al. (2009)
$NaPb_2(CO_3)_2(OH)(s) + 3H^+ \leftrightarrow Na^+ + 2Pb^{2+} + 2HCO_3^- + H_2O$	Not Included in FM4	
Aqueous Dissociation Reactions		
$PbCl^+ \leftrightarrow Pb^{2+} + Cl^-$	-1.50	Powell et al. (2009)
$PbCl_2(aq) \leftrightarrow Pb^{2+} + 2Cl^-$	-2.10	Powell et al. (2009)
$PbCl_3^- \leftrightarrow Pb^{2+} + 3Cl^-$	-2.00	Powell et al. (2009)
$PbOH^+ + H^+ \leftrightarrow Pb^{2+} + H_2O$	7.46	Powell et al. (2009)
$Pb(OH)_2(aq) + 2H^+ \leftrightarrow Pb^{2+} + 2H_2O(l)$	16.94	Powell et al. (2009)
$Pb(CO_3)(OH)^- + 2H^+ \leftrightarrow Pb^{2+} + HCO_3^{1-} + H_2O(l)$	13.44	Powell et al. (2009)
$Pb(CO_3)Cl^- + H^+ \leftrightarrow Pb^{2+} + HCO_3^- + Cl^-$	3.87	Powell et al. (2009)
$PbCO_3(aq) + H^+ \leftrightarrow Pb^{2+} + HCO_3^-$	3.89	Powell et al. (2009)
$Pb(CO_3)_2^{2-} + 2H^+ \leftrightarrow Pb^{2+} + 2HCO_3^-$	10.55	Powell et al. (2009)
$PbSO_4(aq) \leftrightarrow Pb^{2+} + SO_4^{2-}$	-2.72	Powell et al. (2009)

Note:

- All of Powell et al.'s data were derived using the SIT model, which is not internally consistent with the Pitzer derived parameters of DATA0.FM1.
- There are no Pitzer data for the lead system.

Iron System: Included Thermodynamic Data

Reaction	Source		Source	
Solid Dissolution Reactions	Included	Log K	Proposed	Log K
$Fe(OH)_2(s) + 2H^+$ (ferrous hydroxide) $\leftrightarrow Fe^{2+} + 2H_2O$	Kim et al. (2017)	12.89	Domski(2018)	12.83
$Fe_2Cl(OH)_3(s) + 3H^+$ (hibbingite) $\leftrightarrow 2Fe^{2+} + Cl^- + 3H_2O$	Kim et al. (2017)	17.08	Domski(2018)	17.01
$FeCO_3(s) + H^+$ (siderite) $\leftrightarrow Fe^{2+} + HCO_3^-$	Stumm and Morgan (1996)	-0.12	Lemire et al. (2013)	-0.35
$Fe_2CO_3(OH)_2(s) + 3H^+$ (chukanovite) $\leftrightarrow 2Fe^{2+} + HCO_3^- + 2H_2O$	Kim et al. (2017)	12.32	Domski (2018)	12.23
Aqueous Dissociation Reactions				
$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$	Shock et al. (1997)	9.31	Lemire et al. (2013)	9.10
$Fe(OH)_2(aq) + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$	Stumm and Morgan (1996)	20.82	Lemire et al. (2013)	20.85
$Fe(OH)_3^- + 3H^+ \leftrightarrow Fe^{2+} + 3H_2O$	Baes and Mesmer (1976)	31.0	Baes and Mesmer (1976)	31.0
$FeCO_3(aq) + H^+ \leftrightarrow Fe^{2+} + HCO_3^-$	Bruno et al. (1992)	4.83	Lemire et al. (2013)	5.06
$Fe(CO_3)_2^{2-} + 2H^+ \leftrightarrow Fe^{2+} + 2HCO_3^{1-}$	Kim et al. (2017)	13.89	Lemire et al. (2013)	13.62

In order to align with AP-182 (reviewed by Carlos Jove-Colon), we have adapted the thermodynamic data of Kim et al. (2017) alongside the Pitzer parameters previously identified in APP GEOCHEM for the iron system, and under which Kim et al.'s (2017) thermodynamic data were derived for the iron system.

Iron System: Included Pitzer Data

I	j	α_1/α_2^A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Source
Fe^{2+}	Cl-	2.0/12.0	0.373	1.135	0	-0.022	Moog et al. (2004)
Na^+	$Fe(CO3)_2^{-2}$	2.0/12.0	-0.23	6.26	0	0	Kim et al. (2017)

i	j	$\theta_{cc'}$ or $\theta_{aa'}$	Source
Na^+	Fe^{2+}	0.110	Moog et al. (2004)
Mg^{2+}	Fe^{2+}	0.145	Moog et al. (2004)
K^+	Fe^{2+}	0.0274	Moog et al. (2004)
Ca^{2+}	Fe^{2+}	0.0811	Moog et al. (2004)

I	j	k	Ψ_{ijk}	Source
Fe^{+2}	Na^+	Cl^-	-0.0161	Moog et al. (2004)
Fe^{+2}	K^+	Cl^-	-0.0252	Moog et al. (2004)
Fe^{+2}	Mg^{+2}	Cl^-	-0.0299	Moog et al. (2004)
Fe^{+2}	Ca^{+2}	Cl^-	-0.0160	Moog et al. (2004)

Summary

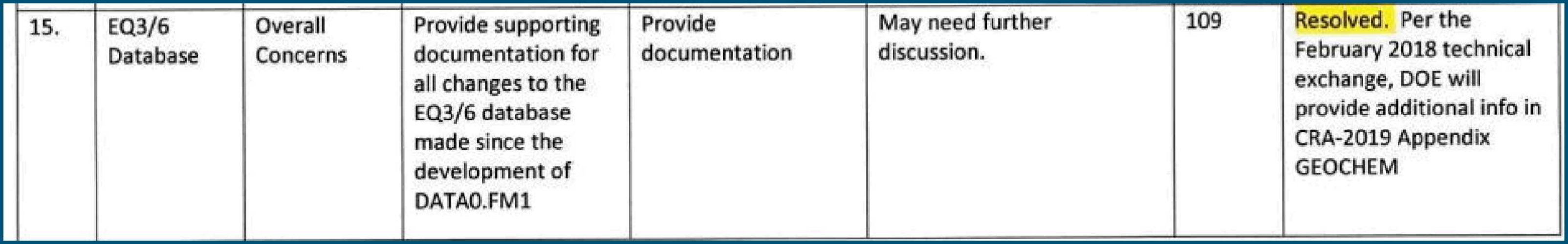
- The inorganic data is the same in both FM1 and FM4 (Harvie et al. 1984).
- Hydromagnesite5424 Log K updated to Robie & Hemmingway (1973) value as per EPA's request.
- The borate system in FM4 is the same as FM1 (Felmy and Weare, 1986) with no additions.
- EDTA and citrate updated to Hummel et al. (2005) and SNL derived values.
- Oxalate data that was originally sourced from Domski (2018) in early drafts of APP GEOCHEM was changed to AP-182 value(s) due to issues found during the creation of DATA0.FM4. This is a deviation from early drafts of APP GEOCHEM.
- The lead system log K values added using Powell et al. (2009) data.
- The lead system only includes thermodynamic data, and no Pitzer data.
- Iron thermodynamic data that was originally sourced from Domski (2018) and Lemire et al. (2013) in early drafts of APP GEOCHEM was changed to Kim et al. (2017) due to procedural issues in light of AP-182. This is a deviation from early drafts of APP GEOCHEM.

Summary (continued)

- The iron system includes both thermodynamic data, and Pitzer data.
- The thermodynamic data for the lead and system was derived using the SIT model.
- The addition of the lead and iron systems to DATA0.FM4 allow the inclusion of additional waste inventory materials to the baseline solubility model.

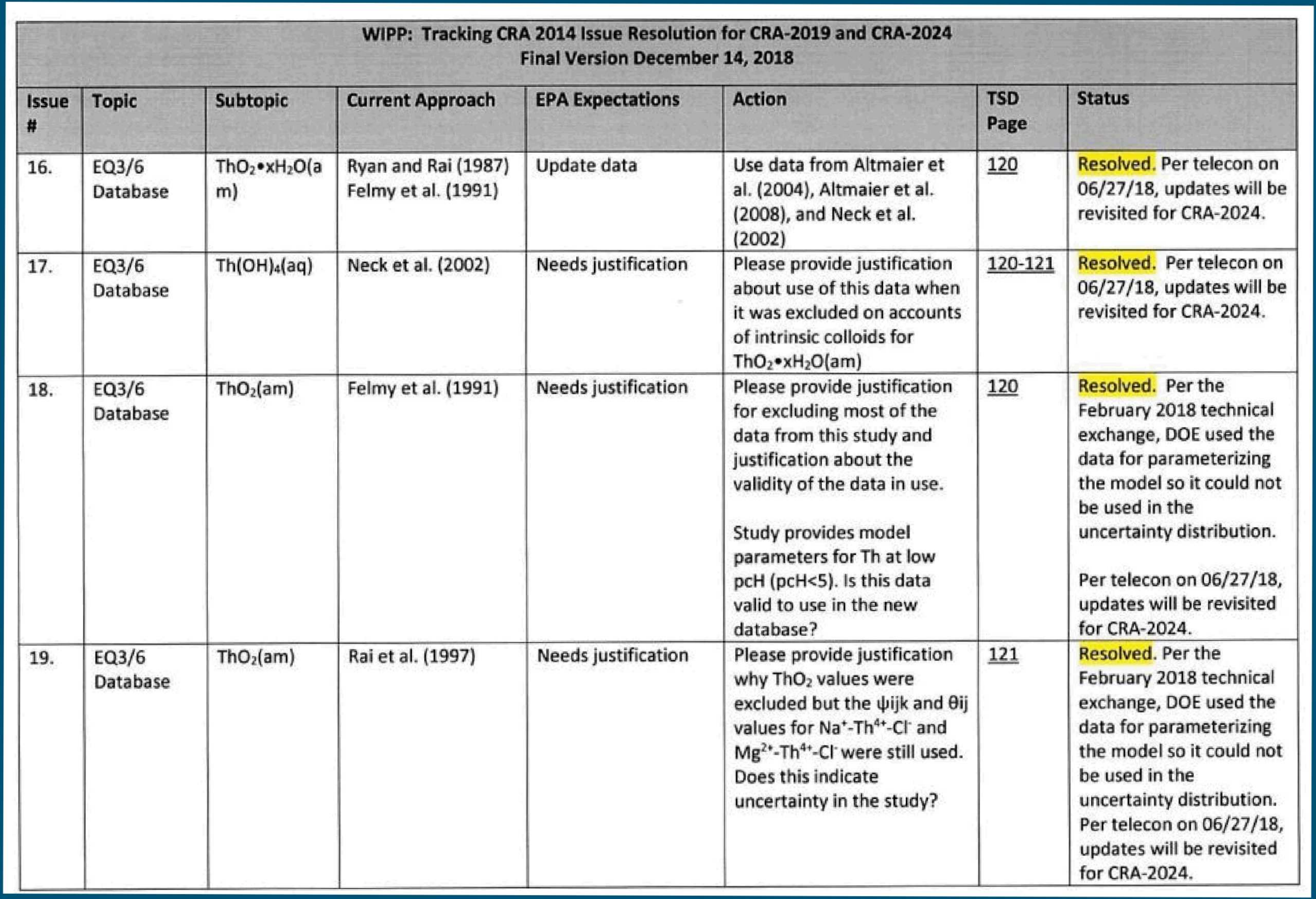
EPA Database Issues from Peake (12/2018)

- Peake (2018) outlined the issues with the EQ3/6 database, and the status of those issues. All of the EPA's issues have been resolved, with the majority deferred to CRA-2024.
- It should be noted that issues, 16, 17, 18 and 19, are actually uncertainty analysis issues, not database issues.



