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subject: Evaluation of the An(III) - Borate interaction, Revision 1

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1. Introduction

This memo is intended to address the Environmental Protection Agency's (EPA) continuing questions concerning the impact of boron on +III actinide complexation, as applied to Waste Isolation Pilot Plant (WIPP) Performance Assessment (PA) calculations. In issue #35 of their letter (Peake 2022) on technical issues associated with the CRA-2019, the EPA wrote "*Am(III)-borate aqueous speciation and solid phases are not included in the WIPP thermodynamic database*"… "*Evaluate available data and include these species and solid phases if sufficient data are available*". The EPA's technical issue here specifically concerns the complexation of americium in the +III oxidation state, Am(III), with boron. As correctly stated in the EPA letter, WIPP-PA currently excludes Am(III)-borate complexation. Further, in EPA's Technical Support Document (TSD) on the actinide source term (U.S. Environmental Protection Agency 2022), EPA wrote that the following issue was considered "*Continue evaluating the potential effects of borate on actinide aqueous speciation and solid phase solubilities*" and later in Section 7.5 of this TSD "*Borate in WIPP brines is unlikely to significantly increase Am(III) concentrations under WIPP repository conditions (Hinz et al. 2015), but borate may have small effects on Am(III) aqueous speciation and solubility.*"

[1] SNL WIPP: Sandia National Laboratories at the Waste Isolation Pilot Plant (WIPP). WIPP is located ~26 miles southeast of Carlsbad, New Mexico, U.S.A., built 2,150 feet underground in the Salado Formation, a Permian evaporite deposit in the northern Delaware Basin.

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For the purposes of WIPP-PA, data from a variety of actinide analogs in the +III oxidation state are used to parameterize the WIPP geochemistry model for An(III) ≡ actinides in the +III oxidations state. This memo provides a literature review on An(III) - borate interaction under WIPP-relevant conditions and gives recommendations on whether WIPP PA should include An(III)-borate species and solid-phase values in the WIPP thermodynamic database, for use in WIPP-PA.

WIPP-relevant conditions are summarized in Table SOTERM-1 and Table SOTERM-2 of U.S. Department of Energy (2019), and cross-referenced references listed therein. These conditions include strongly reducing conditions, a slightly alkaline pH ≈ 9, low carbonate concentrations due to the presence of the brucite-hydromagnesite buffer, brine compositions as discussed in Section 2, atmospheric pressure for the purpose of determining actinide solubilities, and an ambient temperature around 27 °C.

2. Origin of Boron in WIPP Brines

The Ochoan evaporate section of the Delaware basin includes both the Castile and Salado formations, with the Castile lying stratigraphically below the Salado. For both the Salado and Castile brines, the evidence suggests that the original source of boron is sea water that evaporated to form evaporite minerals (Powers, Lambert et al. 1978, Stein 1985), with perhaps a separate (and presumably minor) contribution due to sea water or partially-evaporated sea water leaching borate from sedimentary and igneous rock native to the Delaware basin during the late Permian (Popielak, Beauheim et al. 1983).

ERDA-6 is the name given to a well that was drilled in the Castile formation (Popielak, Beauheim et al. 1983); ERDA comes from the Energy Research and Development Administration, a predecessor to the DOE. The Castile consists of thick beds of anhydrite interbedded with halite (Popielak, Beauheim et al. 1983). The Castile is significant in that pressurized brine pockets, which have been found reasonably close to the WIPP site and below the WIPP-repository stratigraphy, have been found in this formation. The Castile formation is believed to have formed in the initial stages of the evaporitic deposition of the Delaware basin and was likely deposited in deep (up to 1000's ft) water (Popielak, Beauheim et al. 1983). Castile brine has been found to occur below fractured anhydrite beds, and typically in sections that have undergone significant deformation and inclination (Popielak, Beauheim et al. 1983). Brine sampling that came to define the ERDA-6 brine came from the ERDA-6, WIPP-12 and Union wells (Brush 1990) drilled into the Castile formation.

