



Department of Energy
 Carlsbad Field Office
 P. O. Box 3090
 Carlsbad, New Mexico 88221

AUG 24 2009

Ms. Elizabeth Cotsworth, Director
 Office of Radiation and Indoor Air
 U. S. Environmental Protection Agency
 1200 Pennsylvania Ave.
 Washington, DC 20460

Subject: Response to Environmental Protection Agency Letter Dated May 21, 2009 Regarding Compliance Recertification Application

Dear Ms. Cotsworth:

In response to the Environmental Protection Agency (EPA) letter dated May 21, 2009, the U. S. Department of Energy (DOE) is providing information that responds to a subset of the questions included in the enclosure to that letter. DOE determined after review of the EPA letter dated May 21, 2009, that the response to many of the items listed required additional analysis or significant effort. In order to allow time for those additional analyses, while at the same time responding to the EPA's requests in a timely manner, DOE will respond in a phased approach.

This submittal includes two enclosures. The first enclosure is a hard copy of the responses. The second enclosure (on compact disc) provides the references for documents identified in the first enclosure.

If you have any questions regarding these responses, please contact Russ Patterson at (575) 234-7457.

Sincerely,

David C. Moody
 Manager

Enclosures

cc:
 T. Peake, EPA *ED
 C. Byrum, EPA ED
 R. Lee, EPA ED
 V. Daub, CBFO ED
 R. Nelson, CBFO ED
 G. Basabilvazo, CBFO ED
 R. Patterson, CBFO ED
 S. Kouba, WRES ED
 A. Chaves, WRES ED
 T. Klein, WRES ED
 CBFO M&RC
 *ED denotes electronic distribution

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EPA Comment**1-23-1 New Compliant Performance Assessment**

EPA believes it is necessary to perform a new performance assessment to capture changes since the last recertification, as was done in 2004. The Agency also believes that even though our CRA-2009 review is not yet complete, it is necessary to notify DOE of this need as soon as possible. In particular, changes in the waste inventory since the 2006 performance assessment baseline calculations must be addressed. Specifically, the organic chemical materials have, in some cases, significantly increased and their impact (e.g., solubilities, etc.) needs to be incorporated into the CRA-2009 performance assessment calculations to verify continued compliance with our regulations. As in the past, DOE is expected to find and correct errors in the previous performance assessments. DOE is also expected to include the new Culebra hydrology model peer reviewed in 2008 and to include the most recent parameters, such as the updated drilling rate and revised borehole plugging patterns.

DOE Response

The DOE will perform a new PA, referred to as the 2009 Compliance Recertification Application Performance Assessment Baseline Calculation (PABC-2009) that captures the additional information requested by the EPA.

EPA Comment
1-23-4

AP-137 (Clayton 2008), includes the statement on pages 17 and 18 that the ligand concentrations were expected to increase from the 2004 to 2007 inventories. Clayton (2008) indicated that the effects of increased ligand concentrations would be evaluated using bounding estimates of the mean DBR and total releases at higher organic ligand concentrations. DOE (CRA-2009, Section 24.6.1) notes the existence of the 2007 inventory data, and states, "The DOE anticipates this inventory update will have only a small impact on normalized releases relative to the CRA-2009 PA, and will not be significant for compliance."

The ligand concentrations have significantly increased since the CRA-2004, PABC inventory (Table 1, below). Higher ligand concentrations, particularly EDTA, would be likely to affect actinide solubilities based on calculations conducted during review of the CRA-2004 PA. DOE should provide evidence supporting their statement that the inventory update will not have a significant impact on normalized releases.

Table 1. Changes in Reported Ligand Inventories Between the CRA-2004 PABC and 2007

Ligand	PABC and CRA-2009 Inventory (kg, Leigh 2005 ERMS 539550)	2007 Inventory (kg, DOE 2008)	Change
Acetic acid	142	14,100	99.3×
Sodium acetate	8,510	31,400	3.69×
Citric acid	1190.5	5,680	4.77×
Sodium citrate	400	2,560	6.40×
Sodium EDTA	25.6	423	16.5×
Oxalic acid	13,796	29,500	2.14×
Sodium oxalate	33,940	658	0.019×

