SAND2022-14863C

Sandia National Laboratories

EPA Technical Exchange: Thermodynamic Database Issue Resolution

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10/25/2022

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Outline

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  - Am(III) Model (Issue #11)
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  - Calcite Saturation (Issue #6)
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- EPA low Priority Issues (25, 28, 30-33, 35, 36, 50)

Database Parameters

EDTA Parameters (Issue #5)

EPA Expectation:

Revise the database and demonstrate that available experimental data can be adequately modeled.

DOE Path Forward:

- DATA0.FM6 is based on DATA0.FM1

Database Parameters

EDTA Parameters (Issue #5) (continued)

Reactions	log K	Source
$H_4EDTA(aq) = 4H^+ + EDTA^{-4}$,	-23.03	Choppin et al. (2001)
$H_3EDTA^- = 3H^+ + EDTA^{-4}$	-20.53	Choppin et al. (2001)
$H_2EDTA^{-2} = 2H^+ + EDTA^{-4}$	-17.45	Choppin et al. (2001)
$HEDTA^{-3} = H^+ + EDTA^{-4}$	-10.57	Choppin et al. (2001)
$CaEDTA^{-2} = Ca^{+2} + EDTA^{-4}$	-10.12	Analogue to MgEDTA in Giambalvo (2002, Org.)
$AmEDTA^- = Am^{+3} + EDTA^{-4}$	-18.97	Giambalvo (2002, Org.)
$ThEDTA(aq) = Th^{+4} + EDTA^{-4}$	-23.55	Giambalvo (2002, Org) + Giambalvo (2002, An(IV)) + Choppin et al. (2001)
$NpO_2EDTA^{-3} = NpO_2^+ + EDTA^{-4}$	-8.53	Giambalvo (2002, Org)
$NpO_2HEDTA^{-2} = NpO_2^+ + H^+ + EDTA^{-4}$	-15.54	Giambalvo (2002, Org)
$NpO_2H_2EDTA^- = NpO_2^+ + 2H^+ + EDTA^{-4}$	-20.86	Giambalvo (2002, Org)

Database Parameters

EDTA Parameters (Issue #5) (continued)

For CRA-2024 the following changes will be implemented:

- $CaEDTA^{2-}$ and $MgEDTA^{2-}$ log β values will be restored to the values in DATA0.FM1
- The binary Pitzer parameters $Na^{+}/CaEDTA^{2-}$ will be restored to the values in DATA0.FM1
- $NaEDTA^{3-}$ will not be included in the database
- $MgHEDTA^{1-}$ and $CaHEDTA^{1-}$ will not be included in CRA-2024
- The binary Pitzer parameters associated with $Mg^{2+}/CaEDTA^{2-}$, $Mg^{2+}/MgEDTA^{2-}$, and ~~$Ca^{2+}/EDTA^{4-}$ will not be included in CRA-2024~~

EPA Database Issues

Pb-Inorganic Model (Issue #8)

EPA Expectation:

Remove lead data from database and omit them from solubility calculations until a complete Pitzer model and evaluation is performed.

DOE Path Forward:

The CRA-2019 non-Pitzer lead model will be replaced with a validated Pitzer based model for the Pb-Cl-CO_3-SO_4-H_2O system.

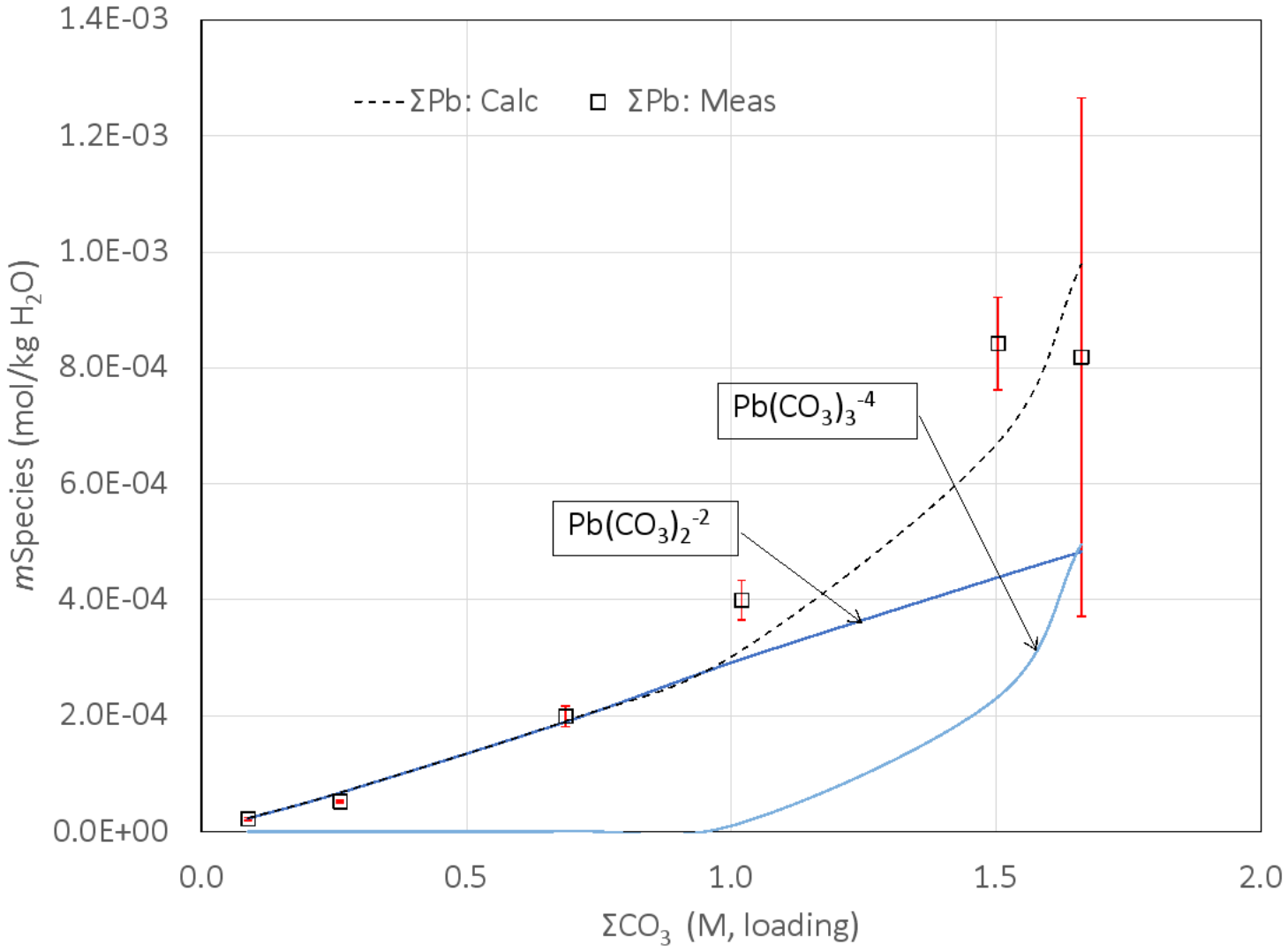
EPA Database Issues: Pb-Inorganic Model (Issue #8)