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The Salado was deposited later than the Castile, also during the late Permian (Holt and Powers 2011). Salado deposition is believed to have also occurred via the evaporation of sea water that was perhaps even more saline than that which led to the Castile formation (Powers, Lambert et al. 1978). The Salado likely deposited from shallow (10's meters) water (Holt and Powers 1990). The particular Salado brine that has been used in PA, Generic Weep Brine (GWB), is formulated to simulate/mimic intergranular Salado brine. That brine lies at the grain boundaries between halite single crystals and tends to "weep" into boreholes and recent excavations. From Power, Lambert et al. (1978): "*Such fluids will tend to be squeezed out of the salt beds over geological time as recrystallization along grain boundaries and other processes permit compaction, just as the residual water in a sandstone is eliminated during the formation of a quartzite.*"

The above discussion indicates that the current consensus on brine flow and accumulation mechanisms are different in the Salado compared to the Castile. As such, two classes of brine are used in Performance Assessment (PA) to represent possible chemistry of the WIPP repository in a simplified manner. These classes of brine are called Generic Weep Brine (GWB) and ERDA-6. Generic Weep Brine is formulated to simulate intergranular Salado brine (Snider 2003). The ERDA-6 brine is formulated to simulate Castile brine (Popielak, Beauheim et al. 1983). Generic Weep Brine has a total boron concentration of $[B]_{tot}$ = 0.16 M, whereas $[B]_{tot}$ = 0.06 M in ERDA-6 (Xiong 2008).

The synthetic brine chemistries used in PA, ERDA-6 and GWB, represent a simplified picture from reality. However, there are clear physical limitations outlined above on what the total borate concentration can be in natural brines that could enter the WIPP repository. Hence, we at least expect the boron concentration in ERDA-6 and GWB to represent probable draws from some underlying distribution of WIPP brine compositions. This premise is important because, as will be shown in later sections, the conclusions related to the impact of boron chemistry on actinide solubility somewhat depend on the total boron concentration in solution.

3. Overview of Borate Chemistry and Speciation

Borate has complex chemical behavior and continues to be the subject of on-going studies within and outside the WIPP project. Boric acid $B(OH)_3$, more specifically orthoboric acid, reacts as a weak Lewis acid (Ingri 1962). Its high acid-dissociation constant (pKa ≈ 8.98) makes it a strong hydroxide acceptor as described in the following reaction.

$$B(OH)_3 + H_2O = B(OH)_4^- + H^+ \quad (1)$$

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Ingri et al. (1957, 1962) postulated that with a total boron concentration of $[B]_{tot} \approx 0.025$ M, tri-, tetra-, and penta- polyborates form in the pH range of 4 – 13; here [X] is the molarity of X in solution with units of M ≡ mol/L. Ingri et al. (1957, 1962) studied the solubility constant of those polyborates enabling Anderson, Eyring et al., (1964) to publish a proposed speciation diagram (see Figure 1 of Anderson, Eyring et al. 1964).

Schott, Kretzschmar et al. (2014) calculated a speciation diagram based on Ingri et al. (1957, 1962), shown in their Fig. 1. That speciation diagram shows the importance of the species $B_4O_5(OH)_4^{2-}$ for $[B]_{tot} = 0.7$ M at $I = 0.1$M for pH = 8 – 10; $I \equiv$ solution ionic strength. Looking at the graph towards acidic conditions, $B_3O_3(OH)_4^-$ peaks, followed by $B_5O_5(OH)_4^-$. At low pH the speciation is dominated by $B(OH)_3$. Looking at the graph towards alkaline pH, after $B_4O_5(OH)_4^{2-}$, there is a small peak due to $B_3O_3(OH)_5^{2-}$. Finally at high pH the speciation is dominated by $B(OH)_4^-$.

Hinz, Altmaier et al. (2015) provide a thermodynamically calculated speciation diagram (also based on Ingri et al. (1957, 1962)) at low ionic strength ($I \approx 0$) for a total borate concentration of $[B]_{tot} = 0.04$ M, and $[B]_{tot} = 0.4$ M. This speciation diagram is given in their Fig. 1. Looking at Fig. 1 (Hinz, Altmaier et al. 2015), at $[B]_{tot} = 0.04$ M the calculated borate speciation is dominated by $B(OH)_3(aq)$ between pH = 4 – 8, and dominated by $B(OH)_4^-$ between pH = 8 – 12. There is a smaller contribution by $B_3O_3(OH)_4^-$ near pH = 8. At $[B]_{tot} = 0.4$ M, the situation is similar at the extremes of pH, but in between there are contributions from $B_5O_6(OH)_4^-$ which peaks in its fraction of total borate at pH ≈ 7, $B_3O_3(OH)_4^-$ which peaks at pH ≈ 8.5, and $B_4O_5(OH)_4^{2-}$ which peaks at pH ≈ 10.

