OFFICE OF RADIATION AND INDOOR AIR
WASHINGTON, D.C. 20460

April 17, 2024

Mr. Michael Gerle, Director
Environmental Regulatory Compliance Division
Carlsbad Field Office
U.S. Department of Energy
P.O. Box 3090
Carlsbad, New Mexico 88221-3090

Re: First set of questions on the RPPCR

Dear Mr. Gerle:

The U.S. Environmental Protection Agency (EPA) has begun its review of the U.S. Department of Energy's (DOE) submittal of the Replacement Panels Planned Change Request (RPPCR). This letter transmits the first set of Agency technical questions and comments (see enclosure). EPA would appreciate a timely response to these questions to help expedite its review.

If you have any questions concerning this request, please contact Jay Santillan at (202) 343-9343 or at Santillan.Jay@epa.gov.

Sincerely,

Tom
Peake

Digitally signed
by Tom Peake
Date: 2024.04.17
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Tom Peake
Director
Center for Waste Management and Regulations

ENCLOSURE
1. First set of technical questions on the RPPCR
2. Ongoing uncertainties related to WIPP chemical conditions and Pu oxidation state

cc: Anderson Ward, DOE CBFO
Justin Marble, DOE EM
Lee Veal, EPA
Ray Lee, EPA

Winifred Okoye, EPA
EPA Docket

Enclosure 1: First set of technical questions on the RPPCR[1]

RPPCR1-OXCUTOFF-1: Sensitivity Study Using OXCUTOFF Parameter

RPPCR1-OXCUTOFF-1a

Please perform a sensitivity calculation demonstrating how releases are affected in a 12-panel and 19-panel repository if 100% of performance assessment (PA) realizations used Pu(III) solids in equilibrium with aqueous Pu(III) consistent with previous EPA analyses (see EPA Air Docket EPA-HQ-OAR-2019-0534-0049). Please also show how releases are impacted if the ratio of realizations between Pu(III) reactions mentioned above and Pu(IV) solids in equilibrium with aqueous Pu(IV) was 75/25 and 50/50, respectively.

As stated in the December 4, 2023 technical exchange, EPA finds that while using 100% Pu(III) in the PA is conservative, it is the most defensible approach to Pu oxidation states given the current data and uncertainties available. DOE has not sufficiently addressed existing uncertainties in both the repository chemical conditions and the experiments (Beam 2023) used in the current iteration of the OXCUTOFF parameter (see Enclosure 2). Some of these uncertainties include:

- *Issues with experiments used to justify the update including questions on representativeness of the Pu concentrations, timescales, and ORP measurements taken, as well as inconsistencies with results from previously performed LANL experiments (i.e., Reed 2006, 2011)*
- *Lack of justification on the iron phases used to represent the upper bound redox conditions in the post-closure repository*
- *Uncertainty about the reactivity of $H_2(g)$ in the repository and the presence of any redox catalysts*
- *Impacts of radiolysis on redox conditions*

In light of these issues, and until they are resolved, the Agency considers the most defensible approach is the use of 100% Pu(III) for Pu oxidation states represented in the OXCUTOFF parameter. The Agency believes DOE must continue to collect experimental data, including data under longer timescales, and perform a peer review before the Agency can accept an update. See Enclosure 2 for a list of some of the ongoing questions and uncertainties EPA has identified on this topic that will need to be addressed.

Beam, J. (2023). "Plutonium Oxidation State Distribution under WIPP Relevant Conditions." Los Alamos National Laboratory report LCO-ACP-31, Revision 1. LA-UR-23-20189 (2023)

Lucchini, J., and J. Swanson. 2023. LANL ACRSP Parameter Recommendations for the CRA-2024 Performance Assessment. LCO-ACP-34. ERMS 578969. Carlsbad, NM: Los Alamos National Laboratory Carlsbad Operations.

Reed, D.R., M. Borkowski, J. Swanson, M. Richmann, H. Khaing, J.F. Lucchini, and D. Ams. 2011. Redox-controlling processes for multivalent metals and actinides in the WIPP. in Redox Phenomena Controlling Systems, M. Altmaier, B. Kienzler, L. Duro, M. Grivé, and V. Montoya (eds.) 3rd Annual Workshop Proceedings, 7th EC Recosy Cooperative Project, Karlsruhe Institute for Technology, March 2011.

Reed, D.T., J.F. Lucchini, S.B. Aase and A.J. Kropf. 2006. Reduction of plutonium(VI) in brine under subsurface conditions. Radiochimica Acta 94:591-597.

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[1] Italicized language is background information for the question or comment provided.

Schramke, J. A., Santillan, E. F. U., & Peake, R. T. 2020. Plutonium oxidation states in the Waste Isolation Pilot Plant repository. Applied Geochemistry, 116, 104561.