15.	EQ3/6 Database	Overall Concerns	Provide supporting documentation for all changes to the EQ3/6 database made since the development of DATA0.FM1	Provide documentation	May need further discussion.	109	Resolved. Per the February 2018 technical exchange, DOE will provide additional info in CRA-2019 Appendix GEOCHEM

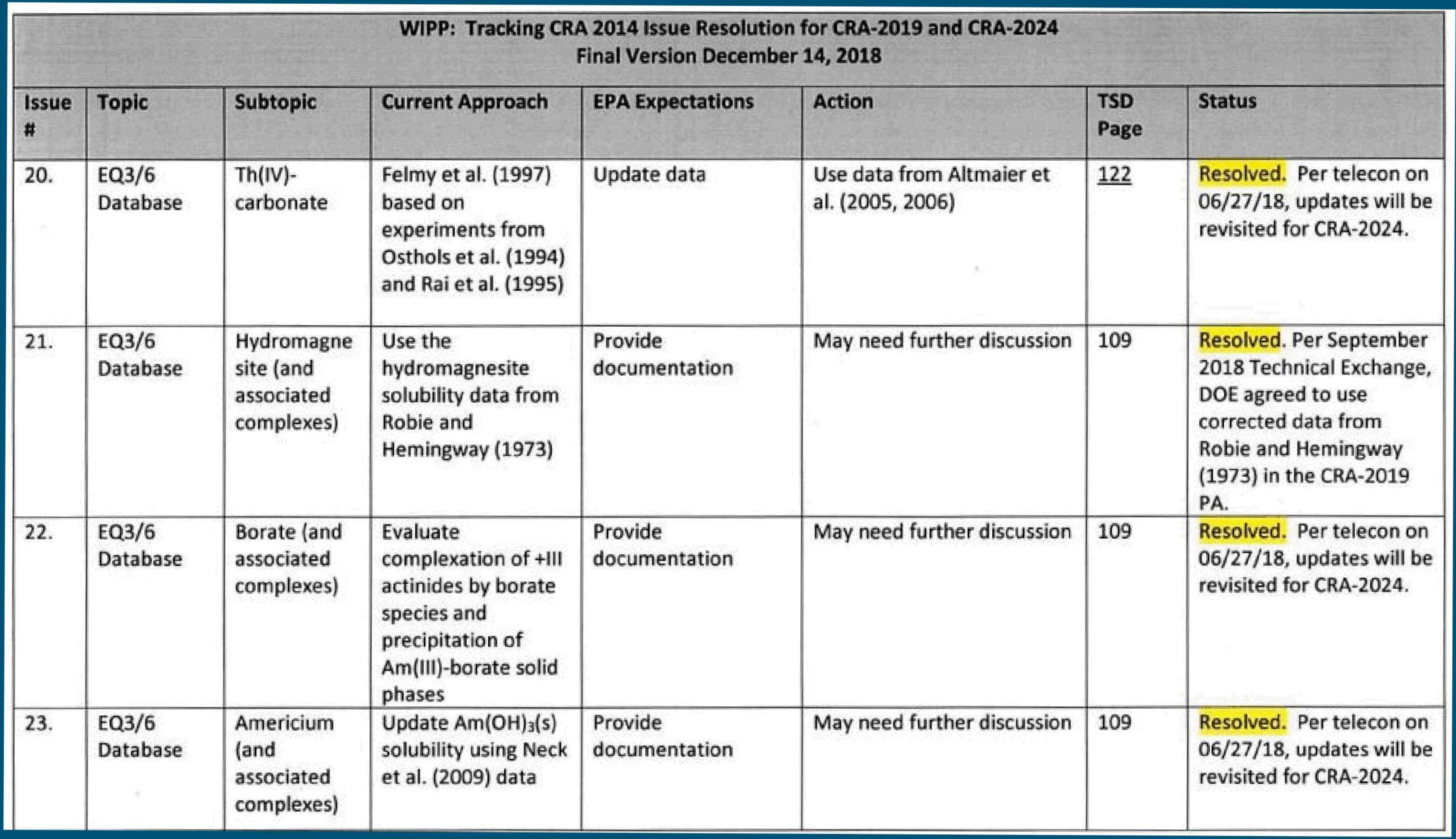
EPA Database Issues from Peake (12/2018) (continued)



WIPP: Tracking CRA 2014 Issue Resolution for CRA-2019 and CRA-2024
Final Version December 14, 2018

Issue #	Topic	Subtopic	Current Approach	EPA Expectations	Action	TSD Page	Status
16.	EQ3/6 Database	$ThO_2 \bullet xH_2O$(am)	Ryan and Rai (1987) Felmy et al. (1991)	Update data	Use data from Altmaier et al. (2004), Altmaier et al. (2008), and Neck et al. (2002)	120	Resolved. Per telecon on 06/27/18, updates will be revisited for CRA-2024.
17.	EQ3/6 Database	$Th(OH)_4$(aq)	Neck et al. (2002)	Needs justification	Please provide justification about use of this data when it was excluded on accounts of intrinsic colloids for $ThO_2 \bullet xH_2O$(am)	120-121	Resolved. Per telecon on 06/27/18, updates will be revisited for CRA-2024.
18.	EQ3/6 Database	ThO_2(am)	Felmy et al. (1991)	Needs justification	Please provide justification for excluding most of the data from this study and justification about the validity of the data in use. Study provides model parameters for Th at low pcH (pcH<5). Is this data valid to use in the new database?	120	Resolved. Per the February 2018 technical exchange, DOE used the data for parameterizing the model so it could not be used in the uncertainty distribution. Per telecon on 06/27/18, updates will be revisited for CRA-2024.
19.	EQ3/6 Database	ThO_2(am)	Rai et al. (1997)	Needs justification	Please provide justification why ThO_2 values were excluded but the ψijk and θij values for Na^+-Th^{4+}-Cl^- and Mg^{2+}-Th^{4+}-Cl^- were still used. Does this indicate uncertainty in the study?	121	Resolved. Per the February 2018 technical exchange, DOE used the data for parameterizing the model so it could not be used in the uncertainty distribution. Per telecon on 06/27/18, updates will be revisited for CRA-2024.

EPA Database Issues from Peake (12/2018) (continued)

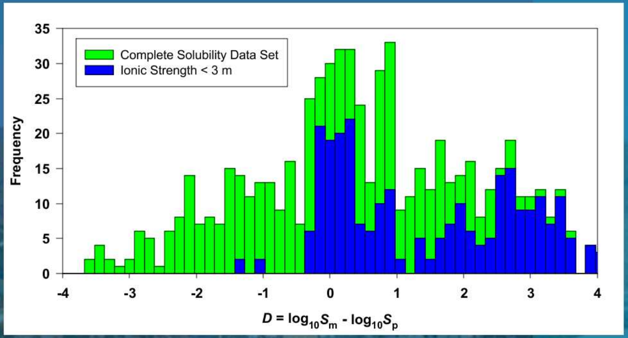


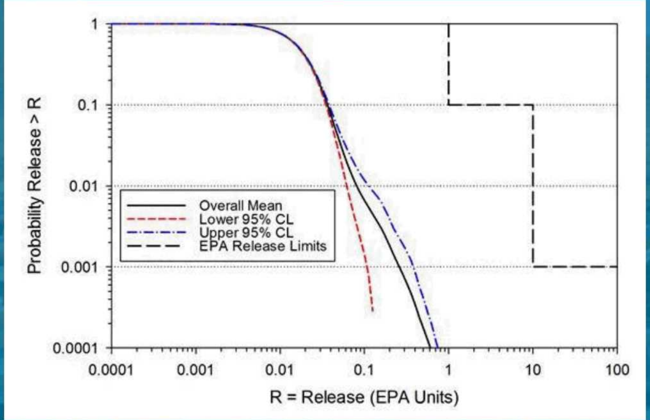
WIPP: Tracking CRA 2014 Issue Resolution for CRA-2019 and CRA-2024
Final Version December 14, 2018

Issue #	Topic	Subtopic	Current Approach	EPA Expectations	Action	TSD Page	Status
20.	EQ3/6 Database	Th(IV)-carbonate	Felmy et al. (1997) based on experiments from Osthols et al. (1994) and Rai et al. (1995)	Update data	Use data from Altmaier et al. (2005, 2006)	122	Resolved. Per telecon on 06/27/18, updates will be revisited for CRA-2024.
21.	EQ3/6 Database	Hydromagnesite (and associated complexes)	Use the hydromagnesite solubility data from Robie and Hemingway (1973)	Provide documentation	May need further discussion	109	Resolved. Per September 2018 Technical Exchange, DOE agreed to use corrected data from Robie and Hemingway (1973) in the CRA-2019 PA.
22.	EQ3/6 Database	Borate (and associated complexes)	Evaluate complexation of +III actinides by borate species and precipitation of Am(III)-borate solid phases	Provide documentation	May need further discussion	109	Resolved. Per telecon on 06/27/18, updates will be revisited for CRA-2024.
23.	EQ3/6 Database	Americium (and associated complexes)	Update $Am(OH)_3(s)$ solubility using Neck et al. (2009) data	Provide documentation	May need further discussion	109	Resolved. Per telecon on 06/27/18, updates will be revisited for CRA-2024.