Felmy and Weare (1986) developed a Pitzer model for the ion system Na-K-Ca-Mg-H-Cl-SO_4-CO_2-$B(OH)_4$-H_2O. These authors extended the Harvie, Moller et al., (1984) ionic system and investigated the borate system at 25°C and up to $I \approx 10$ M. A notable quote from the authors regarding polyborate speciation reads: "*However, as the total boron concentration increases in solution, the acid-base equilibria no longer follows simple, weak acid behavior. This effect has been previously explained by the introduction of strongly complexed polyborate ions, but the exact polyborate species present in solution are difficult to determine. Boron can coordinate to three or four oxygen atoms which allows a variety of theoretical structures to exist, and several different polyborate species have been hypothesized to exist in solution.*" This last sentence is critical and summarizes our (Sandia's) position on borate speciation.

The general speciation scheme gleaned from the above publications rests on the work of Ingri et al. (1957, 1962), although as will be discussed in Section 4.3, some recent corroborating evidence has been

Information Only

obtained by Schott, Kretzschmar et al. (2014). The currently accepted conceptual picture is that $B(OH)_3$ and $B(OH)_4^-$ dominate at low and high pH, respectively, and exist without other borate species in the limit of low $[B]_{tot}$. At higher $[B]_{tot}$, borate tends to dissociate into polyborates that generally exist away from high and low pH. The exact polyborate species stoichiometry remains uncertain in our professional opinion.

4. Literature Review of An(III) – Borate Interactions

In this section, a selected set of papers on An(III) – borate interactions are reviewed. For each paper, we have attempted to summarize the paper's conclusions, followed by our review. The review is not comprehensive at this time.

4.1. Borkowski, Richmann et al. (2010)

4.1.1. Authors' Conclusions

Borkowski, Richmann et al. (2010) measured the stability constant of Neodymium (Nd) with dissolved sodium tetraborate as a function of NaCl ionic strength for determining Pitzer ion-interaction parameters. In their work, concentrations (0 – 0.04 M) of sodium tetraborate ($Na_2B_4O_7.10H_2O$) were dissolved in NaCl solutions of 1 – 5 M. An excess (10mg $Nd(OH)_3$) of Nd solids was introduced into each reactor. The solutions were aged for over 90-120 days prior to analysis. The pcH of solutions were maintained at pcH = 8.6 by a method not stated in the paper, where $pcH \equiv -\log_{10}[H^+]$.

The work of Borkowski, Richmann et al. (2010) shows a relatively small increase of solubility (Factor ≈ 3 – 5) with increasing $[B]_{tot}$ (see Fig. 3 of Borkowski, Richmann et al. 2010). The authors emphasized that sodium tetraborate has a low solubility at a WIPP-relevant pH. As a consequence (according to Borkowski, Richmann et al. 2010), this effect could have prevented further borate complexation in their studies, preventing a significant effect on the overall Nd solubility. Borkowski, Richmann et al. (2010) indicated a complexation constant of 4.99 ± 0.30 for the formation of $NdHB_4O_7^{+2}$. The authors lay out a series of assumptions that were required for determining this complexation constant.

4.1.2. Sandia Review

In Borkowski, Richmann et al.'s (2010) experiment, the concentration of borate was $[B]_{tot} \leq 0.16$ M. There is a general trend of increasing Nd concentration with increasing $[B]_{tot}$ and with increasing ionic strength. These results were obtained for a fixed value of pcH = 8.6. At the highest ionic strength (5M NaCl), the increase in Nd solubility with and without borate is about a factor of 3 – 5. There has been

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some concern related to this work because no final XRD was performed on the solid phase, such that the final Nd solubility-controlling phase is unknown. However, the increase in Nd solubility with increasing borate concentration was observed.

4.2. Study of Hinz, Altmaier et al. (2015)

4.2.1. Authors' Conclusions

Hinz, Altmaier et al. (2015) present their Nd solubility results in the presence of borate in their Fig. 2. They do not present results with $[B]_{tot} = 0$ M for comparison, instead comparing to data from Neck, Altmaier et al. (2009), in which data isn't available for all matrix solutions studied in Hinz, Altmaier et al. (2015). According to the authors, at low borate concentration ($[B]_{tot} = 0.004$ M), borate had little-to-no effect on Nd solubility between pcH = 7 – 9. At higher $[B]_{tot}$, in NaCl solutions, there was a drop in total Nd solubility for pcH $\lesssim$ 9, which is attributed to the precipitation of a Nd-borate solid phase. Above pcH $\approx$ 10, Hinz, Altmaier et al. (2015) write that considerable scatter was observed in the Nd solubility data due perhaps to the low total Nd solubility obtained at these pcH values.