RPPCR1-OXCUTOFF-1b

Please provide documentation, including a timeline, on DOE's plans to conduct a peer review of the WIPP chemical conditions conceptual model prior to submission of the next CRA. DOE has emphasized the oxidative effects of radiolysis, has assumed that hydrogen gas will be unreactive in the repository, and has chosen to use magnetite as an upper bound to redox conditions in the PA to justify that 75% of realizations will use Pu(IV) solids in equilibrium with aqueous Pu(IV). This may constitute a change in the current WIPP chemical conditions conceptual models and is inconsistent with data presented in the literature (see Schramke et al. 2020).

Schramke, J. A., Santillan, E. F. U., Peake, R. T. 2020. Plutonium oxidation states in the Waste Isolation Pilot Plant repository. Applied Geochemistry, 116, 104561.

RPPCR1-PROPMIC-1: Pu(III) PROPMIC and CAPMIC values

Please provide a quantitative assessment on how releases are impacted if the recommended Pu(III) values from Swanson and Lucchini (2023) are utilized for PA vectors that showed only Pu(III) releases. Lucchini and Swanson (2023) recommend a PROPMIC and CAPMIC value of 3.52 and 9.00×10^{-7} M, respectively, for Pu(III). Their recommended values for Pu(IV) are 0.3 and 1.22×10^{-9} M, respectively, and are also the values chosen for all Pu microbial colloids in the RPPCR (Table 4-20 of Brunnell et al. 2023).

The current microbial colloids approach in the PA is that colloid parameter values are element-specific. However, the values that have been recommended in Lucchini and Swanson (2023) also provide oxidation state specific Pu PROPMIC and CAPMIC parameters. Consequently, the RPPCR PA does not utilize a bounding Pu(III) microbial colloids parameter value and could be underestimating releases.

Brunnell, S., Bethune, J., Dochert, P., Kicker, D. Kim, S., King, S. Long, J. Zeitler, T. 2023. Summary Report for the 2023 Replacement Panels Planned Change Request Performance Assessment, Revision 0. Sandia National Laboratories, Carlsbad, NM. ERMS 579729.

Lucchini, J., Swanson, J. 2023. LANL ACRSP Parameter Recommendations for CRA-2024 Performance Assessment, Revision 0. Los Alamos National Laboratories, Carlsbad, NM. LCO-ACP-34.

RPPCR1-Inventory-1: Waste Characteristics

Please provide updated tables that identify and assess waste characteristics for their impact on disposal system performance, with an analysis substantiating all decisions to exclude consideration of a waste characteristic or component.

DOE is required to identify and assess all waste characteristics for their impact on disposal system performance, and to submit an analysis substantiating decisions to exclude consideration of a waste characteristic or component [40 CFR 194.24(b)]. EPA noted during their review of the CRA-2019 that the tables identifying the impacts of waste characteristics have not been updated since CRA-2004 and contained entries inconsistent with the CRA-2019 DPA (Issue #18). EPA and DOE agreed during an October 2022 Technical Exchange meeting that DOE would provide an updated listing of all waste characteristics and components that are included or excluded from consideration along with substantiating analyses for the RPPCR.

RPPCR-Inventory-2: Breakdown of Emplaced and Temporary Storage CH and RH Waste Volumes by Waste Generator Site

Using the RPPCR inventory, please provide a table listing the unscaled volumes of emplaced and temporary storage waste volumes by waste generator site.

EPA noted during their review of the CRA-2019 that DOE provided total unscaled emplaced and temporary storage waste volumes (ATWIR 2022), but unscaled emplaced and temporary storage waste volumes were not provided by waste generator site (Issue #42).

RPPCR1-DBMAR-1: Questions related to the DBMAR.

EPA had previously communicated with DOE several questions on DOE's proposed update to calculating borehole plugging pattern frequency (see Issue 19 in EPA's CRA-2019 Issues Table, Santillan 2023). These questions were sent in a November 2, 2023 email from Jay Santillan to Anderson Ward in anticipation of an update in the RPPCR.

a. Questions Related to the 2021 DBMAR
    i. Please explain the purpose of Order No. 3324, the relationship to NMODC Order R-111-P, and the differences, if any, between the two orders with regards to extractive activities (i.e., oil & gas, potash) in the region and any implications on parameters developed by the DBDSP.
    ii. Please explain the difference between the total number of deep wells in Table 5 of the 2021 DBMAR (34,964 wells) and the total number in Table 6 of the same document (34,839 wells). EPA believes that these two numbers should be the same. EPA also notes that the deep drilling rate of 151.3 boreholes/km^2 reported in Table 6 of the 2021 DBMAR appears to be based on the 34,964 wells in Table 5 rather than the 34,839 deep wells in Table 6.
b. Questions Related to the 2022 DBMAR
    i. Section 2.0 of the 2022 DBMAR contains a statement that the deep drilling rate for 2021 was miscalculated in the 2021 DBMAR and that the miscalculation was subsequently corrected in the 2022 DBMAR, but no further explanation was provided. Please provide a more detailed explanation, including the relevant documentation, of the source of the miscalculation, its correction, and a justification of the correction. According to Table 6 of the 2022 DBMAR, fixing the miscalculation reduced the number of deep boreholes from 34,839 wells reported in the 2021 DBMAR to a recalculated value for 2021 of 29,045 wells , with no further explanation. This is a difference of 5,794 wells removed from the 2021 deep drilling calculation.
    ii. Please explain the difference between the total number of deep wells in Table 5 of the 2022 DBMAR (32,099 wells) and the total number in Table 6 of the same document (32,079 wells).
    iii. Section 2.7 of the 2022 DBMAR states that not many responses have been received from drillers to DOE's annual surveys of Castile brine encounters and that a new approach has been proposed but has not yet been formalized or implemented. Please describe this new approach and when its implementation may be expected.
c. Questions Related to DBMAR Quality Assurance