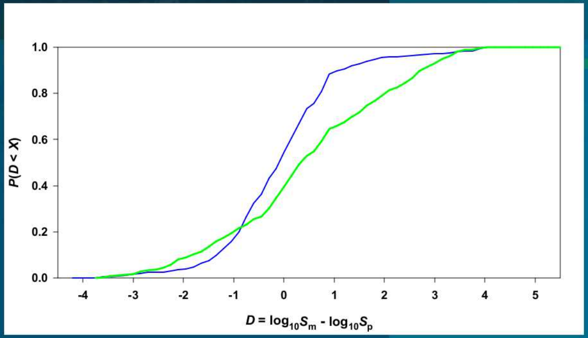
Database Updates for CRA-2024 PA

- CRA-2014 Database updates in accordance with EPA issues.
- Investigate the impact of using SIT data in a Pitzer database via expert elicitation, and/or sensitivity study.
- Evaluate the borate species.
- Evaluate the Ca – Mg – Carbonate system with the possible inclusion of a Ca – Mg solid-solution phase.





Actinide Uncertainty Analysis for CRA-2019 PA



Pertinent Documents

Domski, P.S. 2019. “Uncertainty Analysis of Actinide Solubilities for CRA 2019.” Carlsbad, NM: Sandia National Laboratories. (ERMS# 571179).

Peake, T. 2018. Letter to Mike Brown “2018-12-17 E Letter to CBFO WIPP Issues Summary”. U.S. Environmental Protection Agency, Center for Waste Management and Regulations. December 17, 2018.

All documents are in the WIPP records center

Criteria from Domski (2019)

- G7. Include only results from studies with a characterized solubility-controlling solid for which [the value of the dimensionless standard chemical potential(μ^o/RT) or thermodynamic equilibrium constant (log K)] solubility data is in the WIPP Th(IV) or Am(III) model (i.e., in the EPA-certified thermodynamic database), and in which the quantity of solid initially present was sufficient to prevent complete dissolution of this solid during the experiments.

- G9. Include results from studies with dissolved elements or species that are present in WIPP brines. Exclude studies with dissolved elements or species that are absent in WIPP repository brines and for which our models do not include association/dissociation constants or Pitzer parameters.

Criteria (continued)

G11. Include only results from experimental studies carried out under conditions at or close to those predicted for WIPP disposal rooms. Specifically, include only results from experiments in which:

- (1) $I \geq 3$ m or M,
- (2) pcH = 8.0–11.2, and
- (3) total inorganic C (TIC) = 0.0 - 2×10^{-2} M.

This is the EPA requested update, increasing TIC from 0.014 to 0.02 M.

Actinide Uncertainty Analysis for CRA-2019

- The CRA-2019 Actinide Uncertainty analysis is identical to the SEN4 (Xiong & Domski 2015) uncertainty analysis with two exceptions:
    1. The Khalili (1994) data were not included in the CRA-2019 PA Am(III) uncertainty distribution.
    2. The new QA database DATA0.FM4 was used to simulate the laboratory experiments for CRA-2019 rather than DATA0.FM1.
- No literature search was conducted for CRA-2019 per EPA's direction, and as documented in APPENDIX GEOCHEM.
- The selection criteria were updated per EPA's and DOE's mutual agreement. Moot for CRA-2019 PA.

Am(III) Solubility Model

Twenty-four samples from Khalili et al. (1994) in G-Seep brine which were included in SEN4, per EPA's instructions have since been eliminated based on DOE's reasoning of the poor quality of this data set.

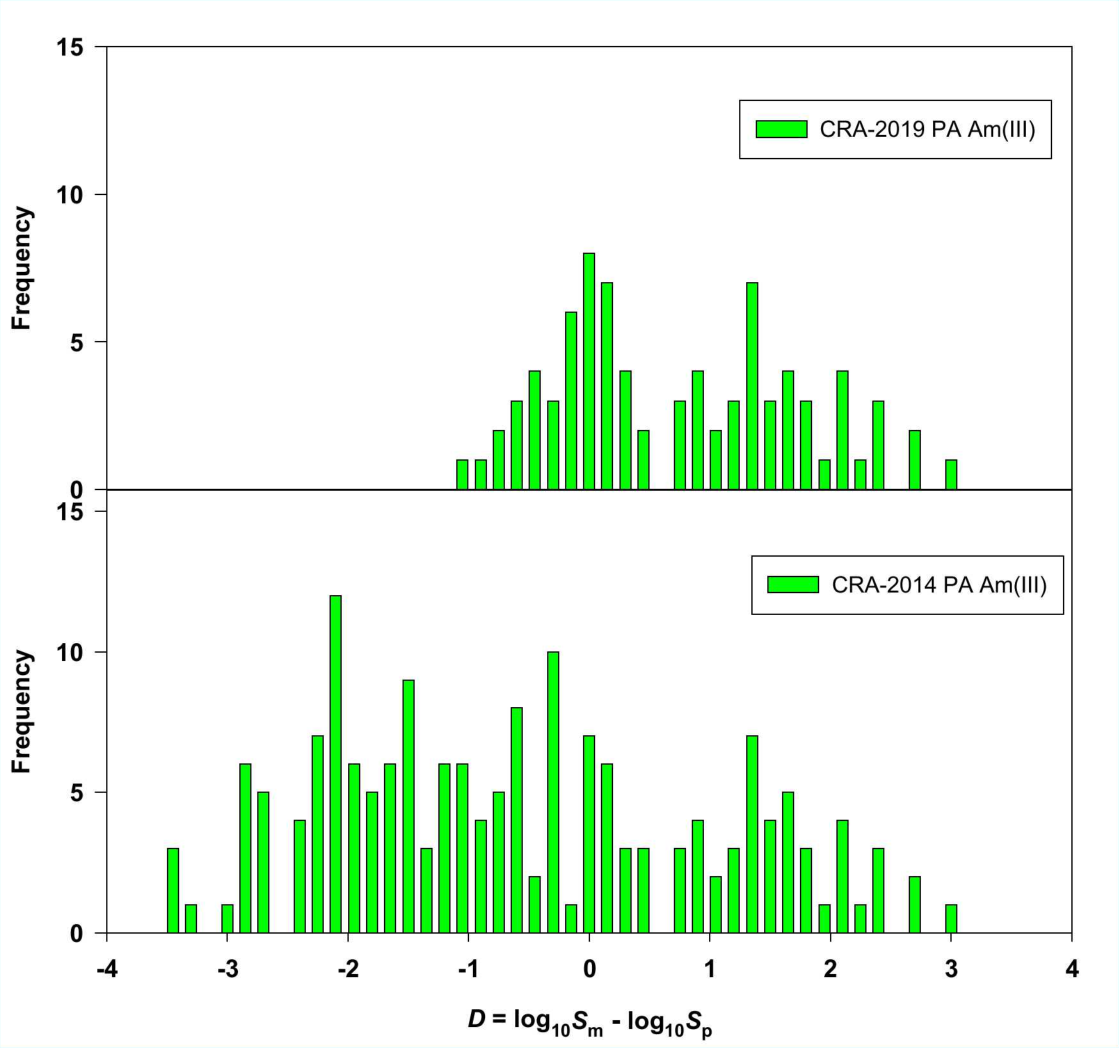
The 15 results in ERDA-6 from Rao et al. (1999), were included in this analysis, per EPA's instructions.

Eight samples in 5M NaCl, 5 samples in 1 M $MgCl_2$, 3 samples in 2.5 M $MgCl_2$, 8 samples in 5 M $MgCl_2$, 9 samples in 1 M $CaCl_2$, 10 samples in 2.5 M $CaCl_2$, and 13 samples in 3.5 M $CaCl_2$, for a total of 56 samples from Neck et al. (2009).

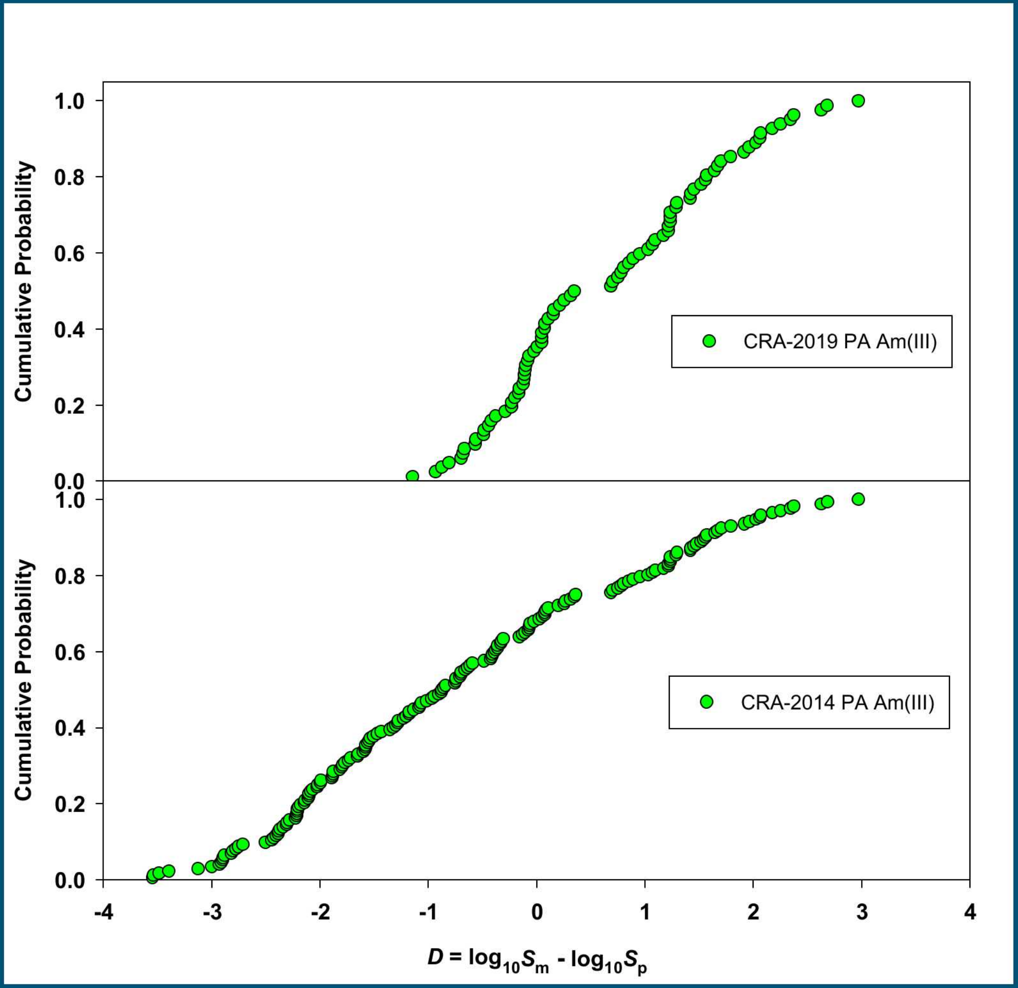
Eleven 5 M NaCl samples of Runde and Kim (1995) were included in this analysis, per EPA's instructions.