To complement the Nd-solubility observations, Hinz, Altmaier et al. (2015) performed a TRLFS (Time Resolved Laser Fluorescence Spectra) study using Cm(III) instead of Nd(III) at pcH = 8, for different salt solutions, varying the concentration of $[B]_{tot}$. The authors were not able to explain the shifts in the TRLFS spectra and fluorescence lifetimes in 0.1 M NaCl. In 5.0M NaCl, the authors conclude that the only explanation for the observed wavelength shift in TRLFS spectra with increasing borate concentration is the formation of a Cm-borate complex. In $MgCl_2$ solutions, the authors conclude the wavelength shift in spectra with increasing borate concentration indicates the formation of a Cm-borate complex.

4.2.2. Sandia review

The data shown in Fig. 2 of Hinz, Altmaier et al. (2015) shows a possible increase in Nd solubility with increasing borate concentration between pcH = 9 – 10. However, the data is indeed scattered, and in general there doesn't appear to be a trend. At lower pcH, the trend is a bit clearer with increasing borate concentration leading to decreased Nd solubility in most experimental cases. Hinz, Altmaier et al.'s (2015) explanation that the reduction in solubility results from the precipitation of a solid Nd-borate phase appears plausible. The TRLFS study provides some evidence that borate is complexing with Cm(III), although alternative explanations for the fluorescence-spectra shifts were not provided in the paper.

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The data in Fig. 2 of Hinz, Altmaier et al. (2015) for 5.0 M NaCl (and other ionic strengths) appears to shows a trend opposite that of Borkowski, Richmann et al. (2010). In Hinz, Altmaier et al. (2015), $[Nd]_{tot}$ drops from 10^{-4} mol/L to $10^{-7.5}$ with $[B]_{tot}$ increasing from 0.04 M to 0.16 M at pcH ≈ 8 – 9; in Borkowski, Richmann et al. (2010), an increase in Nd solubility was observed with increasing $[B]_{tot}$. While we could speculate on potential causes of the discrepancy between the two publications, in the absence of additional experimental data we don't dismiss either publication.

4.3. Study of Schott, Kretzschmar et al. (2014)

4.3.1. Authors' conclusions

Schott, Kretzschmar et al. (2014) performed NMR studies of solutions containing 0.2 – 0.7 M $[B]_{tot}$ at pH = 5 – 6. The pH in this work is reported as what was directly measured via a glass electrode (model un-disclosed) and adjusted in solutions via NaOH and $HClO_4$. Ionic strength was set to 0.1 M using $NaClO_4$. The authors report that at pH = 5 and $[B]_{tot} \lesssim 0.5$ M, no polyborate species were detected (via NMR). Under these conditions the authors conclude the only species is undissociated boric acid ($B(OH)_3(aq)$). At pH = 5 and $[B]_{tot} > 0.5$ M, the authors report that small amounts of polyborates were observed. At pH = 6 and $[B]_{tot} > 0.4$, the authors state that there are three boron species evident in the NMR spectra. The authors assign these peaks to $B(OH)_3$, $B_3O_3(OH)_4^-$, and $B_5O_6(OH)_4^-$.

Schott, Kretzschmar et al. (2014) performed TRLFS spectroscopic studies on the formation of An(III)-borate complexes using Eu(III) as an An(III) analog at low ionic strength (I=0.1 M) and pH < 6. Under acidic conditions, the authors conclude that strong Eu(III) hydroxo complexes can be excluded as well as the formation of any Eu(III) hydroxide solid. Using TRLFS, the authors conclude for $[B]_{tot} \lesssim 0.1$ M, Eu(III) does not form a significant concentration of borate complex. For $[B]_{tot} \gtrsim 0.1$ M, the authors report changes to the TRLFS data with increasing boron concentration, from which the authors conclude the formation of polyborate species and their complexation with Eu(III).

4.3.2. Sandia Review

Schott, Kretzschmar et al. (2014) provides NMR data that is qualitatively consistent with previous speciation schemes. That is, at low pH the NMR data provides corroborating evidence that the detectable majority of dissolved borate species is $B(OH)_3$. At higher pH and $[B]_{tot} > 0.4$, Schott, Kretzschmar et al. (2014) provide corroborating evidence of the presence of polyborate species in solution. The conclusions of Schott, Kretzschmar et al. (2014) appear reasonable and consistent with the law of mass action regarding the formation of polyborates. It is our conclusion that the precise

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speciation of the polyborates remains uncertain. Furthermore, the data in Schott, Kretzschmar et al. (2014) was obtained at relatively low ionic strength, and it's unclear how their conclusions could be affected by higher ionic strengths.