    i. Please provide descriptions and documentation of the QA/QC review and approval process as applied by DOE to the 2021 and 2022 DBMARs including copies of relevant procedures and signed and dated documentation of the technical and QA reviews.

d. Questions Related to the 2018 Oil/Gas/Water Release Incident
    i. 4.1 Section 2.0 of the 2022 DBMAR states that a 2018 oil/gas/water release incident near Mosaic Potash was brought to the attention of the DBDSP by Intrepid Potash. The text states that, while the well was being pumped, limited amounts of water and later an oil/gas/water mixture flowed from zones deep in the well through failed production and intermediate casing strings at 540′ and then into a shallow salt formation where it traveled laterally approximately one mile to a plugged and abandoned 1970s potash core hole, where it migrated to the ground surface. Please provide a more detailed analysis of the incident identifying, for example, the locations of the wells involved, the conditions under which the failure occurred, the strata through which the fluid could have migrated, the condition of the abandoned potash core hole and its plugging configuration, and the estimated volume of fluid loss.
    ii. Please provide an assessment of the potential significance of incidents such as this release of fluids to the surface via an abandoned (and plugged?) potash core hole to the performance of production wells, fluid injection wells (both waterflood and salt water disposal wells), the performance of borehole plugs generally, and the long-term performance of the WIPP.
    iii. Most of the casing failures EPA is aware of in the Permian Basin seem to be related to wells with an “open hole annulus” in the salt section or a lack of cement installed between the steel casing and the borehole. New Mexico, especially in areas with potash resources, has relatively strict well construction requirements (e.g., R-111-P) including a “salt protection string” that cements the annulus through the salt layers. Did the 2018 incident involve a well with an open hole annulus or some other configuration? Has DOE identified any wells (active or plugged) in the area surrounding WIPP with an open-hole annulus/lacking a salt protection string?
    iv. This incident, which occurred 5 years ago, appears to have been brought to the DOE’s attention through a third party rather than directly through the Department’s surveillance program. Given the potential importance of incidents such as this to WIPP performance, what can DOE do to strengthen its data collection approach in light of this incident in the future?

Santillan, J. 2023. Revised CRA-2019 Issues Table. Email from Jay Santillan to Anderson Ward, August 24, 2023.

RPPCR1-EM-1: Questions about the EM survey

a. Please provide copies of any reports or other documentation describing the Phase 1 study of the Electromagnetic (EM) survey performed in 2021 by Zonge International and justifying the selection of the synthetic target depth, thickness, and electrical conductivity used in Phase 1B. The EM survey document provided to EPA in August 2023 is identified as a Phase 1B report and reference is made to a Phase 1 study that assessed the feasibility of detecting deep brine pockets using EM arrays located close to WIPP surface facilities. Please provide a scale plan drawing showing the locations of

EM Loops 1, 2, and 3 relative to the projected locations of the underground facilities including the 19 existing and conceptual underground waste panels.

b. What accounts for the similarity in the general shape and magnitude of the WIPP site response curves for Loops 1 through 3? If the results are strongly influenced by near-surface cultural features, would these features and their effects be expected to be similar at the different loop locations?
c. The slide presentation accompanying the Phase 1B report indicated that Zonge's synthetic signal analysis of the CSEM setup is still ongoing. Please provide copies of any documentation describing this analysis and its conclusions.
d. Please provide a second scale plan drawing showing the LWA boundary, the 19-panel repository layout, and the locations of ERDA-9, WIPP-12, DOE #1, and the Culebra release points.
e. Please provide a detailed justification for applying the legacy PBRINE distribution developed by EPA for the original 10 waste panels to conceptual Panels 13 through 19 in the RPPCR PA.

RPPCR1-DATA0.FM6-1: Documentation for Hydromagnesite5424 Solubility

Please provide a short explanation of the source of the log K value for hydromagnesite5424 in the DATA0.FM6 documentation.