Total of 82 experimental data points for CRA-2019 PA. Early versions of APP GEOCHEM had the total at 75 data points as specified by EPA, this was a counting error by EPA. All of the data originated from digitized versions of figures in reports by Runde and Kim (1994), Rao et al. (1999), and Neck et al. (2009), and EPA simply mis-counted.

Am(III) PDF for CRA-2019 PA and CRA-2014 PA



Am(III) CDF for CRA-2019 PA and CRA-2014 PA



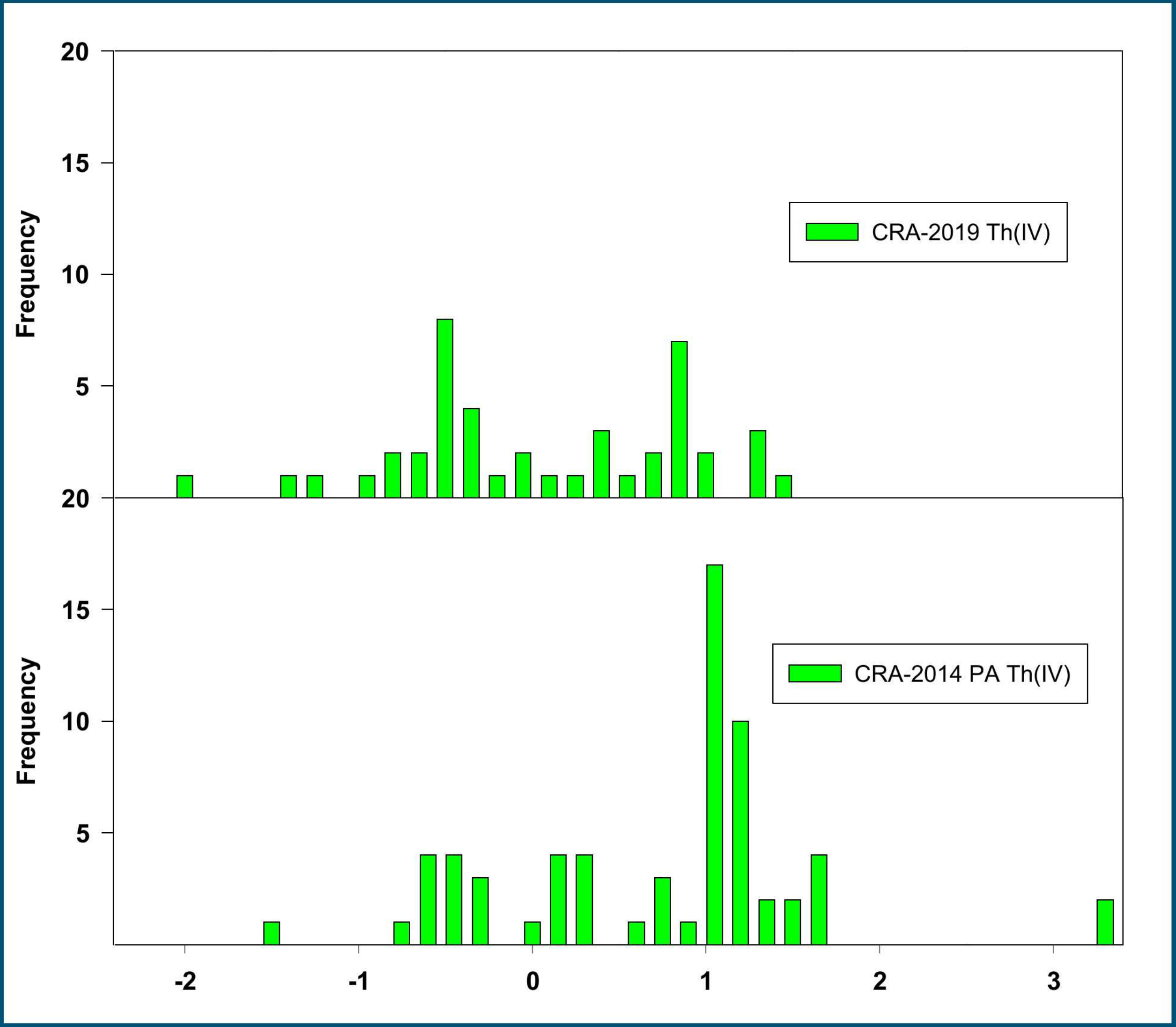
Am(III) Statistics for CRA-2019 PA and CRA-2014 PA

Analysis	Mean	Median	Std Dev	Minimum	Maximum	n
CRA-2014	–0.678	–0.866	1.57	–3.55	2.97	172
CRA-2019	0.651	0.516	1.01	-1.14	2.97	82

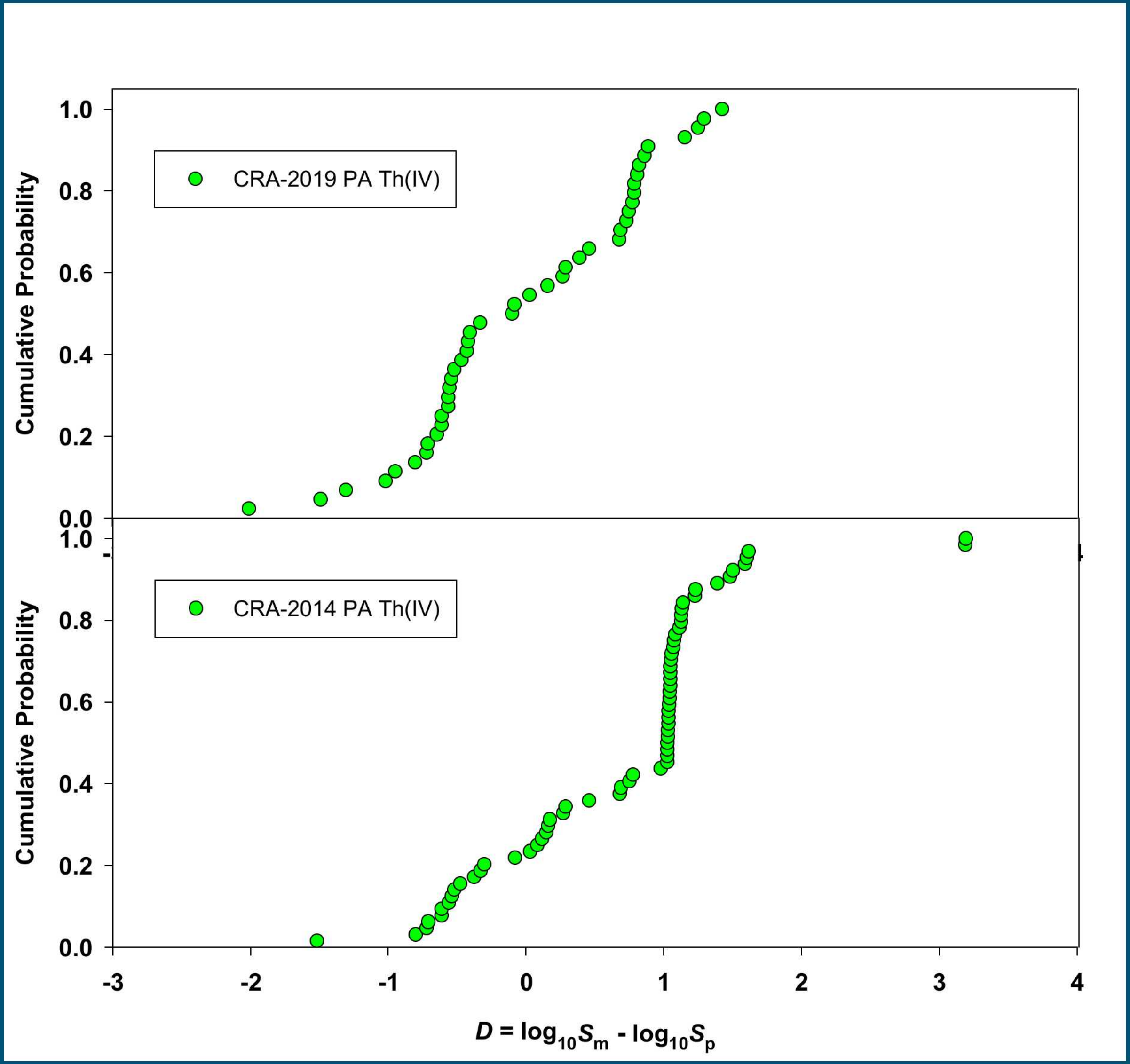
Th(IV) Solubility Model

- The EPA selected the following data sets for construction of An(IV) solubility uncertainty distribution (U.S. EPA, 2016):
  - Inclusion of 18 samples in 3 M NaCl, $8.0 \leq \mathrm{pcH} \leq 11.2$ from Felmy et al. (1991)
  - Inclusion of 5 ultracentrifuged samples in 5 M NaCl and 5 ultracentrifuged samples in 2.5 M $MgCl_2$ from Altmaier et al. (2004)
  - Inclusion of 12 samples in 4 M NaCl with 0.02 M TIC from Altmaier et al. (2006)
  - Inclusion of 4 samples in 5.26 M $CaCl_2$ with $\mathrm{pcH} < 10$ from Altmaier et al. (2008)
- Total of 44 experimental data points, the same data used for SEN4.

Th(IV) PDF for CRA-2019 PA and CRA-2014 PA



Th(IV) CDF for CRA-2019 PA and CRA-2014 PA



Th(IV) Statistics for CRA-2019 PA and CRA-2014 PA

Analysis	Mean	Median	Std Dev	Minimum	Maximum	n
CRA-2014	0.673	1.029	0.869	–1.52	3.19	64
CRA-2019	–0.011	–0.090	0.821	–2.01	1.43	44

Summary and Conclusions

- The CRA-2019 PA actinide uncertainty distribution for Am(III) is the same as the SEN4 distribution with the exception that SEN4 incorporated the Khalili et al., (1994) data which the CRA-2019 PA distribution does not.