DOE Response

Brush et al. (2008) documented the effects of increased EDTA concentration on performance assessment (PA) results. The effect on the mean complementary cumulative distribution functions (CCDFs) for the direct brine releases (DBRs) and total releases were determined at EDTA concentrations of 10 times and 100 times that used for the CRA-2004 PABC (8.14×10^{-6} M). The results of this analysis show that even at increased EDTA concentrations of 100 times that used for the CRA-2004 PABC, the CCDFs for DBRs and total releases are below the release limits. Since the expected increase in the EDTA concentration was on the order of ~10 times the concentration used for the CRA-2004 PABC, the DOE concluded that the increase in EDTA would have a small impact on the normalized releases, but would not endanger compliance and therefore was not significant for compliance. The DOE will perform a new PA that includes an updated EDTA, acetate, citrate and oxalate concentration based on the information provided in the Performance Assessment Inventory Report – 2008 (Crawford et al. 2009). The DOE will document this PA and provide it to the EPA.

References:

Crawford, B. A., Guerin, D., Lott, S. A., McInroy, B., McTaggart, J., Van Soest, G., 2009. *Performance Assessment Inventory Report - 2008*. INV-PA-08, Revision 0, LA-UR-09-02260. Carlsbad, NM: Los Alamos National Laboratory Carlsbad Operations.

Brush, L.J., Y. Xiong, J.W. Garner, T.B. Kirchner and J.J. Long. 2008. *Sensitivity of the Long-Term Performance of the WIPP to EDTA*. ERMS 548398. Carlsbad, NM: Sandia National Laboratories.

EPA Comment
1-C-3 Chemistry Issues

Appendix PA-2009, Section 7.1.1 attributes slower changes in repository pressure after 2,000 years to cessation of room closure, slowing of brine inflow, and consumption of CPR. DOE should provide information regarding whether the slower rates of microbial degradation assumed for the CRA-2004 PABC and the CRA-2009 PA result in the persistence of CPR for longer than 2,000 years in most realizations.

DOE Response

One of the many things that can affect the repository pressure is CPR degradation. Gas generation is dominated by iron corrosion. For the undisturbed scenario, on average three times the amount of gas is generated from iron corrosion compared with CPR degradation (see Section 6.3.5.3 and Table 6-9 in Nemer and Clayton 2008). Figure 1 displays the fraction of the initial CPR remaining in the repository for the undisturbed scenario. CPR persists in all of the vectors for the entire 10,000 year period. Although the CPR persists at times longer than 2,000 years, the degradation of the CPR is minimal for many vectors at longer times.

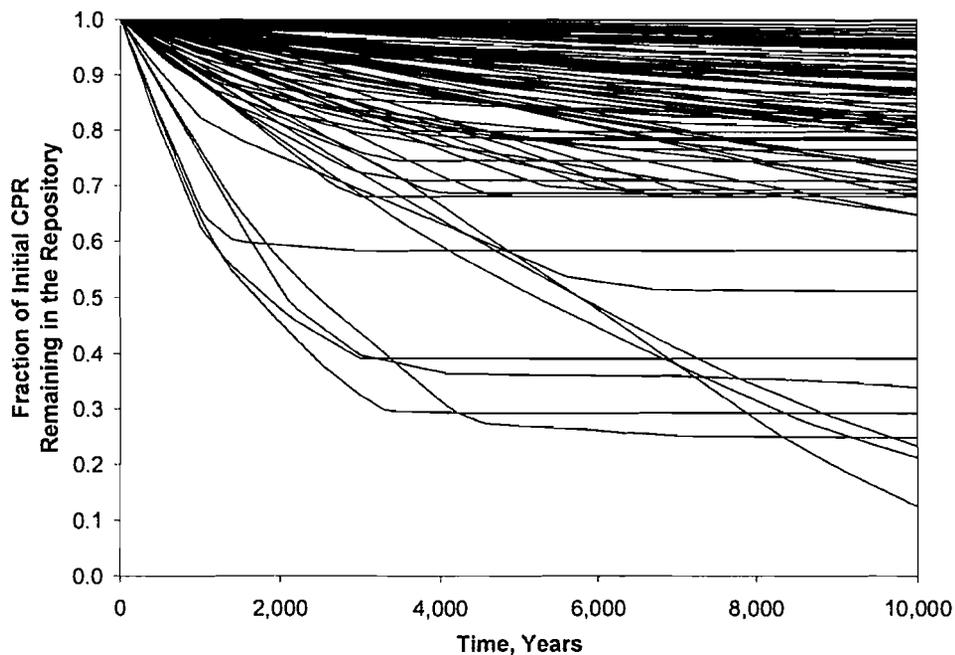


Figure 1. Fraction of initial CPR remaining in the repository as a function of time for the undisturbed scenario, replicate R1.