DOE recalculated the DATA0.FM1 hydromagnesite5424 log K value of 32.25 to a value of 31.49 for DATA0.FM4 (Sisk-Scott 2019). EPA (2022, Attachment B, Section 3.4.1) accepted the recalculated hydromagnesite5424 log K value of 31.39 during its review of DATA0.FM4, noting that the recalculated value was more internally consistent with other thermodynamic data in the database.

During development of the DATA0.FM6 database, DOE appropriately revised the hydromagnesite5424 log K value from the DATA0.FM1 value to 31.49, but this change was not included in Table IX.3.1 of Jang et al. (2021b) or the discussion of database revisions related to magnesium in Domski (2023, Section 3.1.3). The revised hydromagnesite5424 data block is, however, appropriately included in a summary listing of the database revisions to create DATA0.FM6 (Domski 2023, Appendix A) and in the DATA0.FM6 database. To avoid possible confusion regarding the DATA0.FM6 log K value for hydromagnesite5424, DOE should include a short explanation of its source in the DATA0.FM6 documentation.

Domski, P.S. 2023. An Update to the WIPP EQ3/6 Database DATA0.FM1 with the Creation of DATA0.FM6. ERMS 579370, Sandia National Laboratories, Carlsbad, New Mexico.

EPA (U.S. Environmental Protection Agency). 2022. Technical Support Document for Section 194.24, Evaluation of the Compliance Recertification Application (CRA-2019) Actinide Source Term, Gas Generation, Backfill Efficacy, Water Balance, and Culebra Dolomite Distribution Coefficient Values. EPA-HQ-OAR-2019-0534, Office of Radiation and Indoor Air, Washington, DC.

Jang, J., P. Hora, L. Kirkes, C. Miller, and L. Zhang, 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines Under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01. ERMS 576381, Sandia National Laboratories, Carlsbad, New Mexico.

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

RPPCR1-DATA0.FM6-2: XRD Examination of Post-Test Solids

For the following experiments, please provide XRD examination results. If solids characterization results are currently unavailable for these experiments, please indicate when or if reaction product characterization is planned:

a. $PbCl_2$(s)-HCl-H_2O experiments (Jang et al. 2021b, Section V.2.5).
b. $PbCl_2$(s)-NaCl-H_2O experiments (Jang et al. 2021b, Section V.3.5).
c. $PbCl_2$(s)-$MgCl_2$-H_2O experiments (Jang et al. 2021b, Section V.4.5).

Jang et al. (2021b) reported that XRD examination data for solids from some of the lead solubility experiments were not yet available at the time of the report. DOE should provide an update on the availability of the solids characterization data.

Jang, J. P. Hora, L. Kirkes, C. Miller, and L. Zhang. 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines Under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01. ERMS 576381. Sandia National Laboratories, Carlsbad, New Mexico.

RPPCR1-DATA0.FM6-3: WIPP Test Plans Cited in DATA0.FM6 Documentation

a. Please explain whether test plans TP 00-07 (Snider et al. 2004), TP 06-03 (Deng et al. 2007), and TP 14-03 (Jang 2014) are relevant to the development of DATA0.FM6 or whether these test plans should have been omitted from the listing in AP-190 and the title of Jang et al. (2021b).
b. Please explain why the data collected under TP 10-02 (Xiong 2010), TP 14-05 (Brush and Xiong 2014), TP 16-02 (Jang and Kim 2016), and TP 19-01 (Sisk-Scott 2019) were not used for the development of DATA0.FM6.

Analysis Plan AP-190 (Jang et al. 2021a) lists ten WIPP test plans for data that would be evaluated for inclusion in DATA0.FM6. However, the analysis reports by Jang et al. (2021b) and Jang and Foli (2023) list experimental data from only three of these test plans: TP 08-02 (Ismail and Nemer 2008), TP 12-02 (Xiong et al. 2015), and TP 20-01 (Kirkes and Zhang 2020). TP 00-07, TP 06-03, and TP 14-03 do not appear to be designed to collect data relevant to aqueous speciation, solids solubility, or Pitzer parameters and are not addressed elsewhere in the DATA0.FM6 documentation, except for the inclusion of test plan numbers TP 06-03 and TP 14-03 in the title of Jang et al. (2021b). Data collected under TP 10-02, TP 14-05, TP 16-02, and TP 19-01 were not reported to have been included in the development of DATA0.FM6.

Brush, L.H., and Y. Xiong. 2014. Test Plan for the Experimental Determination of the Solubilities of Iron and Lead in the Presence of Dissolved Hydrogen Sulfide Species. Test Plan 14-05. Revision 0. Sandia National Laboratories, Carlsbad, New Mexico.

Deng, H., M. Nemer, and Y. Xiong. 2007. Experimental Study of MgO Reaction Pathways and Kinetics. TP-06-03, Revision 1, Sandia National Laboratories, Carlsbad, New Mexico.