Reaction	Log K (I = 0)	Reference
Aqueous reactions		
$PbCl^+ = Pb^{2+} + Cl^-$	-1.48	GEOC-21-11 (Jang et al., 2021)
$PbCl_2(aq) = Pb^{2+} + 2Cl^-$	-2.03	GEOC-21-11 (Jang et al., 2021)
$PbCl_3^- = Pb^{2+} + 3Cl^-$	-1.86	GEOC-21-11 (Jang et al., 2021)
$PbHCO_3^+ = Pb^{+2} + HCO_3^-$	-1.86	GEOC-22-01 (Jang et al., 2022, in prep)
$PbCO_3(aq) + H^+ = Pb^{+2} + HCO_3^-$	3.88	GEOC-22-01 (Jang et al., 2022, in prep)
$Pb(CO_3)_2^{-2} + 2H^+ = Pb^{+2} + 2HCO_3^-$	10.53	GEOC-22-01 (Jang et al., 2022, in prep)
$Pb(CO_3)OH^- + 2H^+ = Pb^{+2} + HCO_3^- + H_2O$	13.42	GEOC-22-01 (Jang et al., 2022, in prep)
$Pb(CO_3)_3^{-4} + 3H^+ = Pb^{+2} + 3HCO_3^-$	27.19	GEOC-22-01 (Jang et al., 2022, in prep)
Dissolution		
$PbCl_2(s)$ (Cotunnite) $= Pb^{2+} + 2Cl^-$	-4.83	GEOC-21-11
$PbCO_3(s)$ (Cerussite) $+ H^+ = Pb^{+2} + HCO_3^-$	-2.85	GEOC-22-01 (Jang et al., 2022, in prep)
$NaPb_2(CO_3)_2(OH)(s)$ (Abellaite) $+ 3H^+ = Na^+ + 2Pb^{+2} + 2HCO_3^- + H_2O$	2.59	GEOC-22-01 (Jang et al., 2022, in prep)
$2PbCO_3.Pb(OH)_2(s)$ (Hydrocerussite) $+ 4H^+ = 3Pb^{+2} + 2HCO_3^- + 2H_2O$	2.41	GEOC-22-01 (Jang et al., 2022, in prep)
$PbSO_4(s)$ (Anglesite) $= Pb^{+2} + SO_4^{-2}$	-7.77	GEOC-22-01 (Jang et al., 2022, in prep)

i	j	α_1/α_2	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C\phi$	Source
H^+	$PbCl_3^-$	2.0/12.0	0.1077	0.0425	0.00	-0.0035	GEOC-21-11 (Jang et al., 2021)
Na^+	$PbCl_3^-$	2.0/12.0	-0.10025	0.0	0.0	0.0	GEOC-21-11 (Jang et al., 2021)
Mg^{+2}	$PbCl_3^-$	2.0/12.0	0.23015	0.0	0.0	0.0	GEOC-21-11 (Jang et al., 2021)
i	j		θ				
Pb^{+2}	H^+		0.348				GEOC-22-01 (Jang et al., 2022, in prep)

EPA Database Issues: Pb-Inorganic Model (Issue #8)

Pb-CO_3 Model Validation



Database Parameters

Am(III) Model (Issue #11)

EPA Expectation:

Evaluate possible internal inconsistencies in the WIPP Am(III) model.

DOE Path Forward :

- The An(III)-Cl model from Oakes et al., (2021) was evaluated.
- Am(III) model comparison.

Database Parameters

Am(III) Model (Issue #11)

- Part 1: Issues with the $AmCl^{+2}$ and $AmCl_2^{+}$ log K values and Pitzer parameters with respect to the parameters of Konnecke et al., (1997)

- Part 2: Comparison of the Am(III) model in the WIPP thermodynamic database with the model in Neck et al., (2009)

Database Parameters: Am(III) Model (Issue #11, Part 1)

Konnecke

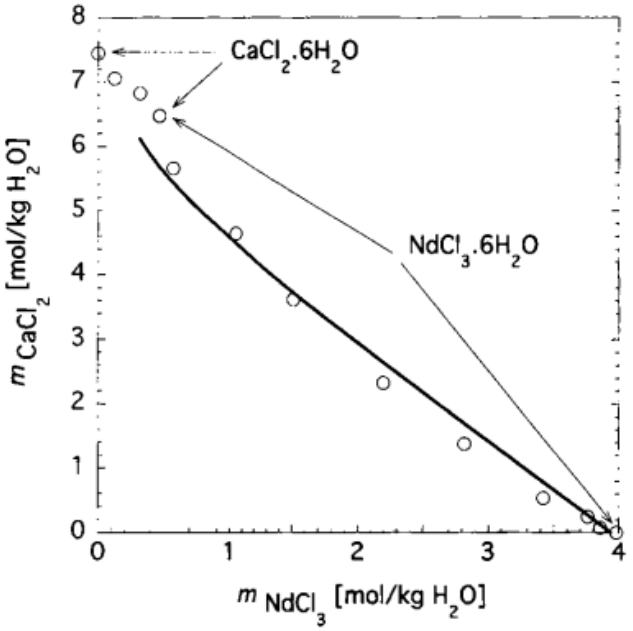


Fig. 3. Experimental and calculated solubilities in the system $CaCl_2-NdCl_3-H_2O$. ○: Shevtsova *et al.* [12], ——: calculated in this work.

Oakes (using Konnecke parameters)

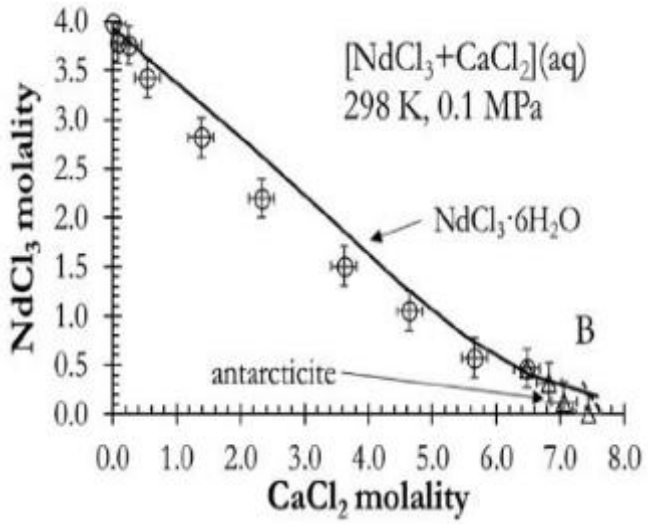
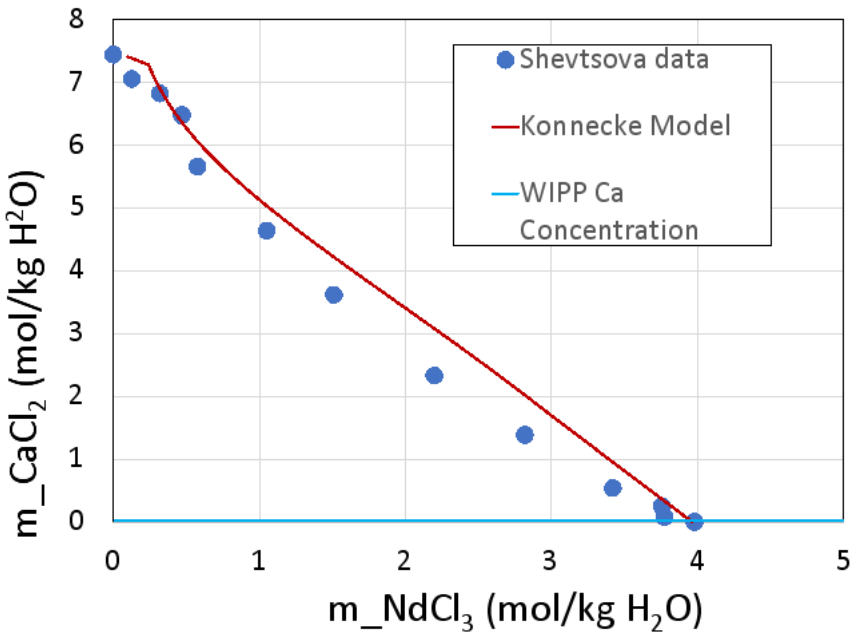


Fig. 9. Comparisons of measured $NdCl_3 \cdot 6H_2O$ and antarcticite solubilities from Shvetsova et al. (1958) to the Könnecke et al. (1997) model that includes their $\theta_{Ca,NdCl}$ and $\theta_{Ca,NdCl_2}$ parameters. This graph should, but does not, replicate Fig. 3 in Könnecke et al. (1997). Könnecke et al. (1997) did not attempt to reproduce antarcticite solubility; that curve is created using the HMW value for $\mu^{\circ}_{CaCl_2 \cdot 6H_2O}/RT$. Short sections of the metastable extensions are shown beyond each 2-solid coexistent point.