References:

Nemer, M. and D. Clayton. 2008. *Analysis Package for Salado Flow Modeling: 2009 Compliance Recertification Application Calculation*. ERMS 548607. Carlsbad, NM: Sandia National Laboratories.

EPA Comment**1-C-4 Chemistry Issues**

Appendix MASS-2009 and Appendix SOTERM-2009 do not address the current assumption that plastic and rubber degradation (if occurring) will take place at the same rate as cellulose degradation, when normalized to the assumed carbon content of the CPR. This assumption has been included in all WIPP performance assessments, and should have been included in the description of the CRA-2009 PA. Another issue is that this assumption may no longer be appropriate, based on: 1) WIPP-specific experimental results (Gillow and Francis 2003) showing much lower plastics and rubber degradation rates, 2) evaluations of literature data regarding plastics and rubber degradation processes that have become available since the CRA-2004 PABC (e.g., SCA 2006), 3) evidence obtained during the CRA-2004 PABC that lower microbial gas generation rates resulted in a slight increase in releases. DOE should evaluate the potential effects on repository releases of lower, more realistic microbial gas generation rates from plastics and rubber degradation.

DOE Response

CRA-2009 Appendix MASS, Section MASS-8.0, Gas Generation discusses gas generation modeling assumptions. This section of MASS states the modeling in the CRA-2009 was unchanged from that used in the CRA-2004 PABC and references Appendix PA, Section PA-4.2.5. This section of Appendix PA specifically describes the assumptions and implementation of Cellulose, Plastic and Rubber (CPR) degradation and shows that the same rate is used for C, P and R, normalized for carbon content. Additionally, Appendix MASS Section 2.0 discusses the changes made to CPR assumptions during the CRA-2004 PABC in Table MASS-3. This table references Leigh et al. 2005, Sections 2.3 and 2.4 which further detailed the implementation of the changes. Appendix SOTERM, Section SOTERM-2.4.1.1 discusses the conceptual model for biodegradation of CPR for the CCA through the CRA-2009.

In regards to comment items 1 and 2, there continues to be a high-level of uncertainty regarding P & R degradation over the 10,000-year time frame. DOE acknowledges the results presented in Gillow and Francis (2003) that show lower potential for P & R degradation however the data is not conclusive enough to justify a value for the rates. To account for the uncertainty, DOE has historically bounded the P & R degradation with a zero rate as a lower bound (for 75% of the vectors) and an equivalent degradation rate equal to the derived C degradation rate as an upper bound (for 25% of the vectors).

For comment item 3, EPA may have misinterpreted the CRA-2004 PABC results when they state that lower gas generation rates resulted in a slight increase in releases. The DOE's analysis of the CPR degradation rate changes (Nemer, Stein and Zelinski 2005; Nemer and Stein 2005) show very little difference between the two PA's intermediate results but did not calculate changes in releases. Pressures tend to increase more slowly in the CRA-2004 PABC due to the new lower gas generation rates, which may reduce

Spallings and Direct Brine Releases that occur at short times. The DOE does not believe that the reduction in the gas generation rates increases releases.

With respect to whether the approach is still appropriate, if the rates were changed to be specific to the carbon source type, the impact of reducing the P&R degradation rate(s) would be a minor reduction in the gas volumes generated. The gas generation from iron corrosion is on average three times greater than that from CPR degradation. This is shown in Table 6-9 (undisturbed scenario) and in Table 6-15 (disturbed scenario) in Nemer and Clayton (2008). Furthermore, the P and R comprise ~68% of the total equivalent carbon but are only modeled to contribute to potential gas generation in 25% of the vectors and since the C rate would not change, this further reduces the impact.

DOE acknowledges the February 2009 EPA letter where they "recommended a more accurate representation of plastic and rubber rate degradation be included in performance assessment calculations." Further the attachment to this letter stated in its conclusion that, "additional evaluation would be required to determine whether such changes [P&R rate change]...are advisable." Because there is great uncertainty in defining P&R degradation in the WIPP environment from short-term experiments and extrapolating them to a 10,000-year rate, the DOE cannot at this time justify a credible change to the rate. The DOE intends to continue its analysis of P&R degradation and may present a planned change request when adequate justification is developed to defend such a change.