Ismail, A.E., and M.B. Nemer. 2008. Iron, Lead, Sulfide and EDTA Solubilities. Test Plan 08-02, Revision 0, Sandia National Laboratories, Carlsbad, New Mexico.

Jang, J.-H. 2014. Experimental Determination of the Existence of a Mobile Colloidal Fraction of Fe(II) Minerals in Two WIPP-Relevant Brines. Test Plan 14-03, Sandia National Laboratories, Carlsbad, New Mexico.

Jang, J., and I. Foli. 2023. Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, Boron, and Calcium in Brines. Revision 1, ERMS 578806, Sandia National Laboratories, Carlsbad, New Mexico.

Jang, J.-H., and S. Kim. 2016. Test Plan for the Measurement of the Concentration of Aqueous Complexes of Iron(II) and Organic Ligands in the Solutions of High Ionic Strength. Test Plan 16-02, Sandia National Laboratories, Carlsbad, New Mexico.

Jang, J., P. Hora, L. Kirkes, C. Miller, and L. Zhang. 2021a. Analysis Plan for Analysis Reports Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in WIPP-Relevant Brines Under Test Plans 00-07, 06-03, 08-02, 10-01, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01. AP-190, Revision 0, Sandia National Laboratories, Carlsbad, New Mexico.

Jang, J., P. Hora, L. Kirkes, C. Miller, and L. Zhang. 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01. Revision 0, ERMS 576381, Sandia National Laboratories, Carlsbad, New Mexico.

Kirkes, L., and L. Zhang. 2020. Solubility and Complexation of Lead in Non-Sulfidic Brines of WIPP Relevance. Test Plan TP 20-01, Sandia National Laboratories, Carlsbad, New Mexico.

Sisk-Scott, C. 2019. Investigation of Neodymium Hydroxide Synthesis and Solubility. Test Plan TP 19-01, Sandia National Laboratories, Carlsbad, New Mexico.

Snider, A., Y. Xiong, and N.A. Wall. 2004. Experimental Study of WIPP Engineered Barrier MgO at Sandia National Laboratories Carlsbad Facility. Test Plan TP 00-07, Revision 3, Sandia National Laboratories, Carlsbad, New Mexico.

Xiong, Y. 2010. Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility. Test Plan TP10-01, Sandia National Laboratories, Carlsbad, New Mexico.

Xiong, Y. J. Jang, and J. Icenhower. 2015. Experimental Investigation of Borate Interactions with Rare Earth Elements Under the WIPP Relevant Conditions at Sandia National Laboratories Carlsbad Facility. Test Plan TP 12-02, Sandia National Laboratories, Carlsbad, New Mexico.

RPPCR1-DATA0.FM6-4: $FeEDTA^{2-}$ Stability Constant

Please provide a review of the available stability constant data for $FeEDTA^{2-}$ to justify the value included in DATA0.FM6.

Jang (2021b) selected a $FeEDTA^{2-}$ $\log \beta^0$ *value of –16.1 from a textbook (Morel and Hering 1993) for inclusion in DATA0.FM6. This value was obtained by Morel and Hering (1993) from a review and compilation by Smith and Martell (1974). Other values have been published for this dissociation constant, including a* $\log \beta^0$ *of –14.94 determined from potentiometric measurements by Clark and Martell (1988). A thorough review of the available literature data is required to justify the* $\log \beta^0$ *included in DATA0.FM6.*

Clark, N.H., and A.E. Martell. 1988. Ferrous Chelates of EDTA, HEDTA, and SHBED. Inorganic Chemistry 27:1297-1298.

Jang, J. 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines Under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-02. ERMS 576381, Sandia National Laboratories, Carlsbad, New Mexico.

Morel, F.M.M., and J.G. Hering. 1993. Principles and Applications of Aqueous Chemistry. John Wiley and Sons.

Smith, R.M., and A.E. Martell. 1974. Critical Stability Constants, Volume 1. Plenum, New York.

RPPCR1-DATA0.FM6-5: FeCitrate$^-$ Stability Constant

Please provide a review of the ferrous iron-citrate aqueous speciation and stability constants to justify the data included in DATA0.FM6.

Jang (2021b) selected a log β^0 *value for the FeCitrate*$^-$*stability constant from the Morel and Hering (1993) textbook. Jang et al. (2021b) used this log* β^0 *and the assumption that the ferrous iron-citrate species would also include FeOHCitrate*$^{2-}$ *to calculate a log* β^0 *of 2.24 for the FeOHCitrate*$^{2-}$ *stability constant. Since publication of Morel and Hering (1993), additional investigations have been conducted to examine aqueous speciation and dissociation constants in the ferrous iron-citrate system, including Königsberger et al. (2000) and Pham and Waite (2008). A review of the available literature data is required to justify the citrate stability constants and aqueous speciation included in DATA0.FM6.*

Jang, J. 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Borate in the WIPP-Relevant Brines Under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-02. ERMS 576381, Sandia National Laboratories, Carlsbad, New Mexico.