SNL EQ3/6 Results



"This graph should, but does not, replicate Fig. 3 in Konnecke et al. (1997)." (Oakes et al., 2021)

Database Parameters: Am(III) Model (Issue #11, Part 1)

Part 1: Issues with the $AmCl^{+2}$ and $AmCl_2^{+}$ log K values and Pitzer parameters with respect to the parameters of Konnecke et al., (1997)

Comparison of CRA-2019 DPA Results

	ERDA-6			GWB		
Model	WIPP	Neck	Oakes	WIPP	Neck	Oakes
Species/DB	DATA0.FM5	DATA0.NK5	DATA0.OK5	DATA0.FM5	DATA0.NK5	DATA0.OK5
$AmCl^{+2}$ Molality	9.84E-13	3.34E-12	2.49E-16	7.68E-13	2.58E-12	1.93E-16
$AmCl_2^{+}$ Molality	3.93E-14	1.33E-13	4.58E-16	2.99E-14	1.00E-13	4.10E-16

*The **total dissolved Am(III) concentration for CRA-2019 DPA was ~ 2 x 10^{-7}** molal. The results show that for expected WIPP conditions, Am(III) – Chloride aqueous species contribution is significantly less than the total solubility of Am(III). Therefore, the differences between the Oakes et al., (2021) and the An(III)-Cl models are found to be inconsequential.*

Database Parameters: Am(III) Model (Issue #11, Part 1)

The issues noted by Oakes et al. (2021) with respect to Konnecke et al. (1997) are insignificant and not relevant to WIPP conditions

- The $AnCl_3.6H_2O(s)$ phase has never been included in the WIPP model
- The solubility of $AnCl_3.6H_2O(s)$ in concentrated $CaCl_2$ solutions is not WIPP relevant when the maximum Ca concentration is ~0.03 m
- Both the WIPP and Oakes models predict $AmCl^{+2}$ and $AmCl_2^{+}$ concentrations < 10^{-13} m

Database Parameters

Am(III) Model (Issue #11, Part 2)

Part 2: Comparison of WIPP Am(III) model with that of Neck et al., (2009)

Am(III) models were tested

- The measured data from Neck et al. (2009) and GEOC-21-11
- By creating phase-stability diagrams of solid phases in relation to expected WIPP conditions
- Re-ran the CRA-2019 DPA actinide solubility model with the Neck model

The DATA0.FM6 update is proposed to include

- Addition of $Am(OH)_3$(am) and $Am(OH)_3$(cr-aged) solid phases

Database Parameters

Am(III) Model (Issue #11, Part 2)

Am(III) Model Parameters – DATA0.FM1 and Neck et al. 2009

Reaction	log K	
	WIPP Model DATA0.FM1	Neck et al. (2009)
Solid Phases		
$Am(OH)_3(am) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	NA	16.9 ± 0.8
$Am(OH)_3(cr\text{-}aged) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	NA	15.6 ± 0.6
Aqueous Species		
$Am(OH)^{2+} + H^+ \rightleftharpoons Am^{3+} + H_2O$	7.56	7.2 ± 0.5
$Am(OH)_2^+ + 2H^+ \rightleftharpoons Am^{3+} + 2H_2O$	15.7	15.1 ± 0.7
$Am(OH)_3(aq) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	25.7	26.2 ± 0.5
$Am(OH)_4^- + 4H^+ \rightleftharpoons Am^{3+} + 4H_2O$	NA	40.7 ± 0.7
$AmCl^{2+} \rightleftharpoons Am^{3+} + Cl^-$	-0.24	-0.24 ± 0.03
$AmCl_2^+ \rightleftharpoons Am^{3+} + 2Cl^-$	0.74	0.74 ± 0.05
$Ca[Am(OH)_3]^{2+} + 3H^+ \rightleftharpoons Am^{3+} + Ca^{2+} + 3H_2O$	NA	26.3 ± 0.5
$Ca_2[Am(OH)_4]^{3+} + 4H^+ \rightleftharpoons Am^{3+} + 2Ca^{2+} + 4H_2O$	NA	37.2 ± 0.6
$Ca_3[Am(OH)_6]^{3+} + 6H^+ \rightleftharpoons Am^{3+} + 3Ca^{2+} + 6H_2O$	NA	60.7 ± 0.5

Database Parameters

Am(III) Model (Issue #11, Part 2)

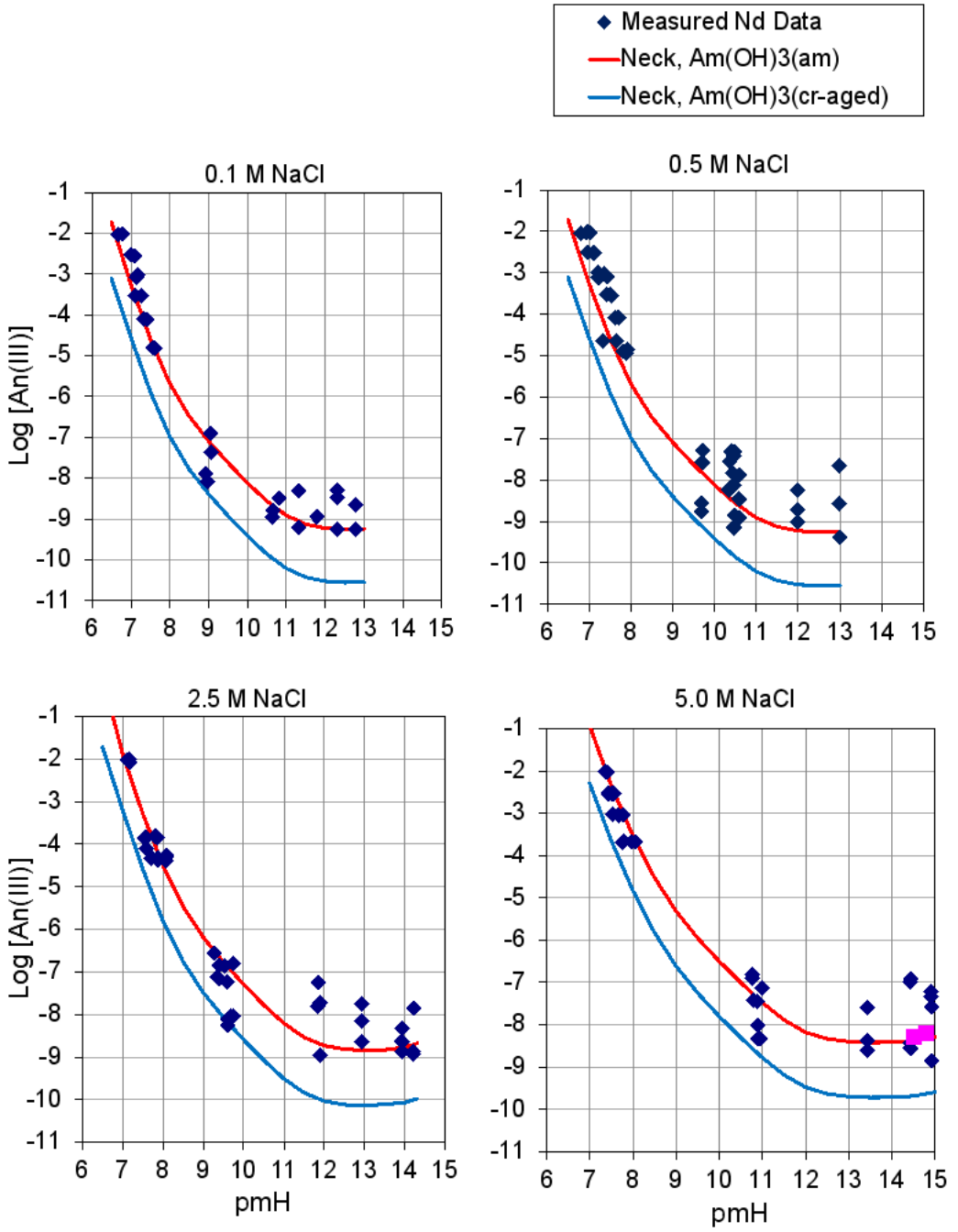
Am (III) Model Parameters retained from DATA0.FM1 for CRA-2024