References:

Edwards, J. 2009. EPA letter from J. Edwards, Radiation Protection Division Acting Director to D. Moody, DOE Carlsbad Field Office Manager submitting report entitled, *Verification of the Waste Isolation Pilot Plant Conceptual Models*, February 3, 2009

Gillow, J.B., and A.J. Francis. 2003. *Microbial Gas Generation under Expected Waste Isolation Pilot Plant Repository Conditions* (Rev. 0, October 6). ERMS 532877. Upton, NY: Brookhaven National Laboratory.

Nemer, M., and D. Clayton. 2008. *Analysis Package for Salado Flow Modeling: 2009 Compliance Recertification Application Calculation*. ERMS 548607. Carlsbad, NM: Sandia National Laboratories

Nemer, M. J. Stein. 2005. *Analysis Package for BRAGFLO: 2004 Compliance Recertification Application Performance Assessment Baseline Calculation*. ERMS 540527. Carlsbad, NM: Sandia National Laboratories.

Nemer, M., J. Stein, and W. Zelinski. 2005 *Analysis Report for BRAGFLO Preliminary Modeling Results With New Gas Generation Rates Based on Recent Experimental Results*. ERMS 539437. Carlsbad, NM: Sandia National Laboratories.

S. Cohen and Associates (SCA). 2006. *Preliminary Review of the Degradation of Cellulosic, Plastic, and Rubber Materials in the Waste Isolation Pilot Plant, and Possible Effects on Magnesium Oxide Safety Factor Calculations (September 11)*. Vienna, VA: SCA.

EPA Comment
1-C-5 Chemistry Issues

It is stated in Appendix PA-2009, Section 2.3.1, that water is neither created nor consumed by microbial reactions. This assumption has been included in the peer reviewed gas generation conceptual model since the CCA. However, new evidence, such as EQ3/6 modeling carried out by Wolery and Sassani (2007), has indicated that CPR degradation could result in significant increases in the amount of brine. DOE should address whether including potential production of water by CPR degradation and consumption of water by brucite hydration and hydromagnesite persistence might significantly affect predictions of repository performance.

DOE Response

Currently it is assumed that water is neither created nor consumed by microbial reactions. Furthermore, the water production/consumption reactions with Mg-based minerals have also been omitted. The effect on repository performance by including potential water producing or consuming reactions (repository water balance) depends upon the condition of the repository. When small amounts of brine enter a dry repository, it will be consumed by the MgO and remain dry, until all of the MgO has been consumed. When the repository is dry, it is assumed that microbial reactions have ceased. The effect on repository performance would be minimal for this case. If a large amount of brine enters the repository that fills the repository, (such as an intrusion into a pressurized brine pocket,) all the MgO would be hydrated and the microbial reactions would proceed. The microbial reactions could produce water and, depending on the ratio of the water produced compared with the amount of brine that entered the repository, might affect the repository performance.

The DOE acknowledges the February 2009 EPA letter where they "recommended that it is necessary and appropriate to include all water balance considerations in the performance assessment calculations." Furthermore, the attachment to this letter stated in its conclusion that, "additional evaluation would be required to determine whether such changes in the repository water balance...are advisable." Because of the uncertainty in the implementation of including the potential production of water by CPR degradation and consumption of water by brucite hydration and hydromagnesite persistence in the WIPP environment, the DOE cannot at this time justify a change to the current implementation. The DOE intends to continue its analysis of the repository water balance and may present a planned change request when adequate justification is developed to defend such a change.

References:

Edwards, J. 2009. EPA letter from J. Edwards, Radiation Protection Division Acting Director to D. Moody, DOE Carlsbad Field Office Manager submitting report entitled, *Verification of the Waste Isolation Pilot Plant Conceptual Models*, February 3, 2009

EPA Comment
1-C-15 Chemistry Issues

In Appendix SOTERM-2009, Table SOTERM-21, the parameter descriptions for PHUMCIM and PHUMSIM indicate "actinide solubilities are inorganic only (complexes with man-made organic ligands are not important); solubilities were calculated assuming equilibrium with Mg-bearing minerals (brucite and magnesite)." DOE should correct these statements to clarify that organic ligands were considered during calculation of the solubilities used with these proportionality constants for the CRA-2004 PABC, and that the solubilities were calculated assuming equilibrium with brucite and hydromagnesite.