Königsberger, L.-C., E. Königsberger, P.M. May, and G.T. Hefter. Complexation of iron(III) and iron(II) by citrate. Implications for iron speciation in blood plasma. Journal of Inorganic biochemistry 78:175-184.

Morel, F.M.M, and J.G. Hering. 1993. Principles and Application of Aqueous Chemistry. John Wiley and Sons.

Pham, A.N., and T.D. Waite. 2008. Oxygenation of Fe(II) in the presence of citrate in aqueous solutions at pH 6.0-8.0 and 25°C. Journal of Physical Chemistry A 112:643-651.

RPPCR1-DATA0.FM6-6: Cotunnite Solubility

Please document the cotunnite log K calculation from the free energy of formation data obtained from Edwards et al. (1992).

Jang et al. (2021b) cites Edwards et al. (1992) as the source for the cotunnite log K of –4.83 used to fit the cotunnite solubility data developed by the WIPP program. Edwards et al. (1992) does not provide a log K for cotunnite, but does provide the cotunnite free energy of formation from Robie et al. (1978). Documentation of the cotunnite solubility constant calculation from the free energy of formation data was not provided.

Edwards, R., R.D. Gillard, P.A. Williams, and A.M. Pollard. 1992. Studies of secondary mineral formation in the PbO-H$_2$*O-HCl system. Mineralogical Magazine 56:53-65.*

Jang, J. 2021b. Analysis Report Documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines Under TPS 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01. Revision 0, ERMS 576381, Sandia National Laboratories, Carlsbad, New Mexico.

Robie, R.A., B.S. Hemingway, and J.R. Fisher. 1978. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. U.S. Geological Survey Bulletin 1452, Washington, DC.

RPPCR1-DATA0.FM6-7: Lead-Carbonate Aqueous Speciation

Please provide a review and evaluation of lead-carbonate aqueous speciation data that has been published since Powell et al. (2009) and explain the reason the $Pb(CO_3)Cl^-$ aqueous species was omitted from the DATA0.FM6 database.

DATA0.FM6 lead-carbonate aqueous species and stability constants were obtained from Powell et al. (2009). More recent investigations have been published that including Easley and Byrne (2011) and Woosley and Millero (2017) that evaluate lead-carbonate aqueous speciation. Both Powell et al. (2009) and Woosley and Millero (2017) included the $Pb(CO_3)Cl^-$ *aqueous species, but this species was not included in DATA0.FM6. Woosley and Millero (2017) determined that this species was important in chloride media, so its inclusion in DATA0.FM6 should be considered.*

Easley, R.A., and R.H. Byrne. 2011. The ionic strength dependence of lead (II) carbonate complexation in perchlorate media. Geochimica et Cosmochimica Acta 75:5638-5647.

Powell, K.J., P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, A.-K. Leuz, S. Sjöberg, and H. Wanner. 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb2+, + OH, Cl-, CO32-, SO42-, and PO4- systems (IUPAC Technical Report). Pure and Applied Chemistry 81:2425-2476.

Woosley, R.J. and F.J. Millero. 2013. Pitzer model for the speciation of lead chloride and carbonate complexes in natural waters. Marine Chemistry 149:1-7.

RPPCR1-DATA0.FM6-8: Hydrocerussite Solubility

Jang et al. (2022) and Domski (2023) cite Edwards et al. (1992) as the source for the DATA0.FM6 hydrocerussite log K value of 2.41:

a. Please provide a review and evaluation of hydrocerussite solubility data published after the Powell et al. (2009) review to provide justification for the hydrocerussite log K value included in DATA0.FM6.

Edwards et al. (1992) provides a hydrocerussite free energy of formation calculated using solubility product values from Bilinski and Schindler (1982). However, the solubility products in Bilinski and Schindler (1982) were determined for ionic strengths of 0.1 M and 0.3 M, and Edwards et al. (1992) does not show the calculations performed to correct these values to zero ionic strength. More recent *publications (e.g., Mendoza-Flores et al. 2017 and Li et al. 2021) indicate that previously reported log K_{sp} values for hydrocerussite may overestimate lead solubilities or indicate that the log K_{sp} value is uncertain.*

b. Please use the available experimental hydrocerussite solubility data to demonstrate that DATA0.FM6-calculated lead concentrations agree with the measured data.

DOE did not demonstrate that hydrocerussite solubility calculations performed with DATA0.FM6 are in reasonable agreement with experimentally measured solubility data or discuss whether sufficient solubility data are available for these comparisons.

Bilinski, H., and P. Schindler. 1982. Solubility and equilibrium constants of lead in carbonate solutions (25°C, I = 0.3 mol dm^{-3}). Geochimica Cosmochimica Acta 46:921-928.

Domski, P.S. 2023. An Update to the WIPP EQ3/6 Database DATA0.FM1 with the Creation of DATA0.FM6. ERMS 570370, Sandia National Laboratories, Carlsbad, New Mexico.