4.4. Study of Xiong, Kirkes et al. (2017)

4.4.1. Authors' Conclusions

Xiong, Kirkes et al. (2017) investigated the $Nd(OH)_3$ solubility in NaCl solutions in equilibrium with borax ($Na_2B_4O_7{\bullet}10H_2O_{(s)}$) in order to examine the effects of borate concentrations on An(III) solubility. The authors' argument is that for high-level-waste (HLW) encapsulated in borosilicate glass, the borate concentration in relevant brines could be higher than the background boron concentration due to the gradual dissolution of the borate-bearing encapsulant glass to form solid phases such as borax and tincalconite ($Na_2B_4O_7{\bullet}5H_2O$). The authors synthesized $Nd(OH)_3(s)$ to be used as the solubility controlling phase by hydrolizing $Nd_2O_3(s)$ in Parr microwave reactors. Steps were taken minimize carbonate contamination.

In NaCl solutions of mNaCl = 0.01 – 0.1 m (here mX is the molality of X in solution with units of m ≡ mol/kg H_2O), the authors observed a $m\mathrm{Nd}_{total}$ 10^{-7} – 10^{-6} m at a pmH ≈ 9.5; pmH ≡ $-\log_{10}mH^+$. The total boron concentration in these experiments is reported to be $m\mathrm{B}_{tot}$ = 0.53 m for mNaCl = 0.01 m and $m\mathrm{B}_{tot}$ = 0.52 m for mNaCl = 0.1 m. The authors report these concentrations are above their corresponding modeling predictions without boron and with boron using $AmB_9O_{13}(OH)_4(cr)$ as the solubility controlling phase (Nd(III) is considered to be an analog for Am(III)). At pmH ≈ 9, the authors report that the Nd concentrations are generally in agreement with the model using $AmB_9O_{13}(OH)_4(cr)$ as the solubility controlling phase, and slightly above that model at pmH ≈ 9.5. At pmH ≈ 6.3 the authors report the Nd concentration is in-line with that of the boron-free model.

In NaCl solutions of mNaCl = 1 – 2.1 m, and pmH ≈ 9, the authors report total Nd concentrations that are in-line with their model assuming $AmB_9O_{13}(OH)_4(cr)$ as the solubility controlling phase. That model lies above (in concentration) their corresponding model without boron. The total boron concentration for these experiments was $m\mathrm{B}_{tot}$ = 0.22 m for mNaCl = 1 m, and $m\mathrm{B}_{tot}$ = 0.18 m for mNaCl = 2.1 m.

In NaCl solutions of mNaCl = 3.2 – 5 m, pmH ≈ 6 – 9, the authors report total Nd concentrations that are consistent with their model with $AmB_9O_{13}(OH)_4(cr)$ as the solubility controlling phase at pmH ≈ 6 – 7.5, and consistent with their model without boron at pmH ≈ 9. The total boron concentration for these

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experiments was mB_{tot} = 0.2 m for mNaCl = 3.2 m, mB_{tot} = 0.16 m for mNaCl = 4.4 m, and mB_{tot} = 0.16 m for mNaCl = 5 m.

4.4.2. Sandia review

Xiong, Kirkes et al. (2017) compare their data to various hypothetical models rather than other experimental data. The solid phase $NdB_9O_{13}(OH)_{4(cr)}$ was not directly observed in the experiment, rather $AmB_9O_{13}(OH)_{4(cr)}$ was used in the model as a possible explanation of the experimental results. The experimental techniques used to minimize carbonate contamination are notable. However, no experiments were performed with a finite carbonate concentration as a "control". The results of Xiong, Kirkes et al. (2017) provide evidence of increased Nd concentrations at relatively high $[B]_{tot}$ relative to the boron-free case, which we at present do not expect under WIPP-relevant conditions.

4.5. Other References

We acknowledge that the literature review contained herein is incomplete. Other papers of interest include Mesmer, Baes et. al (1972), Farmer (1982), Lucchini, Borkowski et al. (2007), Wang and Alekseev (2011), Wang, Kosinski et al. (2013) , Yang, Wang et al. (2013), and the work of the famed minerologist Umberto Sborgi on natural boron minerology.

5. Conclusions

The studies discussed herein provide evidence that the An(III)-borate system under WIPP-relevant conditions is complex and not well understood. The studies reviewed provide evidence that An(III)-borate complexes can form. However, that same evidence does not lead us to conclude An(III)-borate complexation will be significant under WIPP-relevant conditions. The reviewed contradictory Nd solubility measurements under WIPP-relevant conditions support this position. Therefore, it is our professional judgement that insufficient data and theory exist at this time to justify, include, and defend an An(III)-borate model.

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