DOE Response

The description for PHUMCIM in Appendix SOTERM-2009, Table SOTERM-21 should be changed to "Proportionality constant for concentration of actinides associated with mobile humic colloids; in Castile brine; actinide solubilities include organics (complexes with man-made organic ligands); solubilities are calculated assuming equilibrium with Mg-bearing minerals (brucite and hydromagnesite)."

The description for PHUMSIM in Appendix SOTERM-2009, Table SOTERM-21 should be changed to "Proportionality constant for concentration of actinides associated with mobile humic colloids; in Salado brine; actinide solubilities include organics (complexes with man-made organic ligands); solubilities are calculated assuming equilibrium with Mg-bearing minerals (brucite and hydromagnesite)."

[This will be captured as an errata change to Appendix SOTERM.]

EPA Comment**1-C-18 Chemistry Issues - Uncertainties Regarding the Conversion of Hydromagnesite to Magnesite**

In Appendix MgO-2009, Section 4.2.2, DOE claims that hydromagnesite will completely convert to magnesite during the 10,000 year WIPP regulatory time period. However, DOE's evaluation of the likely conversion of hydromagnesite to magnesite ignores information about this issue presented in SCA (2008). As part of a thorough evaluation of the likely conversion rate for hydromagnesite to magnesite, SCA (2008) cited data from Vance et al. (1992) that showed hydromagnesite can persist for as long as 6,200 years. In addition, DOE does not consider that slow CPR degradation will result in continuous brucite carbonation during the 10,000-year regulatory period, rather than hydromagnesite formation that occurs only for a short time following repository closure.

Consequently, even if hydromagnesite formed in the repository converts to magnesite within a few thousand years, hydromagnesite is likely to remain in the repository and would be likely to influence carbon dioxide fugacity for the entire 10,000-year regulatory period. DOE should revise this discussion to show that hydromagnesite is likely to be present in the backfill throughout the WIPP regulatory period.

DOE Response

The EPA has specified that the brucite-hydromagnesite (5424) carbonation reaction (U.S. DOE, 2009, Appendix MgO, Subsection MgO-4.2.1, Equation MgO.7) be used to buffer the CO₂ fugacity (f_{CO_2}) for all compliance-related actinide-solubility calculations since the CCA PAVT (Trovato, 1997; U.S. EPA, 1998) and the DOE has always complied with this specification. The effects on f_{CO_2} , actinide solubilities, and performance assessment (PA) of the DOE's possibly-conservative use of the brucite-hydromagnesite (5424) carbonation reaction instead of the brucite-magnesite reaction (U.S. DOE, 2009, Appendix MgO, Subsection MgO-4.2.2, Equation MgO.8) to buffer f_{CO_2} are described below.

However, the DOE maintains that it is still unclear whether hydromagnesite (5424) will persist or convert to magnesite during the 10,000-year WIPP regulatory period. If hydromagnesite (5424) persists, the brucite-hydromagnesite (5424) carbonation reaction would buffer f_{CO_2} at 3.14×10^{-6} atm in GWB (Salado brine) or ERDA-6 (Castile brine) (U.S. DOE, 2009, Appendix MgO, Subsection MgO-5.1, Tables MgO-7 and MgO-8). If hydromagnesite (5424) converts to magnesite, the brucite-magnesite carbonation reaction would buffer f_{CO_2} at 1.20×10^{-7} atm in GWB or 1.23×10^{-7} atm in ERDA-6 (U.S. DOE, 2009, Appendix MgO, Subsection MgO-5.1, Tables MgO-7 and MgO-8, respectively).

SCA (2008) cited a study by Vance et al. (1992) that demonstrated that hydromagnesite has persisted for 6,200 years in Chappice Lake, a shallow, saline lake in southeast Alberta, Canada. The DOE does not disagree that hydromagnesite has persisted for thousands of years under the conditions characteristic of this lacustrine environment.