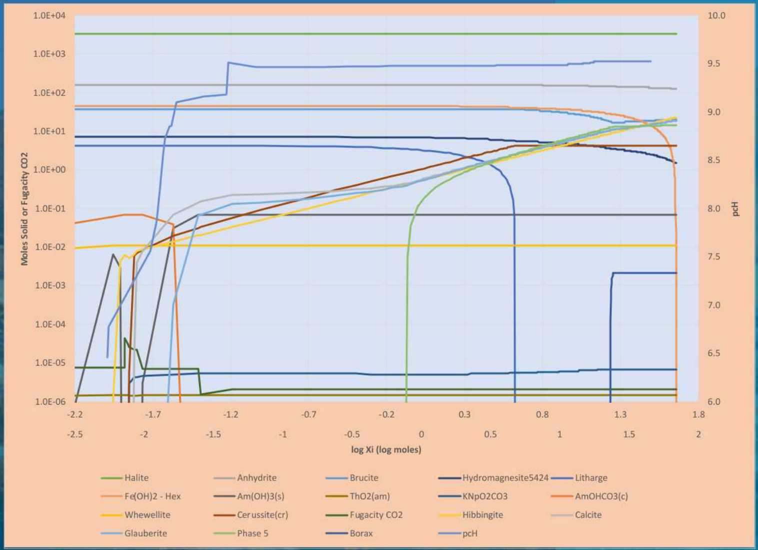
- The CRA-2019 PA actinide uncertainty distribution for Th(IV) is the same as the SEN4 distribution, both in terms of the experimental data and the D values.

- The new QA database, DATA0.FM4, had nominal impact on the uncertainty distributions because the parameters that changed in FM4 compared to FM1 were not used, or had minimal impact on the model results.

- The two deviations from EPA's requests were slight wording change in G7, which is a moot point for CRA-2019, and the number of data for Am(III) which was their error. Neither deviation impacts the CRA-2019 PA uncertainty analysis.

Possible Future of Actinide Uncertainty Analysis

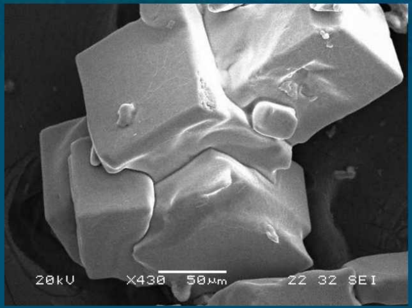
One possibility: Use the baseline solubility model and assign parameter distributions to key variables, such as key mineral phase and aqueous species log K values, that influence actinide solubility. Run N number of simulations each with a unique set of randomly sampled parameters and process the results to produce distributions of actinide solubility, and other key chemical parameters.



$Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O + 6H^+ \leftrightarrow 5Mg^{2+} + 4HCO_3^- + 6H_2O$

Baseline Solubility Model, and Supplemental Information for CRA-2019 PA

$Am(OH)_3(s) + 3H^+ \leftrightarrow Am^{3+} + 3H_2O$



Outline

- CRA-2019 PA Baseline Solubility Model will be presented.
- The supplemental information that provides a road map to the CRA-2019 PA Baseline Solubility Model.

Pertinent Documents

Domski, P.S. and C. Sisk-Scott. 2019. Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4. Carlsbad, NM: Sandia National Laboratories. (ERMS#571178).

Above document can be found in the WIPP records center

Domski, P.S. 2019. Technical Aspects of the Baseline Solubility Model for the CRA-2019 PA. Carlsbad, NM: Sandia National Laboratories. **In Review**

Actinide Baseline Solubility Model for CRA-2019 PA

- Updated organic budget for CRA-2019 (Sisk-Scott, 2019).
- Updated reactant's budget (halite, anhydrite, brucite, hydromagnesite, lead, and iron, based on the quantity of carbon from PAIR 2018 (Van Soest 2018), and scaled to 1 kg brine/water.
- Updated thermodynamic database, DATA0.FM4.
- Updated model to include lead and iron.
- Updated carbonate system assumption.

EQ3NR Inputs

Brine Compositions

- GWB and ERDA-6 (see Table 2, Domski & Sisk-Scott (2019) for comps) entered as molar concentrations.

Organic's Concentrations

- Citrate, Oxalate, EDTA, and Acetate all from Sisk-Scott (2019) and based on Van Soest (2018). Entered as molar concentrations (Table 3 Domski & Sisk-Scott (2019)).

Solubility Controlling Phases

- Am(III) – $Am(OH)_3(s)$
- Th(IV) – $ThO_2(am)$
- Np(V) – $KNpO_2CO_3$
- Phases entered as heterogeneous equilibrium phases

EQ6 Inputs

- Initial solution composition as calculated by EQ3NR in the form of the EQ3NR "pickup" file.
- Amounts (moles) of reactant phases scaled to the masses of carbon (cellulosic, plastic, and rubber) and the 1 kg mass of solvent water used in EQ6.
  - Reactant phases include: Halite, anhydrite, brucite, hydromagnesite5424, litharge, and $Fe(OH)_2$-Hex. See Table 4 of Domski & Sisk-Scott (2019) for amounts.

EQ6 Model

- EQ6 is a reaction path code, in other words it incrementally traces, and records, the evolution of the fluid chemistry and solid phases using a mass balance approach.
- EQ6 was run in “closed system” mode, all reactants and product phases remain in contact with the solution and may dissolve and precipitate as solution properties change. This state of dynamic equilibrium is maintained until all of the reactants are exhausted, or the system reaches equilibrium.
- Phase Suppression: EQ6, and all geochemical codes, allow phases to precipitate once they become saturated based on thermodynamics, i.e., their log K value at a specific temperature. Based on knowledge of kinetics, or other information, the analyst may chose to not allow a phase to precipitate, in EQ6 this is called “suppression”.

EQ6 Model (continued)

Historically calcite has been suppressed in the baseline solubility model.

For CRA-2019 PA calcite has been allowed to precipitate.

CRA-2019 PA GWB Baseline Solubility Outputs

	1 x Volume	2 x Volume	3 x Volume	4 x Volume	5 x Volume
B	0.224	0.231	0.233	0.234	0.235
Na	4.69	4.71	4.71	4.71	4.71
Mg	0.348	0.336	0.332	0.330	0.329
K	0.663	0.682	0.688	0.692	0.694
Ca	1.09E-02	1.07E-02	1.06E-02	1.06E-02	1.05E-02
Fe	2.61E-05	2.61E-05	2.60E-05	2.60E-05	2.60E-05
S	0.232	0.233	0.234	0.234	0.234
Cl	5.40	5.43	5.43	5.44	5.44
Br	3.78E-02	3.88E-02	3.92E-02	3.94E-02	3.95E-02
Pb	1.90E-02	1.90E-02	1.90E-02	1.91E-02	1.91E-02
Th	5.45E-08	5.45E-08	5.45E-08	5.45E-08	5.45E-08
Np	4.02E-07	2.83E-07	2.42E-07	2.21E-07	2.09E-07
Am	1.63E-07	1.58E-07	1.56E-07	1.55E-07	1.54E-07
$f\mathrm{CO}_2$	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
Ionic Strength	6.53	6.55	6.55	6.55	6.55
Pitzer pH	8.82	8.82	8.82	8.82	8.82
pcH	9.54	9.55	9.55	9.55	9.55
a(w)	0.732	0.732	0.732	0.732	0.732
TIC	2.50E-04	2.50E-04	2.50E-04	2.50E-04	2.50E-04

All concentrations in molar quantities

CRA-2019 PA ERDA-6 Baseline Solubility Outputs

	1 x Volume	2 x Volume	3 x Volume	4 x Volume	5 x Volume
B	0.281	0.282	0.282	0.282	0.283
Na	4.66	4.70	4.72	4.72	4.73
Mg	0.435	0.391	0.374	0.365	0.360
K	0.499	0.563	0.590	0.604	0.612
Ca	1.28E-02	1.19E-02	1.16E-02	1.14E-02	1.13E-02
Fe	2.67E-05	2.64E-05	2.64E-05	2.63E-05	2.63E-05
S	0.224	0.228	0.229	0.230	0.231
Cl	5.22	5.29	5.32	5.34	5.35
Br	5.66E-02	6.39E-02	6.69E-02	6.84E-02	6.94E-02
Pb	1.88E-02	1.90E-02	1.90E-02	1.90E-02	1.91E-02
Th	5.44E-08	5.44E-08	5.44E-08	5.44E-08	5.44E-08
Np	1.20E-06	7.27E-07	5.52E-07	4.61E-07	4.05E-07
Am	1.78E-07	1.63E-07	1.58E-07	1.54E-07	1.52E-07
fCO_2	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
Ionic Strength	6.48	6.52	6.53	6.54	6.55
Pitzer pH	8.82	8.82	8.82	8.82	8.82
pcH	9.52	9.53	9.53	9.54	9.54
a(w)	0.732	0.732	0.732	0.732	0.732
TIC	2.50E-04	2.50E-04	2.50E-04	2.50E-04	2.50E-04

All concentrations in molar quantities

Compare CRA-2014 with CRA-2019 1x volume case

	GWB, CRA-2014	GWB, CRA-2019	ERDA-6, CRA-2014	ERDA-6, CRA-2019
B	0.186	0.224	0.062	0.281
Na	4.77	4.69	5.30	4.66
Mg	0.330	0.348	0.136	0.435
K	0.550	0.663	0.096	0.499
Ca	1.11E-02	1.09E-02	1.16E-02	1.28E-02
Fe	-	2.61E-05	-	2.67E-05
S	0.216	0.232	0.182	0.224
Cl	5.36	5.40	5.24	5.22
Br	3.13E-02	3.78E-02	1.09E-02	5.66E-02
Pb	-	1.90E-02	-	1.88E-02
Th	6.05E-08	5.45E-08	7.02E-08	5.44E-08
Np	2.77E-07	4.02E-07	8.76E-07	1.20E-06
Am	2.59E-06	1.63E-07	1.48E-06	1.78E-07
fCO_2	3.14E-06	2.02E-06	3.14E-06	2.02E-06
Ionic Strength	6.44	6.53	5.98	6.48
Pitzer pH	8.82	8.82	8.99	8.82
pcH	9.54	9.54	9.69	9.52
a(w)	0.735	0.732	0.747	0.732
TIC	3.79E-04	2.50E-04	4.54E-04	2.50E-04

All concentrations in molar quantities

Discussion

What do the results show us?