Reaction	Log K	
	WIPP Model DATA0.FM1	Neck et al. (2009)
Solid Phases		
$Am(OH)_3(s) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	14.49	NA
$AmOHCO_3(c) + 2H^+ \rightleftharpoons Am^{3+} + H_2O + HCO_3^-$	1.64	NA
$NaAm(CO_3)_2 \cdot 6H_2O(s) + 2H^+ \rightleftharpoons Na^+ + Am^{3+} + 2HCO_3^- + 6H_2O$	-0.71	NA
Aqueous Species		
$AmCO_3^+ + H^+ \rightleftharpoons Am^{3+} + HCO_3^-$	2.24	NA
$Am(CO_3)_2^- + 2H^+ \rightleftharpoons Am^{3+} + 2HCO_3^-$	7.68	NA
$Am(CO_3)_3^{3-} + 3H^+ \rightleftharpoons Am^{3+} + 3HCO_3^-$	15.8	NA
$Am(CO_3)_4^{5-} + 4H^+ \rightleftharpoons Am^{3+} + 4HCO_3^-$	28.4	NA
$AmSO_4^+ \rightleftharpoons Am^{3+} + SO_4^{2-}$	-3.25	NA
$Am(SO_4)_2^- \rightleftharpoons Am^{3+} + 2SO_4^{2-}$	-3.70	NA
$AmAcetate^{2+} \rightleftharpoons Am^{3+} + Acetate^-$	-2.74	NA
$AmCitrate(aq) \rightleftharpoons Am^{3+} + Citrate^{3-}$	-8.80	NA
$AmEDTA^- \rightleftharpoons Am^{3+} + EDTA^{4-}$	-18.97	NA
$AmLactate^{2+} \rightleftharpoons Am^{3+} + Lactate^-$	-3.71	NA
$AmOxalate^+ \rightleftharpoons Am^{3+} + Oxalate^{2-}$	-6.16	NA

Updated Am(III) system (Issue # 11, part 2)

Comparison of the Neck et al. (2009) model to the Neck et al. training data

Author/Source	Phase	Log K
Neck et al. (2009)	$Am(OH)_3(am)$	16.9
Neck et al. (2009)	$Am(OH)_3(cr\text{-}aged)$	15.6

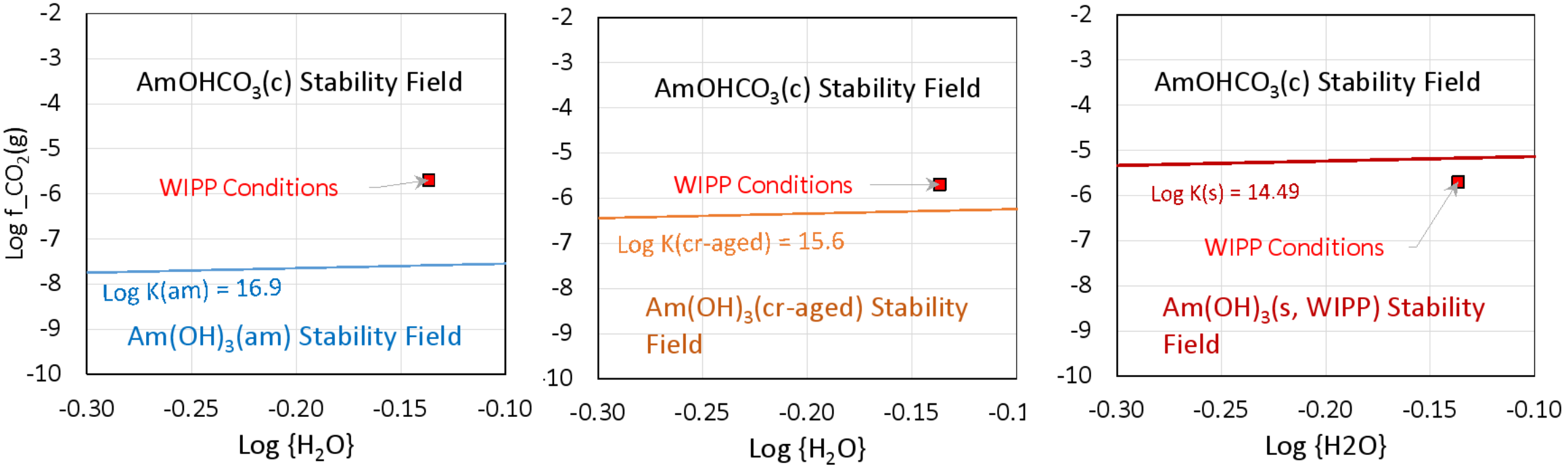


Database Parameters

Part 2: Impact on Am(III) model of including amorphous and crystalline-aged phases

WIPP conditions
- activity of water = 0.73
- f_{CO2}(g) = 2.02E-06

Phase Stability: $Am(OH)_3(x^a)$ and $Am(OH)CO_3(c)$



a – (x) = am, cr-aged, or s

Amorphous or crystalline-aged Am(III)-hydroxide phase → solubility limiting phase is $Am(OH)CO_3$.

Neck et al. stated: *"In the absence of carbonate, silicate, or phosphate, the solubility limiting solid phase is the An(III) hydroxide:*

$$Am(OH)_3(s) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$$*".*

Database Parameters

CRA-2019 DPA Comparison

Column	1	2	3
Database	DATA0.FM5	DATA0.NK5	DATA0.NK5
	gwb_1x.6o	gwb_am.6o	gwb_cr.6o
Suppressed $Am(OH)_3(x)^A$ Phase(s)	none	(s) (cr-aged)	(s)
Am (m)	**1.9E-07**	**1.1E-07**	**1.1E-07**
	erda_1x.6o	erda_am.6o	erda_cr.6o
Am (m)	**3.3E-07**	**2.9E-07**	**2.9E-07**

Solid Phase	Saturation Index (SI)		
$Am(OH)_3(am)$	-[B]	-1.89	-1.89
$Am(OH)_3(cr\text{-}aged)$	-[B]	-0.59	-0.59
$Am(OH)_3(s)$	0.00	0.52	0.52
$AmOHCO_3(c)$	**-0.52**	**0.00**	**0.00**

A - $Am(OH)_3(x)$ x = am, cr-aged, or s.; B - $Am(OH)_3(am)$ and $Am(OH)_3(cr\text{-}aged)$ are not included in DATA0.FM5