However, these conditions are probably not applicable to the possible persistence of hydromagnesite in the WIPP. Chappice Lake is shallow, so its CO₂ fugacity could be controlled by equilibrium with atmospheric CO₂. For example, distilled water in open containers becomes mildly acidic from dissolution of atmospheric CO₂ and formation of carbonic acid. (This does not imply that the waters of Chappice Lake are acidic, only that dissolution of atmospheric CO₂ would be expected.) From 6,200 years ago until the beginning of the Industrial Revolution, the CO₂ concentration of the atmosphere increased from about 270 ppm to roughly 285 ppm (Ruddiman, 2007, Fig. 1.b). Therefore, the average CO₂ concentration during this period was about 275-280 ppm and the average f_{CO_2} was about 3×10^{-4} atm, roughly 100-to-2500 times higher than that expected in the WIPP (see above). Furthermore, ground water flows into Chappice Lake along with surface runoff, so the CO₂ fugacity of this lake could be even higher than that characteristic of equilibrium with atmospheric CO₂. Moreover, the MgO and brucite carbonation experiments carried out for the WIPP Project have shown that the metastable Mg carbonate phases that nucleate, grow, and perhaps even persist depend on the CO₂ fugacity of these experiments (U.S. DOE, 2009, Appendix MgO, Subsection MgO-4.2.1). Therefore, the persistence of hydromagnesite in the sediments of Chappice Lake is not an analog that can be applied to the WIPP.

Slow microbial consumption of cellulosic, plastic and rubber (CPR) materials in the WIPP does indeed result in continuous production of CO₂ and continuous production of hydromagnesite throughout the 10,000-year regulatory period *in some PA vectors*. In other vectors, however, initially rapid CO₂ production followed by early cessation of microbial consumption of CPR materials leaves ample time for essentially complete conversion of hydromagnesite to magnesite.

Therefore, it is still unclear whether hydromagnesite will persist or convert to magnesite during the WIPP regulatory period. The resulting uncertainty in the CO₂ fugacity in the repository (3.14×10^{-6} atm in the case of hydromagnesite; or 1.20×10^{-7} atm or 1.23×10^{-7} atm for magnesite, depending on the brine) could be incorporated in the actinide-solubility calculations in a manner analogous to that of Vugrin et al. (2007), who revised the analysis of the uncertainties inherent in the MgO excess factor by Vugrin et al. (2006). Among other revisions, Vugrin et al. (2007) randomly sampled the uncertainty in the number of moles of CO₂ consumed per mole of MgO (0.8 mole of CO₂ per mole of hydromagnesite (5424) or 1 mole of CO₂ per mole of magnesite).

However, the EPA has specified that the brucite-hydromagnesite (5424) reaction be used to buffer the CO₂ fugacity for all compliance-related actinide-solubility calculations since the CCA PAVT (Trovato, 1997; U.S. EPA, 1998). This specification is reasonable because, to the extent that hydromagnesite converts to magnesite during the regulatory period, it adds some additional conservatism to PA in the case of the +IV actinides. The solubilities predicted for Th(IV), U(IV), Np(IV), and Pu(IV) in GWB with organic ligands for the CRA-2004 PABC were 4.57×10^{-8} M for the brucite-magnesite carbonation reaction and 5.64×10^{-8} M for the brucite-hydromagnesite (5424) buffer (Brush, 2005, Table 5, FMT Runs 5 and 7). Those predicted for ERDA-6 with organic

ligands were 4.84×10^{-8} M for the brucite-magnesite buffer and 6.79×10^{-8} M for the brucite-hydromagnesite (5424) buffer (Brush, 2005, Table 5, FMT Runs 9 and 11).

On the other hand, the CO₂ fugacity does not affect the solubilities of the +III actinides significantly. The solubility predicted for Am(III) and Pu(III) in GWB with organic ligands for the CRA-2004 PABC was 3.87×10^{-7} M for both the brucite-magnesite and the brucite-hydromagnesite (5424) carbonation reactions. Therefore, increasing the CO₂ fugacity from 1.20×10^{-7} atm to 3.14×10^{-4} atm does not change the solubility of Am(III) and Pu(III) in GWB at all. The solubilities predicted for Am(III) and Pu(III) in ERDA-6 with organic ligands were 2.87×10^{-7} M for the brucite-magnesite buffer and 2.88×10^{-7} M for the brucite-hydromagnesite (5424) buffer (Brush, 2005, Table 5, FMT Runs 5, 7, 9, and 11). Clearly, the slight difference in the solubility of Am(III) and Pu(III) in ERDA-6 from 2.87×10^{-7} M to 2.88×10^{-7} M would have no discernible effect on the mean complementary cumulative distribution functions for direct brine releases or for total releases, and thus would have no discernible effect on the long-term performance of the WIPP with respect to the containment requirements.