- Very little change in the bulk solution chemistry compared to CRA-2014 PA. Why? Because the major element chemistry in FM4 is the same as in FM1.

What about the actinides?

- Am(III) decreased by approximately a factor of 16 due to changes in the log K values of $MgEDTA^{2-}$ and $CaEDTA^{2-}$ increasing their stability, and thus decreasing Am(III) solubility.
- Th(IV) decreased slightly in response to changes in the carbonate system equilibrium. The log K of hydromagnesite5424 was changed in FM4, and by allowing calcite to form the equilibrium is being determined the calcite – brucite – hydromagnesite system. Also reflected in the lower fCO_2 and TIC in the CRA-2019 data.
- Np(V) increased due to slight changes in the acetate availability.

Discussion (continued)

It’s very interesting how similar the equilibrium chemistry of GWB and ERDA-6 for CRA-2019 PA are to one another, why is this and what does it mean?

- The reason for the similar chemistry observed for different starting compositions, GWB and ERDA-6, is the very high rock to water ratio of the modeled system. Converting moles of the all of the reactants to kilograms we have about 235 kg of reactants (rock) to 1 kg of solution. At this very high rock to water ratio the equilibrium chemistry should be dominated by the rock as its composition is fixed, and the solution must come into equilibrium with the rock.
- What does this imply? It implies that the starting composition of the brines are of secondary importance, and perhaps moving to a single average starting brine composition is warranted.

Conclusions

Despite the changes between CRA-2014 PA and CRA-2019 PA actinide baseline solubility models the results are similar, both in terms of actinide solubilities and bulk chemistry.

Supplemental Information

The CRA-2019 actinide baseline solubility model is a major departure compared to the CRA-2014 model.

- Updated Pitzer-thermodynamic database, DATA0.FM4, (Domski, 2019) which includes various updates to solid and aqueous species log K values, and the addition of new solid phases and aqueous species.
- The addition of iron and lead chemical systems to DATA0.FM4, and the subsequent inclusion of lead and iron to the model are a significant change to the solubility model.
- The calcite assumption, i.e., allowing calcite to form in the baseline solubility model is a departure from the past.
- Carbonate phase, is calcite the proper phase to precipitate?

CRA-2019 Baseline Solubility Model

- The results of initial model runs, which included lead and iron with calcite suppressed, raised red flags such that to gain an understanding of how the changes to the model effected the model output the model had to be deconstructed.
- This was accomplished by setting up a matrix of runs of increasing complexity and carefully examining the model output to determine causes of significant change.

EQ3/6 Run Matrix

	Tests Database				Tests Reactants			Tests Calcite Assumption		Tests Carbonate Phase
Matrix Column	1	2	3	4	5	6	7	8	9	10
Organic/Reactant Budget	CRA-2014	CRA-2014	CRA-2019	CRA-2019	CRA-2019	CRA-2019	CRA-2019	CRA-2019	CRA-2019	CRA-2019
Database	DATA0.FM1	DATA0.FM4	DATA0.FM1	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.SSL
Reactants[1]	default	default	default	default	+lead	+iron	+lead & iron	default	+lead & iron	+lead & iron
Calcite	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	precipitate	precipitate	precipitate

1 - Default reactants are halite, anhydrite, brucite, and hydromagnesite

Note: Yellow shaded column 1 is the CRA-2014 PA case, and the light green shaded column 9 is the CRA-2019 PA case.

Database Comparison

- Starting Solutions: GWB and ERDA-6 1x Volume case
- Organics Budget: CRA-2014 PA and CRA-2019 PA
- Reactants: Default Suite (halite, anhydrite, brucite, & hydromagnesite)
- Database: DATA0.FM1 and DATA0.FM4
- Calcite: Suppressed

Database Results: GWB 1x Volume Case

Matrix Column	1	2	3	4
Organic Budget	CRA-2014 PA	CRA-2014 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM1	DATA0.FM4	DATA0.FM1	DATA0.FM4
Reactants	default	default	default	default
Calcite	suppressed	suppressed	suppressed	suppressed
File Name	gwb2014.6o	gw14fm4.6o	gw19fm1.6o	gw19fm4.6o
B	0.186	0.186	0.186	0.186
Na	4.77	4.77	4.76	4.76
Mg	0.330	0.330	0.334	0.333
K	0.550	0.550	0.550	0.550
Ca	0.0111	0.0111	0.0111	0.0111
Fe	-	-	-	-
S	0.216	0.217	0.216	0.216
Cl	5.36	5.36	5.36	5.36
Br	0.0313	0.0313	0.0313	0.0313
Pb	-	-	-	-
Th	6.05E-08	5.52E-08	6.05E-08	5.52E-08
Np	2.77E-07	3.86E-07	3.04E-07	4.27E-07
Am	2.59E-06	1.62E-07	2.74E-06	1.62E-07
fCO_2	3.14E-06	2.02E-06	3.14E-06	2.02E-06
IS(M)	6.44	6.44	6.43	6.44
Pitzer pH	8.82	8.82	8.82	8.82
pcH	9.54	9.54	9.54	9.54
Mass of solvent water (kg)	0.737	0.737	0.737	0.737
a(w)	0.735	0.735	0.735	0.735
TIC(M)	3.79E-04	2.44E-04	3.79E-04	2.44E-04

Database Results: ERDA-6 1x Volume Case

Matrix Column	1	2	3	4
Organic Budget	CRA-2014 PA	CRA-2014 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM1	DATA0.FM4	DATA0.FM1	DATA0.FM4
Reactants	default	default	default	default
Calcite	Suppressed	Suppressed	Suppressed	Suppressed
File Name	erda_2014.6o	er14fm4.6o	er19fm1.6o	er19fm4.6o
B	0.062	0.062	0.062	0.062
Na	5.30	5.31	5.30	5.30
Mg	0.136	0.132	0.134	0.134
K	0.096	0.096	0.096	0.096
Ca	0.0116	0.0118	0.0119	0.0119
Fe	-	-	-	-
S	0.182	0.180	0.179	0.179
Cl	5.24	5.24	5.23	5.23
Br	0.0109	0.0109	0.0109	0.0109
Pb	-	-	-	-
Th	7.02E-08	6.24E-08	7.06E-08	6.24E-08
Np	8.76E-07	1.18E-06	9.72E-07	1.28E-06
Am	1.48E-06	9.53E-08	1.76E-06	9.54E-08
fCO_2	3.14E-06	2.02E-06	3.14E-06	2.02E-06
IS(M)	5.98	5.97	5.97	5.97
Pitzer pH	8.99	9.00	9.00	9.00
pcH	9.69	9.70	9.70	9.70
Mass of solvent water (kg)	0.888	0.888	0.888	0.888
a(w)	0.747	0.747	0.747	0.747
TIC(M)	4.54E-04	2.96E-04	4.59E-04	2.96E-04

Effect of the Database: FM1 Versus FM4

- Comparison of the model results confirm that the major ion chemistry and chemical properties are nearly identical regardless of which database was used for the calculation.
- The biggest difference are the Am(III) concentrations which are ~ 16x less calculated using FM4 compared to FM1. The source of this decrease was a change in the log K values of $MgETDA^{2-}$ and $CaEDTA^{2-}$ in DATA0.FM4. The stability of both of these aqueous species was increased in FM4 which resulted in more EDTA complexing with Mg^{2+} and Ca^{2+} and less with Am(III) which decreases its solubility (Domski & Sisk-Scott, 2019).

Lead and Iron Comparison

- Starting Solutions: GWB and ERDA-6 1x Volume case
- Organics Budget: CRA-2019 PA
- Reactants: Default Suite (halite, anhydrite, brucite, & hydromagnesite) with the addition of lead and iron, singly and together.
- Database: DATA0.FM4
- Calcite: Suppressed

Effect of Lead and Iron: GWB 1x Volume Case

Matrix Column	4	5	6	7
Organic Budget	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4
Reactants	default	+lead	+iron	+lead & iron
Calcite	suppressed	suppressed	suppressed	suppressed
File Name	gw19fm4.6o	gw19fm4p.6o	gw19fm4f.6o	gwb2019.6o
B	0.186	0.185	0.111	0.111
Na	4.76	4.75	5.38	5.38
Mg	0.333	0.335	0.013	0.013
K	0.550	0.547	0.329	0.329
Ca	0.0111	0.0112	0.0188	0.0188
Fe	-	-	9.08E-06	9.08E-06
S	0.216	0.215	0.142	0.142
Cl	5.36	5.39	5.34	5.34
Br	0.0313	0.0312	0.0188	0.0188
Pb	-	1.83E-02	-	4.14E-04
Th	5.52E-08	5.50E-08	9.81E-08	9.81E-08
Np	4.27E-07	4.27E-07	1.54E-07	1.54E-07
Am	1.62E-07	1.60E-07	3.05E-08	3.05E-08
fCO_2	2.02E-06	2.02E-06	2.02E-06	2.02E-06
IS(M)	6.44	6.43	5.92	5.92
Pitzer pH	8.82	8.82	9.54	9.54
pcH	9.54	9.54	10.26	10.26
Mass of solvent water (kg)	0.737	0.740	1.24	1.24
a(w)	0.735	0.735	0.745	0.745
TIC(M)	2.44E-04	2.49E-04	1.07E-03	1.08E-03

Effect of Lead and Iron: ERDA-6 1x Volume Case

Matrix Column	4	5	6	7
Organic Budget	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4
Reactants	default	lead	iron	lead & iron
Calcite	Suppressed	Suppressed	Suppressed	Suppressed
File Name	er19fm4.6o	er19fm4p.6o	er19fm4f.6o	erda2019.6o
B	0.062	0.062	0.043	0.043
Na	5.30	5.31	5.49	5.49
Mg	0.134	0.129	0.011	0.011
K	0.096	0.096	0.066	0.066
Ca	0.0119	0.0120	0.0162	0.0163
Fe	-	-	9.11E-06	9.11E-06
S	0.179	0.179	0.132	0.132
Cl	5.23	5.24	5.27	5.27
Br	0.0109	0.0109	0.0075	0.0075
Pb	-	5.27E-03	-	4.05E-04
Th	6.24E-08	6.26E-08	9.90E-08	9.90E-08
Np	1.28E-06	1.25E-06	7.72E-07	7.72E-07
Am	9.54E-08	9.28E-08	2.94E-08	2.94E-08
fCO2	2.02E-06	2.02E-06	2.02E-06	2.02E-06
IS(M)	5.97	5.96	5.76	5.76
Pitzer pH	9.00	9.01	9.54	9.54
pcH	9.70	9.71	10.24	10.24
Mass of solvent water (kg)	0.888	0.888	1.29	1.29
a(w)	0.747	0.747	0.750	0.750
TIC(M)	2.96E-04	2.99E-04	1.09E-03	1.09E-03

Lead and Iron Discussion

- Lead has virtually no impact on the solution chemistry. Litharge (PbO) dissolves until cerussite ($PbCO_3$) saturates at which point it precipitates in a 1:1 ratio until the litharge is exhausted.
- The primary effects of iron dissolution ($Fe(OH)_2$ dissolution) are the increase in pH, TIC, and mass of solvent water, which can be explained in terms of the mineral reactions. The secondary effects include the decrease in conservative ion (B and Br) concentrations by dilution, decrease in Am(III) concentration because of increased pH, and the increase in Th(IV) via hydroxide and carbonate complexation.