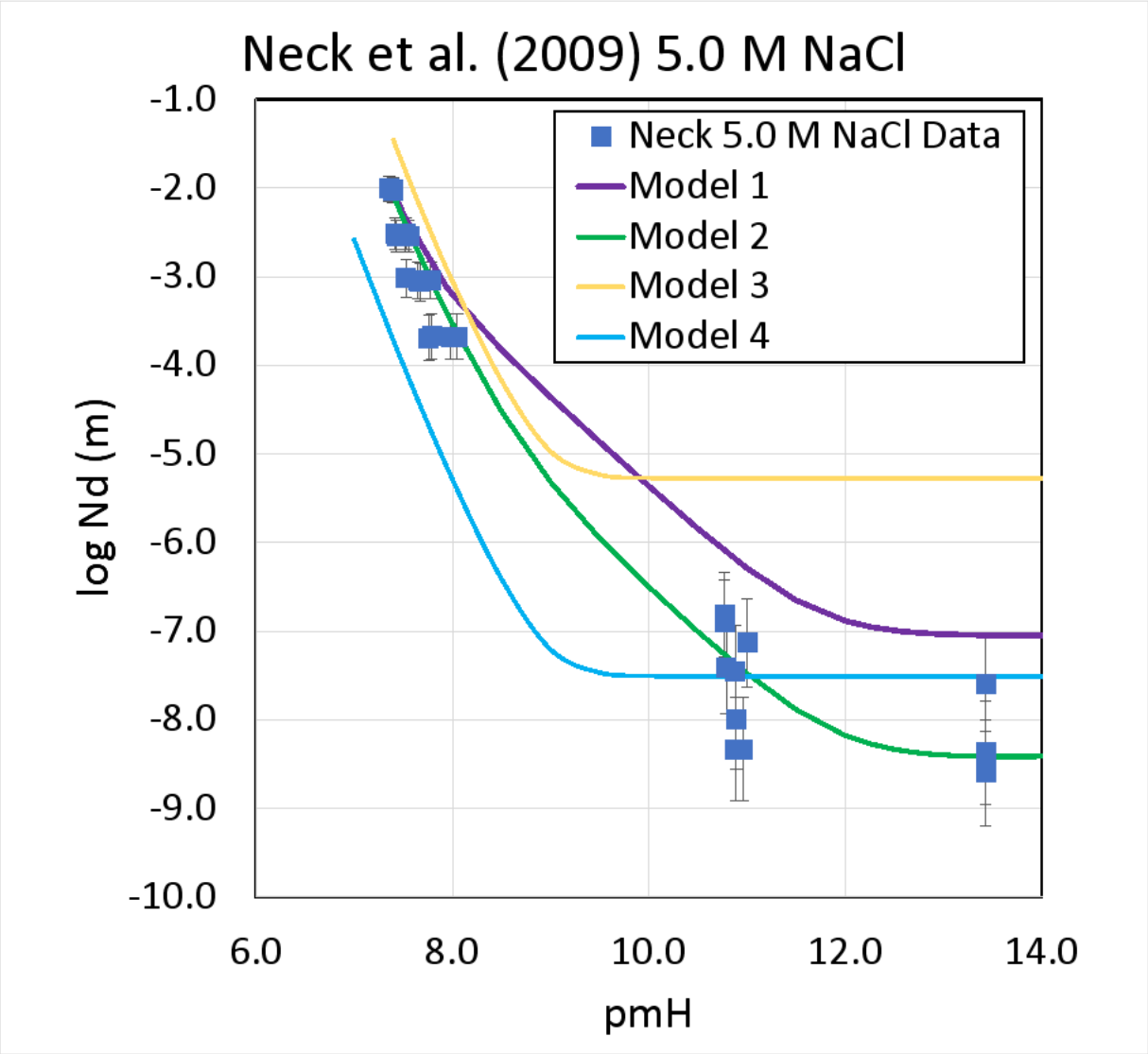
Model Comparison Am(III) system (Issue # 11, Part 2)

Comparison of various models to the Neck et al. 5M NaCl data

Model 1: **DATA0.FM1 with the $Am(OH)_3(am)$ log K (16.9)** of Guillaumont et al. (2003) from GEOC 21-11 (ERMS 576381)

Model 2: **DATA0.FM1 with the Neck et al. (2009) model** fully implemented (i.e., Log K values of aqueous species and Pitzer parameters), using the $Am(OH)_3(am)$ log K value of Guillaumont et al. (2003) as recommended by Neck, and documented in Domski (2021).

Model 3 and 4: **Oakes et al. (2021)** fully implemented as a singular set of parameters with no other parameters included. **Model 3 uses Oakes amorphous phase $Am(OH)_3(am)$** and **Model 4 uses the crystalline phase $Am(OH)_3(cr)$.**



Model Comparison Am(III) system (Issue # 11, Part 2)

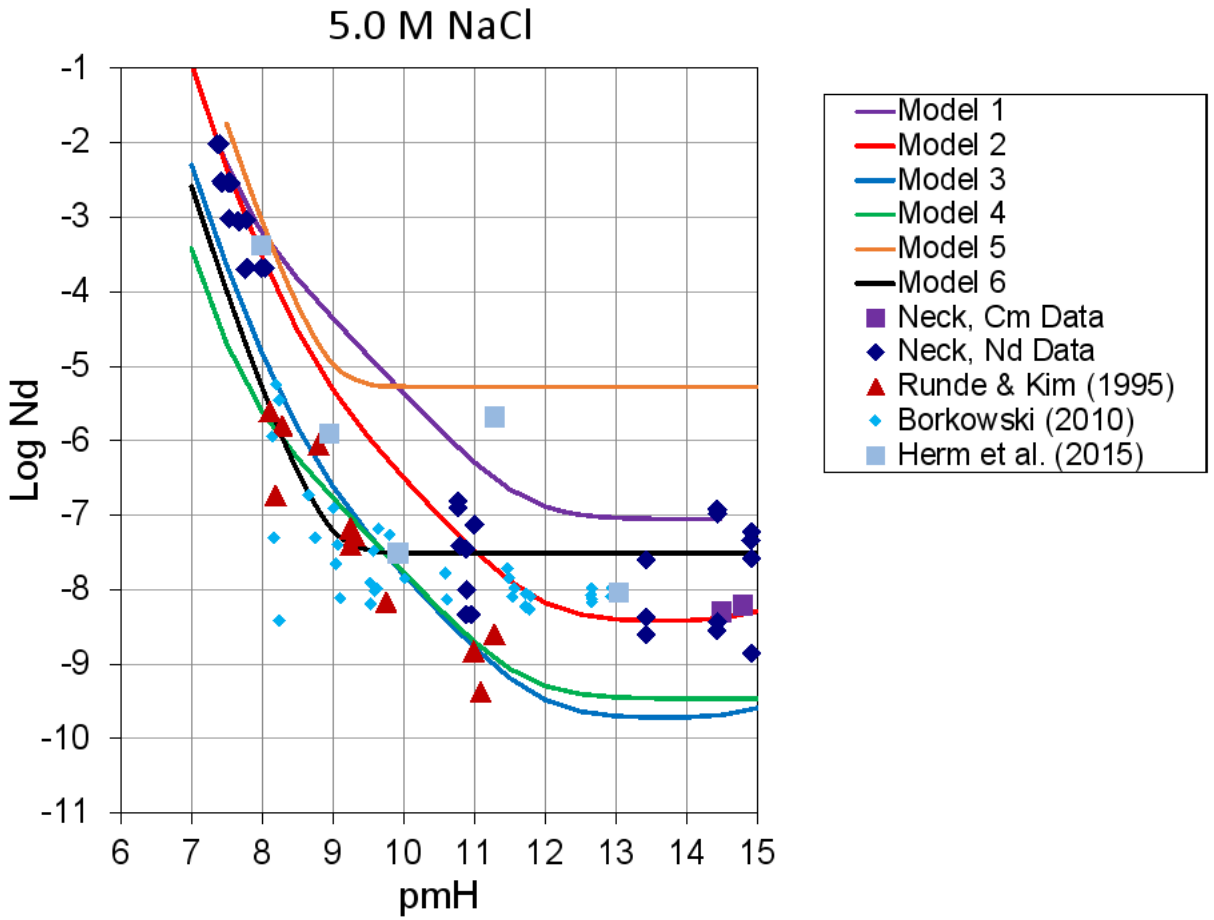
Comparison of various models to selected available data