The following statement should be added at the end of Subsection 4.2.2 of Appendix MgO-2009 to clarify the text in this subsection: “Based on the evidence discussed above, the DOE concludes that it is still unclear whether hydromagnesite will persist or convert to magnesite during the 10,000-year WIPP regulatory period. However, the EPA has specified that the brucite-hydromagnesite (5424) reaction be used to buffer the CO₂ fugacity for compliance-related actinide-solubility calculations since the CCA PAVT (Trovato, 1997; U.S. EPA, 1998).”

[This will be captured as an errata change to Appendix MgO.]

References

Ruddiman, W.F. 2007. “The Early Anthropogenic Hypothesis: Challenges and Responses” *Reviews in Geophysics*. Vol. 45, no. 4, RG4001, doi:10.1029/2006RG000207, 37 pp.

SCA (S. Cohen and Associates). 2008. “Review of MgO-Related Uncertainties in the Waste Isolation Pilot Plant.” U.S. EPA contractor report, January 24, 2008. Vienna, VA: S. Cohen and Associates.

Trovato, E.R. 1997. Untitled letter to G. Dials with enclosures (parameters that are no longer of concern and parameters that DOE must use for the PAVT), April 25, 1997. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air. ERMS 247206.

U.S. DOE. 2009. *Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application for the Waste Isolation Pilot Plant*. DOE/WIPP 09-3424. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

U.S. EPA. 1998. "Technical Support Document for Section 194.24: EPA's Evaluation of DOE's Actinide Source Term." EPA Air Docket A-93-02-V-B-17. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air.

Vance, R.E., R.W. Mathewes, and J.J. Clague. 1992. "7000 Year Record of Lake-Level Change on the Northern Great Plains: A High-Resolution Proxy of Past Climate," *Geology*. Vol. 20, no. 10, 879-992.

Vugrin, E.D., M.B. Nemer, and S.W. Wagner. 2006. "Uncertainties Affecting MgO Effectiveness and Calculation of the MgO Effective Excess Factor," Rev. 0. Analysis report, November 17, 2006. Carlsbad, NM: Sandia National Laboratories. ERMS 544781.

Vugrin, E.D., M.B. Nemer, and S.W. Wagner. 2007. "Uncertainties Affecting MgO Effectiveness and Calculation of the MgO Effective Excess Factor," Rev. 1. Analysis report, June 26, 2007. Carlsbad, NM: Sandia National Laboratories. ERMS 546377.

EPA Comment**1-C-19 Chemistry Issues - Differences between the Actinide Solubilities Calculated for the CRA-2004 PA and the CRA-2004 PABC**

In Appendix MgO-2009, Section 5.1, DOE states that the actinide solubilities in WIPP brines calculated for the CRA-2004 PA and CRA-2004 PABC differed because of "changes in the thermodynamic databases for the An(III), An(IV), and An(V) models." The thermodynamic database for the An(IV) model changed between these two PA calculations when the chemical potential (μ^0/RT) for $\text{Th}(\text{OH})_4(\text{aq})$ was revised. On the other hand, the An(III) and An(V) solubility results changed because of a recalculation of ligand concentrations. EPA was not informed of any changes to the thermodynamic data for the An(III) and An(V) oxidation states. DOE should either correct this statement or document the revised thermodynamic data.

DOE Response

The statement that, "The An(III), An(IV), and An(V) solubilities predicted for the CRA-2004 PA and PABC calculations are different for both brines because of changes in the thermodynamic databases for the An(III), An(IV), and An(V) models between these calculations" (U.S. DOE, 2009, Appendix MgO, Subsection 5.1, p. MgO-32), is incorrect. It should state, "The An(III) solubilities predicted for the CRA-2004 PA and PABC calculations are different for both brines because of an increase in the concentration of EDTA (compare Brush and Xiong, 2005, Table 4, columns labeled "CRA-2004 PA" and "PABC").* The An(IV), solubilities predicted for the CRA-2004 PA and PABC calculations are different for both brines because of changes in the thermodynamic database for An(IV). The An(V) solubilities predicted for the CRA-2004 PA and PABC calculations are different for both brines because of the inclusion of the solubility-limiting phase whewellite ($\text{Ca-oxalate}\cdot 2\text{H}_2\text{O}$) in the FMT database, which decreased the dissolved oxalate concentration despite an increase in the concentration of oxalate prior to precipitation of whewellite (compare Brush and Xiong, 2005, Table 4, columns labeled "CRA-2004 PA" and "PABC")."

*[This will be captured as an errata change to Appendix SOTERM.]