Lead and Iron Discussion (continued)

The cause of the increase in pH, TIC, and mass of water can be traced to two mineral dissolution reactions. The first reaction is the dissolution of hydromagnesite(5424) which on a per mole dissolution basis acts to remove six moles of hydrogen ion, adds four moles of bicarbonate, and adds six moles of water to solution, via:

$$Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O + 6H^+ \leftrightarrow 5Mg^{2+} + 4HCO_3^- + 6H_2O$$

The dissolution of ferrous hydroxide ($Fe(OH)_2$-Hex) removes two moles of hydrogen ion, and contributes two moles of water per mole of dissolved ferrous hydroxide, via:

$$Fe(OH)_2(s) + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$$

Together these two reactions account for the increase in pH, TIC, and solvent water mass, and the decrease in Am(III) solubility and increase in Th(IV) solubility.

Calcite Assumption

- Calcite has not been incorporated in the baseline solubility calculations since CRA-2004 PA non-microbial vectors when the brucite – calcite carbonation reaction was used to buffer fCO_2. Since that time calcite has not been allowed to form and the brucite – hydromagnesite5424 buffer has been the preferred reaction.

- Brush et al., (2006) argued that some carbonate phase either aragonite, a calcite polymorph of slightly lower solubility, or a magnesian calcite would likely form in the WIPP repository environment, rather than pure calcite. However, Xiong and Lord (2006) observed calcite precipitation in XRD patterns of their study of carbonation products of MgO in GWB and ERDA-6.

- The suppression of calcite is a legacy assumption that has been carried forward without reevaluation until now, the CRA-2019 PA baseline solubility analysis.

Calcite Assumption (continued)

- Why now? Why suddenly change a model assumption that has been in place since 2004?
  - Because of red flags:
    1. With the addition of the iron reactant the pH and total inorganic carbon (TIC) increased beyond what has been previously observed in these calculations.
    2. The pH and TIC increase resulted in the saturation state of calcite to be 50x supersaturated.

- Does it make sense to allow calcite to form?
  - There was a gross disequilibrium in the carbonate system and some carbonate phase would surely form in a natural environment.
  - Is calcite the correct phase, or should some other carbonate form?
    - Maybe yes, maybe no, but calcite is the simplest choice available in DATA0.FM4, and Occam’s razor would chose calcite over other alternatives available in DATA0.FM4.

Calcite Assumption

- Starting Solutions: GWB and ERDA-6 1x Volume case
- Organics Budget: CRA-2019 PA
- Reactants: 1)Default suite; and 2) the default suite with lead and iron.
- Database: DATA0.FM4
- Calcite: Suppressed and not suppressed.

Results Calcite Assumption: GWB 1x Volume

Matrix Column	4	8	7	9
Organic Budget	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4
Calcite	suppressed	Not suppressed	suppressed	Not suppressed
Lead/Iron[A]	default	default	+lead & iron	+lead & iron
File Name	gw19fm4.6o	gw19f4c.6o	gwb2019.6o	gwb_1x.6o
B	0.186	0.229	0.111	0.224
Na	4.76	4.69	5.38	4.69
Mg	0.333	0.347	0.013	0.348
K	0.550	0.677	0.329	0.663
Ca	0.0111	0.0109	0.0188	0.0109
Fe	-	-	9.08E-06	2.61E-05
S	0.216	0.232	0.142	0.232
Cl	5.36	5.37	5.34	5.40
Br	0.0313	0.0386	0.0188	0.0378
Pb	-	-	4.14E-04	1.90E-02
Th	5.52E-08	5.46E-08	9.81E-08	5.45E-08
Np	4.27E-07	4.00E-07	1.54E-07	4.02E-07
Am	1.62E-07	1.65E-07	3.05E-08	1.63E-07
fCO_2	2.02E-06	2.02E-06	2.02E-06	2.02E-06
IS(M)	6.44	6.54	5.92	6.53
Pitzer pH	8.82	8.82	9.54	8.82
pcH	9.54	9.54	10.26	9.54
Mass of solvent water (kg)	0.737	0.597	1.24	0.61
a(w)	0.735	0.732	0.745	0.732
TIC(M)	2.44E-04	2.43E-04	1.08E-03	2.50E-04

Results Calcite Assumption: ERDA-6 1x Volume

Matrix Column	4	8	7	9
Organic Budget	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA	CRA-2019 PA
Database	DATA0.FM4	DATA0.FM4	DATA0.FM4	DATA0.FM4
Calcite	suppressed	Not suppressed	suppressed	Not suppressed
Lead/Iron^A	Not included	Not included	+lead & iron	+lead & iron
File Name	er19fm4.6o	er19f4c.6o	erda2019.6o	erda_1x.6o
B	0.062	0.281	0.043	0.281
Na	5.30	4.66	5.49	4.66
Mg	0.134	0.435	0.011	0.435
K	0.096	0.512	0.066	0.499
Ca	0.0119	0.0127	0.0163	0.0128
Fe	-	-	9.11E-06	2.67E-05
S	0.179	0.224	0.132	0.224
Cl	5.23	5.18	5.27	5.22
Br	0.0109	0.0581	0.0075	0.0566
Pb	-	-	4.05E-04	1.88E-02
Th	6.24E-08	5.45E-08	9.90E-08	5.44E-08
Np	1.28E-06	1.20E-06	7.72E-07	1.20E-06
Am	9.54E-08	1.81E-07	2.94E-08	1.78E-07
fCO_2	2.02E-06	2.02E-06	2.02E-06	2.02E-06
IS(M)	5.97	6.48	5.76	6.48
Pitzer pH	9.00	8.82	9.54	8.82
pcH	9.70	9.52	10.24	9.52
Mass of solvent water (kg)	0.888	0.164	1.29	0.168
a(w)	0.747	0.732	0.750	0.732
TIC(M)	2.96E-04	2.44E-04	1.09E-03	2.50E-04

Discussion

- What do the results show, and what does it mean?
  - First of all, for the runs without lead and iron, i.e., runs similar to CRA-2014 and before, allowing calcite to form had a negligible impact on the bulk fluid chemistry and the actinide solubility. Why is this important? It is important because it demonstrates that the model is robust and that calcite precipitation would not have changed previous PA's had it been allowed. In other words it implicitly provides justification for allowing calcite to precipitate in the current PA without negatively reflecting on the assumptions of past PA's.
  - For the runs that include lead and iron, by allowing calcite to precipitate the pH, TIC, and calcite saturation return to expected values, and the carbonate system is in equilibrium. Why is this important? Because suppressing calcite formation results in unrealistic fluid compositions that are indefensible.

Discussion (continued)

Are there any negative impacts by allowing calcite to precipitate?

- The solvent mass of water is decreased via the precipitation of hydrated phases, with Phase 5 consuming the most water:

$$3Mg^{2+} + Cl^{-} + 9H_2O \leftrightarrow Mg_3Cl(OH)_5 \bullet 4H_2O + 5H^{+}$$

Is this realistic?

- Maybe, but maybe not. Brush et al. (2006) stated that some form of Ca – Mg carbonate phase would be the most stable phase in the WIPP environment, in which case Phase 5 precipitation would likely be mitigated.

Carbonate Phase Identity

- To test how carbonate phase identity effected the model output DATA0.FM4 was copied to DATA0.SSL, a non-QA database, and a solid solution phase added. For this example the phase calcite/hydromagnesite5424 (cal-hydromag) was added, the log K for this phase is calculated internally by EQ6 using the endmember log K values already included in DATA0.FM4. This solid phase can be thought of as a hybrid of the two pure end members described in the EQ6 outputs in terms of mole fractions of the endmembers.
- In the EQ6 runs for GWB and ERDA-6 the solid solution phase Cal-Hydromag was the preferred carbonate phase to form rather than calcite, and confirmed Brush et al.'s (2006) hypothesis that a high magnesian calcite phase would be favored in these conditions.

Carbonate Phase

	GWB		ERDA-6	
Database	DATA0.FM4	DATA0.SSL	DATA0.FM4	DATA0.SSL
Carbonate Phase	Calcite	Calcite-Hydromag	Calcite	Calcite-Hydromag
B	0.224	0.130	0.281	5.05E-02
Na	4.69	4.85	4.66	5.03
Mg	0.348	0.320	0.435	0.294
K	0.663	0.383	0.499	0.078
Ca	1.09E-02	1.05E-02	1.28E-02	1.00E-02
Fe	2.61E-05	2.50E-05	2.67E-05	2.43E-05
S	0.232	0.216	0.224	0.198
Cl	5.40	5.36	5.22	5.28
Br	3.78 E-03	2.18 E-03	5.66 E-03	8.81E-03
Pb	1.90E-02	2.47E-02	1.88E-02	2.31E-02
Th	5.45E-08	5.28E-08	5.44E-08	5.39E-08
Np	4.02E-07	6.70E-07	1.20E-06	3.20E-06
Am	1.63E-07	1.51E-07	1.78E-07	1.41E-07
fCO_2	2.02E-06	1.43E-06	2.02E-06	1.38E-06
Ionic Strength	6.53	6.34	6.48	6.15
pH^A	8.82	8.82	8.82	8.82
pcH	9.54	9.53	9.52	9.51
Mass of solvent water (kg)	0.610	1.06	0.168	1.095
a(w)	0.732	0.738	0.732	0.745
Total Inorganic Carbon	2.50E-04	1.79E-04	2.50E-04	1.75E-04

Discussion

What do the results show?