Model 1: **DATA0.FM1 with the $Am(OH)_3$(am) log K (16.9)** of Guillaumont et al. (2003) from GEOC 21-11 (ERMS 576381)

Model 2 and 3: **DATA0.FM1 with the Neck et al. (2009) model** fully implemented (i.e., Log K values of aqueous species and Pitzer parameters), Model 2 using the $Am(OH)_3$(am) log K,and Model 3 $Am(OH)_3$(cr-aged) values of Guillaumont et al. (2003) as recommended by Neck, and documented in Domski (2021).

Model 4: **DATA0.FM1**

Model 5 and 6: **Oakes et al. (2021)** fully implemented as a singular set of parameters with no other parameters included. **Model 5 uses Oakes amorphous phase $Am(OH)_3$(am)** and **Model 6 uses the crystalline phase $Am(OH)_3$(cr).**



The observed scatter in the measured $Am(OH)_3$(solid) solubility data is significant

EPA Database Issues

Earlandite (Issue #29)

EPA Expectation – Revise database to be consistent with available data, include earlandite solubility.

DOE Path Forward : Earlandite will be included in CRA-2024.

- *Earlandite is a potential solubility-controlling phase for citrate.*
- *It was shown that earlandite does not control citrate solubility in the response to EPA completeness question CC2-GEOCHEM-13, nor does it impact actinide solubilities in the CRA-2019.*
- $Ca_3(Citrate)_2 \cdot 4H_2O(s) \leftrightarrow 3Ca^{+2} + 2Citrate^{-3} + 4H_2O$; **log K = -17.90** *(Hummel et al., 2005)*

Actinide Solubility Model Assumptions

Calcite Saturation (Issue #6)

EPA Expectation:

Assume slight oversaturation with respect to calcite, consistent with the presence of known calcite precipitation inhibitor (Mg^{2+} & Fe^{2+}) in WIPP brines.

DOE Path Forward:

The literature[1] indicates that calcite precipitation is inhibited in the presence of Mg and Fe ions, but that aragonite has been observed to form. The WIPP database contains aragonite, a calcite polymorph with slightly higher solubility. Suppressing calcite and allowing aragonite to form eliminates the issues caused by calcite precipitation.

[1]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 (ERMS: 544785)

Actinide Solubility Model Assumptions

Calcite Saturation (Issue #6)

- Preliminary CRA-2019 actinide solubility runs, which included lead and iron reactants, produced high pcH (~10.5) conditions and unrealistically high carbonate concentrations resulting in calcite supersaturation (SI ≈ 1.7). By allowing calcite to precipitate the pcH decreased to ~9.5, and the carbonate concentration decreased into the range expected for the MgO buffer. However, a side effect of calcite precipitation was increased brucite and hydromagnesite dissolution resulting in Phase 5 saturation/precipitation, which uses 9 moles of water per mole of Phase 5. This additional sink for water has the potential to impact the water budget of the repository.
- Inhibition of calcite precipitation with aragonite precipitation, in the presence of Mg^{2+} and Fe^{2+} ions and/or other dissolved constituents has been documented (ERMS: 544785) for natural systems and engineered systems. Aragonite is a more soluble polymorph of calcite, and allowing it to form in place of calcite results in less hydromagnesite dissolution, and hence, lower Phase 5 saturation. For CRA-2024 calcite will be suppressed and aragonite allowed to form should it become saturated.

Actinide Solubility Model Assumptions

Phase-5 (Issue #7)

EPA Expectation:

Verify Phase-5 solubility by comparing calculated solubilities with experimental data.

DOE Path Forward :

Domski and Nemer, (in review) compared the WIPP phase-5 and phase-3 model to three sets of measured data, and Nemer and Domski, (in review) re-fit the log K values for both phases. The literature implies that phase-5 is metastable with respect to phase-3 on the time-scale of lab experiments. Phase-5 and phase-3 are similar in solubility; allowing phase-3 to form by suppressing phase-5 will lessen the water-balance issue.

Actinide Solubility Model Assumptions

Phase-5 (Issue #7)

The magnesium oxy-chloride phases, or Sorel cement phases,
Phase-3: $Mg_2Cl(OH)_3.4H_2O$ and Phase-5: $Mg_3Cl(OH)_5.4H_2O$

Phase-3 & phase-5 form in high Mg - Cl - high ionic strength environments such as the WIPP with the MgO engineered barrier.

Nine moles of water are consumed per mole of phase-5 and seven moles of water per mole of phase-3

Phase-5: $3Mg^{2+} + Cl^- + 9H_2O \rightleftharpoons Mg_3Cl(OH)_5.4H_2O) + 3H^+$

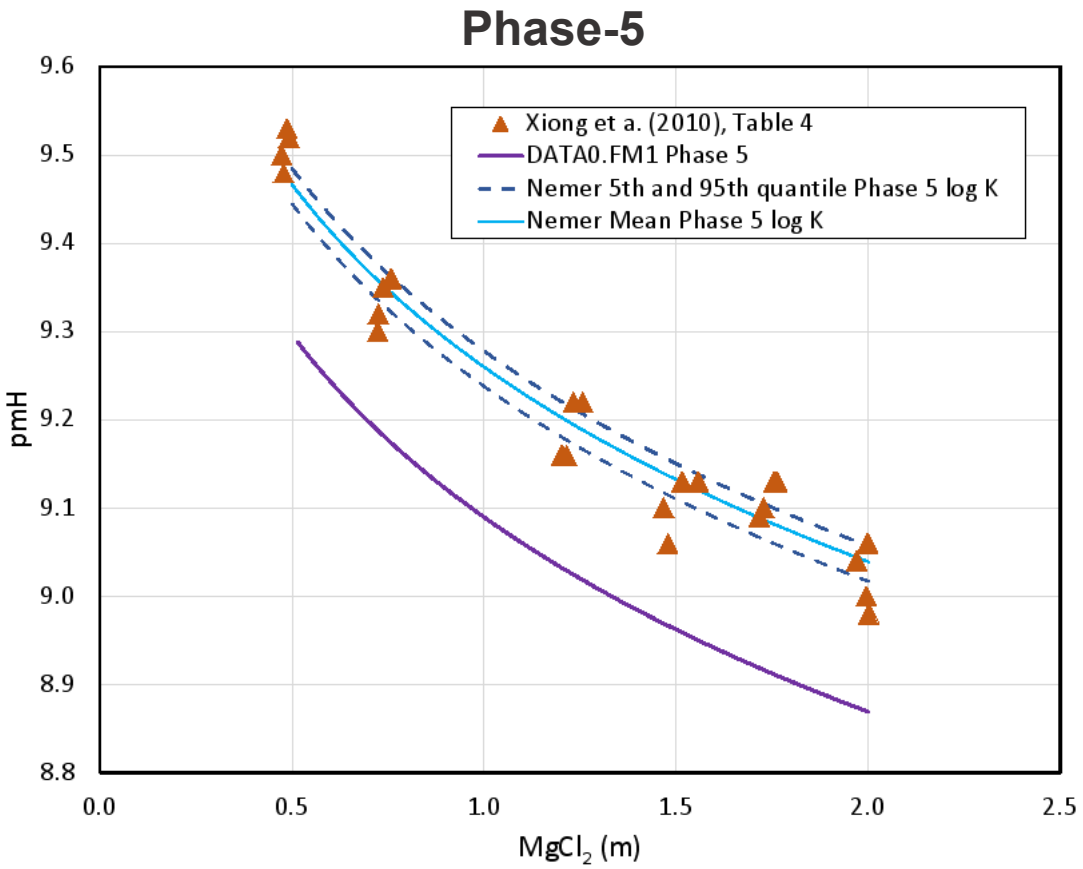
Phase-3: $2Mg^{2+} + Cl^- + 7H_2O \rightleftharpoons Mg_2Cl(OH)_3.4H_2O) + 5H^+$