Edwards, R., R.D. Gillard, P.A. Williams, and A.M. Pollard. 1992. Studies of secondary mineral formation in the PbO-H_2O-HCl system. Mineralogical Magazine 56:53-65.

Jang, J. 2022. The $PbCO_3$(s) - $NaHCO_3$ – Na_2CO_3 – H_2O Experiment (Revision 0): Addendum to Xiong (2015a, b). ERMS 578642, Sandia National Laboratories, Carlsbad, New Mexico.

Li , X., B. Azimzadeh, C.E. Martinez, and M.B. McBride. 2021. Pb mineral precipitation is solutions of sulfate, carbonate, and phosphate: measured and modeled Pb solubility and Pb^{2+} activity. Minerals 11:620.

Mendoza-Flores, A., M. Villalobos, T. Pi-Puig, and N.V. Martínez-Villegas. 2021. Revised aqueous solubility product constants and a simple laboratory synthesis of the Pb(II) hydroxycarbonates: Plumbonacite and hydrocerussite. Geochemical Journal 51:315-328.

Powell, K.J., P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, A.-K. Leuz, S. Sjöberg, and H. Wanner. 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} systems (IUPAC Technical Report) Pure and Applied Chemistry 81:2425-2476.

RPPCR1-DATA0.FM6-9: Cerussite Solubility

Please provide a review of the available cerussite solubility data available since the Powell et al. (2009) review to provide justification for the solubility data included in DATA0.FM6. If sufficient data are available from experimental studies that include Li et al. (2021), please provide verification calculations demonstrating that DATA0.FM6 can reasonably simulate experimentally measured cerussite solubilities.

Li et al. (2021) reported results from lead-carbonate solubility experiments that showed cerussite was precipitated from solution at pH values from 6 to 8. Their evaluation of these data showed that the available cerussite log K_{sp} values tended to overestimate cerussite solubility.

Li, X, B. Azimzadeh, C.E. Martinez, and M.B. McBride. 2021. Pb mineral precipitation in solutions of sulfate, carbonate, and phosphate: measured and modeled Pb solubility and Pb^{2+} activity. Minerals 11:620.

Powell, K.J., P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, A.-K. Leuz, s. Sjöberg, and H. Wanner. 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: the Pb^{2+} *+* OH^-*,* Cl^-*,* CO_3^{2-}*,* SO_4^{2-}*, and* PO_4^{3-} *systems (IUPAC Technical Report). Pure and Applied Chemistry 81:2425-2476.*

RPPCR1-REFERENCES-1: Document Request

Please provide the following documents:

Carrier, W D. 2003. Goodbye, Hazen; Hello, Kozeny-Carman. ASCE Journal of Geotechnical and Geoenvironmental Engineering, November, pp. 1054-1056.

U.S. Department of Agriculture Soil Conservation Service (USDA). 1991. Measurement and Estimation of Permeability of Soils for Animal Waste Storage Facility Design, Technical Note 717 prepared by South National Technical Center.

Enclosure 2: Ongoing uncertainties related to WIPP chemical conditions and Pu oxidation state

Questions and uncertainties on the ongoing Pu-239 Experiments (Beam 2023)

- What evidence is available that magnetite will form in the WIPP repository environment? What is the evidence that it is the upper limit of redox conditions?
  - How can the hydrogen overpressure and possible reactivity of H_2(g) on actinide surfaces be addressed?
  - Are the conditions in the Pu-239 plus magnetite experiments likely to be widespread?
- Are the dissolved Fe^{2+}/magnetite redox couple in the experiments pe/Eh values consistent with the ORP measurements in the experiments with magnetite?
- The table below compares ongoing Pu-239 experiments with PA baseline values. How representative are plutonium concentrations measured in the experiments to repository conditions?

Beam (2023) (Fe(II/III) + organics, pcH 9-10)	PA Baseline Concentration
[Pu] = 2×10^{-5}M	[An(III)] = 3.56×10^{-7} M to 2.14×10^{-6} M [An(IV)] = 5.50×10^{-8} M to 5.84×10^{-8} M

- Does the effect of organic ligands on plutonium concentrations in the experiments indicate that aqueous plutonium is present in the Pu(III) oxidation state?
- How will longer experimental times (>205 days) compare to experiments conducted by Reed et al. (2006, 2011) which showed that experimental results can evolve over a time period of years?
- How do the ongoing Pu-239 experiments compare to the latest PAIR inventory by year (2033, 2133, 2383,3033, 7033, 12033) in terms of ratios of:
  - Total Ci to iron mass?
  - Total Ci to iron surface area?
- How will decreasing radiolysis over the repository's 10,000 years impact plutonium oxidation states?
  - How will radiolysis and resulting redox conditions vary between panels that contain surplus plutonium and panels without surplus plutonium?