- The results show that regardless of what carbonate phase is allowed to form, either pure calcite, or a Ca-Mg carbonate phase the bulk chemistry and actinide solubility is virtually the same for both.
- The results show that when a Ca – Mg carbonate is allowed to precipitate in place of pure calcite, the water consumption via Phase 5 precipitation was averted as Phase 5 never reaches saturation, and the mass of solvent increases via ferrous hydroxide dissolution.

What does it mean?

- It means that the model is robust, and regardless of which carbonate phase forms the chemistry and actinide solubilities are virtually constant.

Conclusions

- The baseline solubility model was extensively exercised to gain an understanding of how changes to the model since CRA-2014 PA affected the model results.
- The results showed
  - The database had negligible impact on the bulk chemistry and a moderate effect on actinide solubility, most notable a decrease in Am(III) by ~16x.
  - Inclusion of a lead reactant, PbO, had no effect on either bulk chemistry or actinide solubilities.
  - The iron reactant, $Fe(OH)_2$, had a strong impact on the bulk chemistry creating diseqilibrium in the carbonate system, with strong impacts on actinide solubility.
  - Allowing calcite to precipitate mitigated the effects of iron dissolution and eliminated the carbonate system disequilibrium.
  - A mixed phase Ca – Mg carbonate maybe more realistic phase than calcite for future PA’s.
- Overall the baseline solubility model for CRA-2019 PA is robust and defensible.

References

Baes, C. F.; Mesmer, R. E. 1976. The Hydrolysis of Cations. WileyInterscience: New York.

Brush, L.H., Y.-L. Xiong, J.W. Garner, A. Ismail, G.T Roselle, 2006. "Consumption of Carbon Dioxide by Precipitation of Carbonate Minerals Resulting from Dissolution of Sulfate Minerals in the Salado Formation In Response to Microbial Sulfate Reduction in the WIPP." Analysis report. Carlsbad, NM: Sandia National Laboratories. ERMS 544785.

Domski, P.S. 2019. "An Update to the EQ3/6 Pitzer Thermodynamic Database DATA0.FM1 with the Creation of DATA0.FM4". Carlsbad, NM: Sandia National Laboratories. (ERMS#571052).

Domski, P.S. 2019. "Official Release of the Qualified Pitzer Thermodynamic Database, DATA0.FM4, for EQ3/6 under AP-183, Revision 1. Carlsbad, NM: Sandia National Laboratories. (ERMS#571051).

Domski, P.S. 2018. Memo on the estimation of the solubility product (Log Ksp) for Ca2EDTA.7H2O, and Pitzer rameters for the Na+ / CaEDTA2- ir. Carlsbad, NM: Sandia National Laboratories. (ERMS#570202).

Felmy, A. R., and J. H. Weare. 1986. The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California. *Geochimica et Cosmochimica Acta* 50: 2771-2783.

Felmy, A. R., Mason, M. J. 2003. An Aqueous Thermodynamic Model for the Complexation of Sodium and Strontium with Organic Chelates Valid to High Ionic Strength. I. Ethylenedinitrilotetraacetic Acid (EDTA) Journal of Solution Chemistry, Vol. 32, No. 4, April 2003.

Giambalvo, E. R. 2002a. Memorandum to L.H. Brush (Subject: Recommended Parameter Values for Modeling An(III) Solubility in WIPP Brines). 25 July 2002. ERMS 522982. Carlsbad, NM: Sandia National Laboratories.

Giambalvo, E. R. 2002b. Memorandum to L.H. Brush (Subject: Recommended Parameter Values for Modeling An(IV) Solubility in WIPP Brines). 26 July 2002. ERMS 522986. Carlsbad, NM: Sandia National Laboratories.

References (continued)

Giambalvo, E. R. 2002c. Memorandum to L.H. Brush (Subject: Recommended Parameter Values for Modeling An(V) Solubility in WIPP Brines). 26 July 2002. ERMS 522990. Carlsbad, NM: Sandia National Laboratories.

Giambalvo, E. R. 2002d. Recommended μ°/RT Values for Modeling the Solubility of Oxalate Solids in WIPP Brines, Giambalvo to Brush, 31July02, ERMS 523057.

Giambalvo, E. R. 2002e. Release of FMT Database FMT_021120.CHEMDAT, Giambalvo memo to Brush 20November02, ERMS 526372.

Giambalvo, E. R. 2002f. Recommended Parameter Values for Modeling Organic Ligands in WIPP Brines. Carlsbad, NM: Sandia National Laboratories. ERMS 522981.

Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O System to High Ionic Strengths at 25 □ C," Geochimica et Cosmochimica Acta. Vol. 48, no. 4, 723 751.

Hummel, W., Anderegg, G., Puigdomenech, I., Rao, L., Tochiyama, O. (2005). Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Zr, Ni and Se with Selected Organic Ligands. Chemical Thermodynamics, Volume 9, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, Elsevier B.B. Amsterdam, The Netherlands, p. 1088.

Jang, J-H. and S. Kim. 2016. "Derivation of Pitzer Interaction rameters and Thermodynamic Properties for the Aqueous Species of Ferrous Iron and Their, Revision 2". Carlsbad, NM: Sandia National Laboratories. (ERMS# 567283).

Jang, J-H. 2019. "Analysis Plan for Derivation and Addition of Equilibrium Constants and Pitzer Interaction rameters to the WIPP Geochemical Thermodynamic Database". AP-182 (2019). Carlsbad, NM: Sandia National Laboratories. (ERMS# 571074).

References (continued)

Khalili, F.I., V. Symeopoulos, J.-F. Chen, and G.R. Choppin. 1994. "Solubility of Nd in Brine," Radiochimica Acta. Vol. 66/67, 51-54.

Kim, S., C. Marrs, M. Nemer, and J-H. Jang 2017. "Solubility Model for Ferrous Iron Hydroxide, Hibbingite, Siderite, and Chukanovite in High Saline Solutions of Sodium Chloride, Sodium Sulfate, and Sodium Carbonate. Carlsbad, NM: Sandia National Laboratories. (ERMS# 569090).

Lemire, R. J.; Berner, U.; Musikas, C.; Palmer, D. A.; Taylor, P.; Tochiyama, O. Chemical Thermodynamics of Iron, Part 1. In Organisation for Economic Co-operation and Development; Perrone, J., Ed.; Nuclear Energy Agency, 2013; Vol. 13a, Chemical Thermodynamics.

Moog, H. C., Hagemann, S., and Rumyantsev, A. V., 2004. Isopiestic investigation of the systems FeCl2-(Na, K, Mg, Ca)Cln-H2O at 298.15 K. ZEITSCHRIFT FUR PHYSIKALISCHE CHEMIE-INTERNATIONAL JOURNAL OF RESEARCH IN PHYSICAL CHEMISTRY & CHEMICAL PHYSICS 218, 1063-1087.

Peake, T. 2018. Letter to Mike Brown "2018-12-17 E Letter to CBFO WIPP Issues Summary". U.S. Environmental Protection Agency, Center for Waste Management and Regulations. December 17, 2018.

Powell, K.J., Brown. P.L., Byrne, R.H., Gajda, T., Hefter. G., Luez, A.-K., Sjoberg, S., and Wanner, H., 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: the Pb2+ + OH-, Cl-, CO32-, SO42-, and PO43- systems (IUPAC Technical Report). Pure and Applied Chemistry 81 (12), 2425-2476.

Rao, L., D. Rai, A.R. Felmy, and C.F. Novak. 1999. Solubility of NaNd(CO3)2·6H2O(c) in Mixed Electrolyte (Na-Cl-CO3-HCO3) and Synthetic Brine Solutions, Actinide Speciation in High Ionic Strength Media: Experimental and Modeling Approaches to Predicting Actinide Speciation and Migration in the Subsurface. Proceedings of an American Chemical Society Symposium on Experimental and Modeling Studies of Actinide Speciation in Non-Ideal Systems, Held August 26-28, 1996, in Orlando, Florida. Eds. D.T. Reed, S.B. Clark, and L. Rao. New York, NY: Kluwer Academic/Plenum Publishers. 153 169.

References (continued)

Robie, R. A., and B. S. Hemingway. 1973. The enthalpies of formation of nesquehonite, $MgCO_3 \cdot 3H_2O$, and hydromagnesite, $5MgO \cdot 4CO_2 \cdot 5H_2O$. *Journal of Research of the U. S. Geological Survey*, 1: 543-547.

Runde, W., and J. I. Kim. 1995. Untersuchungen der Übertragbarkeit von Labordaten natürliche Verhältnisse. Chemisches Verhalten von drei- und fünfwertigem Americium in salinen NaCl-Lösungen. (Study of the Extrapolability of Laboratory data to Natural Conditions: Chemical behavior o Trivalent and Pentavalent Americium in Saline NaCl Solutions). RCM-01094, Munich: frg: Institut für Radiochemie, Technische Universität München. ERMS 241862.

Sisk-Scott, C. 2019 "Analysis Plan to Update the WIPP Geochemical Thermodynamic Database (DATA0.FM1) to Data0.FM4 for CRA-2019". AP-183, Revision 1. Carlsbad, NM: Sandia National Laboratories. (ERMS#571001).

U.S. EPA. 2016. "Reference and Data Selection for the CRA-2014 PABC Actinide Solubility Uncertainty Distributions", an attachment with an e-mail from EPA to DOE on September 30, 2016. Carlsbad, NM: Sandia National Laboratories. ERMS 567126.

Van Soest, G.D. 2018. Performance Assessment Inventory Report – 2018, INV-PA-18, Rev. 0. LA-UR-18-31882. Carlsbad, NM: Los Alamos National Laboratory – Carlsbad Operations.

Xiong, Y.-L. 2004. A Correction of the Molecular Weight of Oxalate in FMT_021120.CHEMDAT, and Incorporation of Calcium Oxalate Monohydrate (Whewellite) into CHEMDAT with Its Recommended Dimensionless Standard Chemical Potential Value, Xiong to Brush, 8 June 2004, ERMS 535813.

Xiong, Y.-L., and P.S. Domski, 2015. "Uncertainty Analysis of Actinide Solubilities in Response to EPA Completeness Comments 3-C-4 and 3-C-5 for CRA 2014". Carlsbad, NM: Sandia National Laboratories. ERMS: 565125.