Actinide Solubility Model Assumptions

Phase-5 (Issue #7)

Variable	Mean (dimensionless)	Variance (dimensionless)	5'th q (dimensionless)	95'th q (dimensionless)
$log_{10}K$	43.81	1.51×10^{-3}	43.75	43.87
σ	0.04	3.42×10^{-5}	0.03	0.05

- SNL used the phase-5 experimental data from Xiong et al. (2010) and the phase-3 experimental data of Altmaier et al. (2003) and Pannach et al. (2017), to fit the log K values of the two phases. **A simplified Bayesian-inverse analysis was used to estimate the log K values, their uncertainty, and the uncertainty in the underlying experimental data (not shown).**
- This is a new approach for SNL geochemistry that provides an estimate of both the thermodynamic parameters and, importantly, **their uncertainty**.



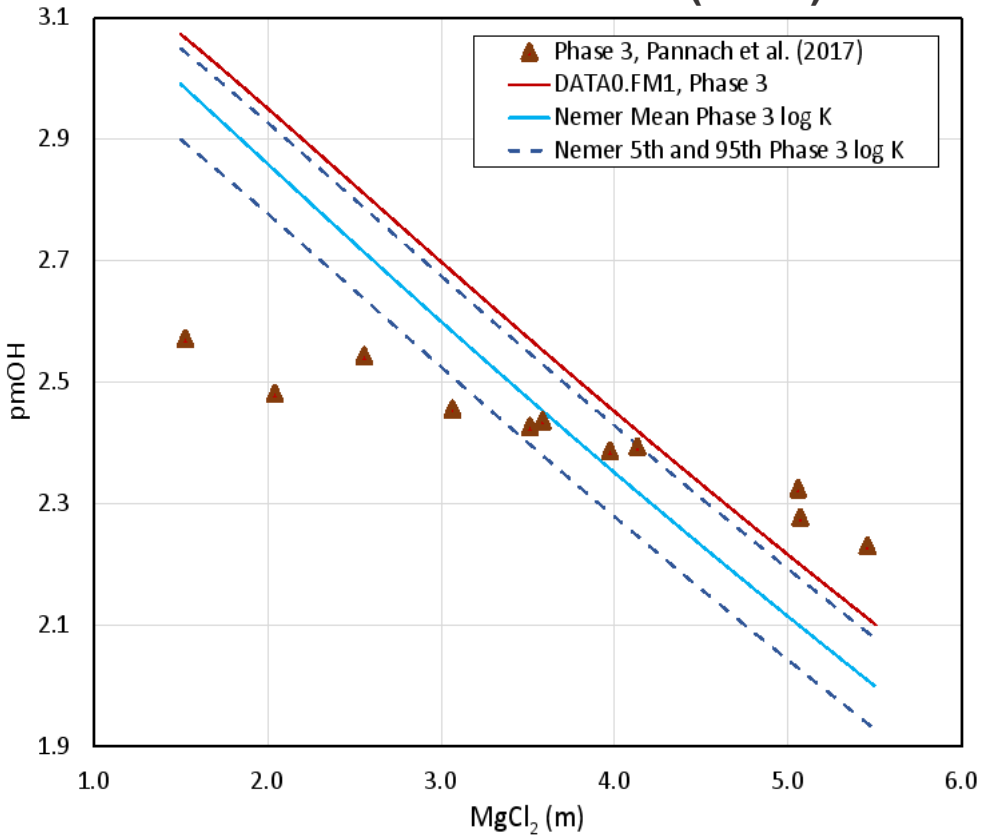
Actinide Solubility Model Assumptions

Phase-5 (Issue #7)

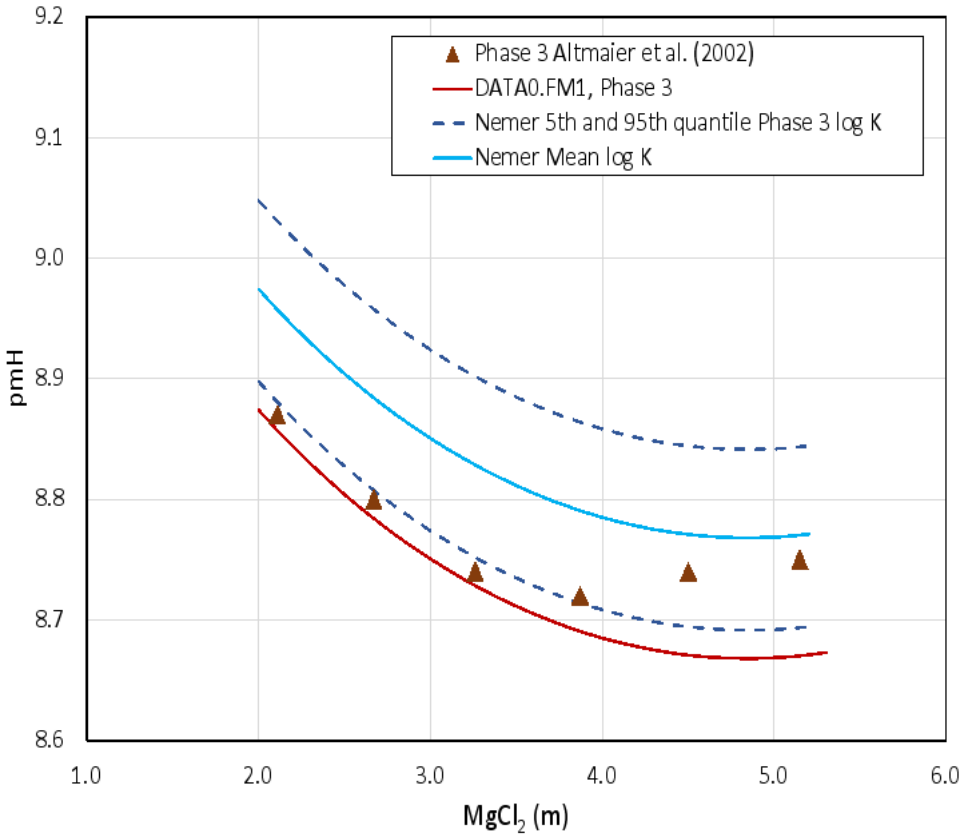
Variable	Mean (dimensionless)	Variance (dimensionless)	5'th q (dimensionless)	95'th q (dimensionless)
$log_{10}K$	26.33	0.019	26.10	26.55
σ	0.18	0.012	0.14	0.25

Although the Pannach et al. data visually appears to be poorly represented by the model, **nearly all of the experimental data fits within the calculated posterior predictive distribution at the 95% confidence interval** (not shown, under review)

Pannach et al. (2017)



Altmaier et al. (2003)



Actinide Solubility Model Assumptions

Phase-5 (Issue #7) Conclusions

- Altmaier et al., (2003) investigated the solubility and stability of brucite and phase-3 in NaCl and $MgCl_2$ solutions. Solid analysis (XRD & SEM) during and after testing did not observe phase-5 at any time.
- Pannach et al., (2017) studied the solubility and occurrence of Mg oxy-chloride phases in $MgCl_2$ solutions at temperatures ranging from 298 to 393 K. At 298 K, it was found that brucite was stable in $MgCl_2$ solutions up to 1.5 m before transforming to phase-3. *Phase-5 was observed to form early in the experiments, but was metastable, and transformed to phase-3 over short time frames.*
- Because the literature indicates phase-5 is metastable w.r.t phase-3, and we have no experimental data to contradict this finding **at this time**, phase-5 will be suppressed for CRA-2024

EPA low Priority Issues

Silica (Issue #25)

EPA Expectation – Evaluate the available high ionic-strength silica data for inclusion in the WIPP thermodynamic database and actinide solubility calculations.