References

Brush, L.H., and Y.-L. Xiong, 2005. "Calculation of Organic-Ligand Concentrations for the WIPP Performance-Assessment Baseline Calculations." Analysis report, May 4, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539635.

U.S. DOE. 2009. *Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application for the Waste Isolation Pilot Plant*. DOE/WIPP 09-3424. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

EPA Comment**1-C-20 Chemistry Issues - Uncertainties in the Compositions of CPR Materials**

In the discussion of MgO uncertainties (Appendix MgO-2009, Section 6.2.4.4), DOE does not include the uncertainties associated with the chemical composition of the cellulose, plastics, and rubber in the WIPP inventory. DOE should acknowledge this uncertainty in the discussion.

DOE Response

The DOE did not include uncertainties associated with the chemical compositions of the cellulosic, plastic and rubber (CPR) materials in the WIPP inventory in its discussion of the 2006 assessment of the uncertainties related to the MgO excess factor (U.S. DOE, 2009, Appendix MgO, Subsection 6.2.4.4, pp. MgO-68 to MgO-77; Vugrin et al. 2006) or in its discussion of the 2007 revision of this assessment (U.S. DOE, 2009, Appendix MgO, Subsection 6.2.4.5, pp. MgO-77 to MgO-79; Vugrin et al., 2007).

The DOE has used the formula $C_6H_{10}O_5$ for cellulosic materials and the equation,

$$\text{total cellulose (kg)} = \text{actual cellulose (kg)} + 1.7 \text{ plastics (kg)} + \text{rubbers (kg)} \quad (1)$$

to convert the masses of plastic and rubber materials in the WIPP inventory to the C-equivalent mass of cellulosic materials in the inventory (Wang and Brush, 1996, Equation 6, p. 4; and Appendix I.5, p. 14) since the WIPP CCA PA.

The following statement should be added at the end of the first paragraph of Subsection 6.2.4.4.1 of Appendix MgO-2009, “Vugrin et al. (2006) did not include uncertainties associated with the chemical compositions of the CPR materials in the WIPP inventory. However, the DOE acknowledges that there are uncertainties associated with the chemical compositions of these materials.”

[This will be captured as an errata change to Appendix MgO.]

References

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Wang, Y. and L.H. Brush. 1996a. "Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment." Memorandum to M.S. Tierney, January 26, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 231943.

EPA Comment
1-C-21 Chemistry Issues

Appendix PA-2009, Table PA-10 does not include units for the concentrations, which should be moles/L.

DOE Response

The units moles/L should be added to Appendix PA-2009, Table PA-10.

[This will be captured as an errata change to Appendix PA.]

EPA Comment
1-C-22 Chemistry Issues

Appendix PA-2009, Section 4.9 includes a statement that releases are controlled almost entirely by direct releases to the surface as cuttings, cavings, and spallings. DOE should correct this statement to include cuttings, cavings, and direct brine release, as explained in Appendix PA-2009, Section 9.0.

DOE Response

In Appendix PA-2009, Section 4.9, page PA-162, line 2, the phrase “cuttings, cavings, and spallings” should be changed to “cuttings, cavings, and direct brine releases”.

[This will be captured as an errata change to Appendix PA.]

EPA Comment
1-C-23 Chemistry Issues

To facilitate EPA's technical review, DOE should provide EPA with copies of all FMT input and output files used to update the actinide solubility uncertainty analysis (Comment 1-23-3), evaluations of the effects of ligand inventory changes on actinide solubility (Comment 1-23-4), or any other solubility calculations performed for the CRA 2009 PABC. In addition, if the FMT database is modified from the version used for the CRA-2004 PABC (FMT_050405.CHEMDAT), DOE should provide the revised database and documentation of all changes.

DOE Response

The actinide solubility uncertainty analysis is currently under way. Upon completion of the analysis, the FMT input and output files will be provided to the EPA. The input and output files used in the evaluation of the effects of ligand inventory changes on actinide solubility (Brush et al. 2008) are on the attached CD. The FMT database used for the ligand inventory analysis and the solubility uncertainty analysis is the same version used for the CRA-2004 PABC, therefore, no revised database or documentation of database modifications will be provided.

References:

Brush, L.J., Y. Xiong, J.W. Garner, T.B. Kirchner and J.J. Long. 2008. *Sensitivity of the Long-Term Performance of the WIPP to EDTA*. ERMS 548398. Carlsbad, NM: Sandia National Laboratories.