Questions and uncertainties on WIPP repository chemical conditions

- What iron phases control Pu oxidation states at WIPP?
  - How much metallic iron remains in the repository for most PA realizations?
  - If multiple iron phases are present in the repository (e.g., $Fe(OH)_2$(s) and metallic iron), what reaction(s) will control actinide oxidation states?
  - What are the impacts of radiolysis on iron phases?
- Can metals and other surfaces in the repository catalyze Pu(IV) reduction to Pu(III) via H_2(g) and other reductants?
  - What is the available literature that addresses whether surfaces such as PuO_2, metallic iron, $Fe(OH)_2$(s), magnetite, or other waste or packaging materials could catalyze the reduction reaction?
  - Can iron metal surfaces in the WIPP repository could catalyze H_2 (g) reduction of Pu similar to the limiting effects of high H_2 pressures on spent fuel leaching (e.g., Fors et al. 2009, Pastina and LaVerne 2021)?

DOE should also perform the following:

- A comprehensive literature review on Pu oxidation states that gives a review of the available plutonium oxidation states literature including the effects of
  - Isotopes/radiolysis
  - WIPP-relevant solids and aqueous species, especially iron
  - Experiment duration
- A peer review of the WIPP chemical conditions that evaluate at minimum:
  - *The actinide oxidation states assumed to be present in the repository solids and brines*. Additional experimental data have become available since the CCA. The data should be evaluated along with the potential effects of radiolysis on actinide oxidation states. Plutonium oxidation states are the most important to PA, but the expected oxidation states of neptunium and uranium should also be considered.
  - *The oxidation state analogy assumption*. The CCA conceptual model includes the assumption that actinides present in the same oxidation state will form the same aqueous species and solid phases and will be dissolved in WIPP brines at the same concentration. Modeled releases from the repository are dominated by americium and plutonium. Americium(III) concentrations are appropriately modeled using data developed from experiments with americium(III), neodymium(III), and curium(III), which are well-established analogues. Plutonium(III) concentrations, however, are also based on the americium(III) model, and plutonium(IV) concentrations are based on modeled thorium(IV) concentrations. These analogues may not accurately predict dissolved plutonium concentrations. Whether adequate experimental data are available for development of plutonium(III) and plutonium(IV) solubility models should be assessed by the peer review panel.
  - *The CCA assumption that anoxic corrosion of steel will produce* $Fe(OH)_2(s)$ *or FeS(s)*. DOE believes that magnetite is a realistic anoxic corrosion product under WIPP repository conditions. Magnetite formation instead of $Fe(OH)_2(s)$ or FeS(s) would affect both the stoichiometry of the anoxic corrosion gas generation reactions and redox conditions in the repository. The available data should be reviewed to determine the iron solid phases that will realistically form in the long-term WIPP repository.
  - *Assumed lack of* $H_2(g)$ *reactivity under repository conditions*. DOE assumes that $H_2(g)$ in the repository will not reduce Pu(IV) to Pu(III) because “there has been no direct evidence of hydrogen gas to reduce Pu(IV) to Pu(III) at temperatures close to 25°C” (Beam 2023). This assumption was not included in the peer-reviewed CCA Chemical Conditions conceptual model. Some studies have reported that $H_2(g)$ can become reactive at temperatures close to 25°C, possibly activated by ionizing radiation or mineral surfaces such as $UO_2(s)$. There is also evidence that surface-mediated reduction of plutonium to Pu(III) in the presence of iron oxides or hydroxides, including magnetite, is caused by electron transfer or electron shuttling on the iron mineral surfaces. The available data regarding the possible reactivity of $H_2(g)$ in the repository environment and the potential for iron metal and iron oxide/hydroxide or other mineral surfaces to facilitate plutonium reduction through electron transfer or electron shuttling should be reviewed.

Beam, J. (2023). “Plutonium Oxidation State Distribution under WIPP Relevant Conditions.” Los Alamos National Laboratory report LCO-ACP-31, Revision 1. LA-UR-23-20189 (2023)

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Pastina, B., & LaVerne, J. A. (2021). An Alternative Conceptual Model for the Spent Nuclear Fuel–Water Interaction in Deep Geologic Disposal Conditions. Applied Sciences, 11(18), 8566.

Reed, D.R., M. Borkowski, J. Swanson, M. Richmann, H. Khaing, J.F. Lucchini, and D. Ams. 2011. Redox-controlling processes for multivalent metals and actinides in the WIPP. in Redox Phenomena Controlling Systems, M. Altmaier, B. Kienzler, L. Duro, M. Grivé, and V. Montoya (eds.) 3rd Annual Workshop Proceedings, 7th EC Recosy Cooperative Project, Karlsruhe Institute for Technology, March 2011.

Reed, D.T., J.F. Lucchini, S.B. Aase and A.J. Kropf. 2006. Reduction of plutonium(VI) in brine under subsurface conditions. Radiochimica Acta 94:591-597.