DOE Path Forward :

The significance of silica will be evaluated before considering inclusion into the database in CRA-2029.

EPA low Priority Issues

Solids (Issue 28)

Conceptual Model: Equilibrium is assumed between repository brine, waste, and the Salado minerals, and either magnesite or hydromagnesite.
Thermodynamic equilibrium is assumed for dissolution and precipitation of actinide-bearing solid phases.

EPA Expectation – Recalculate the initial moles of solids to be consistent with the brine volume.

DOE Path Forward : The simulations are of a “well-mixed” batch reactor, and the input brines are of constant composition, therefore the reactants are scaled correctly.

EPA low Priority Issues

Available Data for Database (Issue #30)

Systems to be included in the thermodynamic database should align with FEPs, chemical condition conceptual model assumptions and dissolved actinide source term conceptual model assumptions.

EPA Expectation– Revise the database to be consistent with available data.

DOE Path Forward : The systems included in the database are carefully evaluated, conceptually and experimentally, in accordance with WIPP conditions, mineral and brine compositions, and waste inventory.

EPA low Priority Issues

An-Acetate (Issue # 31)

EPA Expectation – Assess whether additional Am(III)-acetate and Th(V)-acetate species should be added to the database.

DOE Path Forward : Acetate is a weak ligand. Further evaluations will be conducted to understand the chemical affinity of acetate before CRA-2029.

EPA low Priority Issues

Fe-Sulfate (Issue 32)

EPA Expectation – Add Fe(II)-sulfate Pitzer parameters and solid phases to the WIPP thermodynamic database.

DOE Path Forward : Fe(II)-sulfate will be included in DATA0.FM6.

EPA low Priority Issues

Fe-Sulfate (Issue 32)

Reaction	Log K (I = 0)	Reference
Dissolution		
$FeSO_4.H_2O(s)$ (Szomolnokite) = $Fe^{+2} + SO_4^{-2} + H_2O$	-0.90	GEOC-22-01 (Jang et al., 2022, in prep)
$FeSO_4.7H_2O(s)$ (Melanterite) = $Fe^{+2} + SO_4^{-2} + 7H_2O$	-2.20	GEOC-22-01 (Jang et al., 2022, in prep)
Aqueous Reaction		
$FeEDTA^{-2} = Fe^{+2} + EDTA^{-4}$	-16.1	GEOC-21-11 (Jang et al., 2021)
$FeCitrate^{-} = Fe^{+2} + Citrate^{-3}$	-5.7	GEOC-21-11 (Jang et al., 2021)
$FeOHCitrate^{-2} + H^{+} = Fe^{+2} + Citrate^{-3} + H_2O$	2.24	GEOC-21-11 (Jang et al., 2021)

EPA low Priority Issues

Fe/Pb – Organics (Issue 33)

EPA Issue # 33 – Iron and lead interactions with organic ligands should not be included in actinide solubility calculations without also including the effects of sulfide and phosphate.

DOE Path Forward: The DOE will conduct experiments on metal-sulfide systems prior to their addition to the database; conceptually, phosphate needs further understanding relative to WIPP chemistry.

EPA low Priority Issues

Am-Borate (Issue #35)

EPA Issue # 35 – Am-Borate – Evaluate available data and include these species and solid phases if sufficient data are available.

DOE Path Forward: The literature shows that under WIPP chemical conditions, borate complexation is weak.

EPA low Priority Issues

Am-Borate (Issue #35)

A literature review was performed in order to assess the An(III)-borate interactions (Rhino, 2022). Below is a summary of our initial conclusions from the literature review:

- The literature indicates a weak chemical affinity, i.e., interaction or complexation. We believe the interaction is weaker than carbonation or hydroxylation.
- Potential formation of an An(III)-Borate solid phase occur at high borate concentrations, making the solid less relevant under WIPP-relevant conditions.
- Evaluation of the potential effects of borate on An(III) solubility will continue as new information becomes available.

At this time, no An(III) – borate model is recommended for the WIPP thermodynamic database.

EPA low Priority Issues

Th(IV)-Carbonate (Issue #36)

EPA Expectation – Update Th(IV)-carbonate to be consistent with Altmaier et al. (2006) data.

DOE Path Forward: The Th(IV)-carbonate species specified by EPA are not expected to have a significant effect on Th(IV) solubility, therefore, no action will be taken for CRA-2024.

EPA low Priority Issues

Cements (Issue #50)

EPA Issue # 50 – Re-assess potential effects of cements on actinide solubility calculations if cement inventory increases significantly.

DOE Path Forward: The DOE addressed and resolved this issue in EPA completeness question CC5-GEOCHEM-26 for CRA-2019 DPA. In the TSD, the EPA states: *"Knerr (2021e) provided calculations that included the assumption that the cement wastes contained 67% portlandite, which is significantly greater than the portlandite content of up to 10% estimated by Storz (1996)."*

"The results indicate that even at the relatively high portlandite percentages assumed for cementitious wastes by Knerr (2021e), portlandite in the WIPP inventory is unlikely to significantly affect brine chemistry and actinide solubilities."

The DOE will compare the 2024 cement inventory to the 2019 inventory and take action if the cement inventory is substantially increased.

Thank you!

Actinide Baseline Solubility Calculation

Step 1: Initial Solutions

- EQ3NR is used to equilibrate and speciate the brine compositions (ERDA -6 & GWB) with the inventory scaled masses of the organic ligands (acetate, oxalate, citrate, and EDTA).
- The actinide concentrations are set via equilibrium with solubility controlling phases ($Am(OH)_3(x)$, $ThO_2(am)$, and $KNpO_2CO_3$).
- The conditions of low pH and high carbonate concentration of the initial solution ensures that an excess mass of actinides dissolve in this step.
- These dissolved concentrations are then passed to Step 2 and are subject to the evolving chemical environment of the reacting solution and where the stable solubility controlling phase may form.

Actinide Baseline Solubility Calculation

Step 2: Final Equilibrium System

- Using EQ6, the initial solution compositions from Step 1 are reacted with:
  - Inventory-scaled masses of the MgO barrier (50% brucite and 50% hydromagnesite)
  - Iron and lead reactants representing the waste containers and radiation shielding
  - Salado Formation minerals halite and anhydrite
- The model includes the effects of organic ligand complexation and mineral phase dissolution and precipitation.
- The model provides the actinide solubilities and the expected repository conditions which include:
  - the equilibrium pH
  - fCO2(g)
  - activity of water
  - total inorganic carbon
  - ionic strength
  - the concentration of all dissolved constituents
  - the solid phase budget