UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
AIR AND RADIATION

FEB 22 2010

Dave Moody, PhD.
Manager, Carlsbad Field Office
U.S. Department of Energy
P.O. Box 3090
Carlsbad, NM 88221-3090

Dear Dr. Moody:

The U.S. Environmental Protection Agency (EPA) received the U.S. Department of Energy's (DOE) 2009 Compliance Recertification Application for the Waste Isolation Pilot Plant (WIPP) on March 24, 2009. On May 21, 2009, July 16, 2009, and October 19, 2009 we provided you with comments related to completeness of the Compliance Recertification Application documentation. In our ongoing review, we have identified additional information needed to constitute a complete application.

The enclosed completeness comments and questions focus on repository chemistry related to the +III oxidation state actinides, with additional questions on thorium aqueous speciation and colloid formation. In particular, we have closely examined a report titled *Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendation* by Borkowski et al. (2008). The authors appear to have measured greater actinide +III solubilities than would be predicted by the FMT chemical modeling computer code used in the performance assessment.

Some aspects of the neodymium(+III) solubility experiments discussed in Borkowski et al. raise questions about the applicability of the results to WIPP repository conditions. One example is the use of $NdOHCO_3(s)$ as the starting material in the undersaturation experiments when $Nd(OH)_3(s)$ is likely to be the stable solid phase under WIPP conditions. Other aspects of the experiments that make the applicability of the results to WIPP conditions somewhat uncertain include the lack of data for GWB brine at pcH values expected in repository brines and the absence of data about final carbonate concentrations in some of the experiments. A number of the enclosed completeness comments and questions focus on these potential issues; we need to understand the implications of the Borkowski et al. results and their potential impact on performance assessment predictions.

Our review of the 2009 Compliance Recertification Application will continue as we receive additional information. If you have any questions regarding these issues, please contact Tom Peake at (202) 343-9765.

Sincerely,

Thomas E Kelly

Tom Kelly, Acting Director
Office of Radiation and Indoor Air

cc: Electronic Distribution
Frank Marcinowski, DOE/EM
Russ Patterson, DOE,CBFO
Steve Zappe, NMED
Nick Stone, EPA Region 6
Jonathan Edwards, EPA HQ
EPA Docket

Enclosure: CRA-2009 Fourth (4) Completeness Letter

Chemistry (C) Issues

Neodymium(III) Chemistry Review Comments

These supplemental completeness comments result from review of the Borkowski et al. (2008) report on solubility experiments with neodymium(III) in NaCl, GWB and ERDA-6 brines. A conference call was held between an EPA contractor on January 19, 2010 with Los Alamos National Laboratory staff to discuss WIPP repository chemistry and is referenced in these completeness comments. The focus of this conference call was to discuss the potential effects of the neodymium(III) solubility data on the actinide solubilities modeled for WIPP PA and, in particular, early questions related to Borkowski et al. (2008). Discussion topics included the extrapolation of the neodymium(III) solubility results in GWB at lower pcH to the higher pcH conditions expected in the WIPP repository, aqueous speciation of +III actinides in WIPP brines including the effects of borate, the effects of higher organic ligand concentrations on the total mobilized +III actinides calculated for the CRA-2009 PABC, and the status of the two documents that had not yet been received by EPA (Completeness Comment 1-23-2b and 1-23-2c). Some clarifying comments to EPA's first completeness letter comment 1-23-6 were provided in a January 25, 2010 email to DOE. Additional completeness comments regarding thorium(IV) aqueous speciation and colloid formation are provided here as the result of an initial review of DOE's response provided on November 25, 2009 to Completeness Comment 1-23-3.

4-C-26. On page 12 of Borkowski et al. (2008), the americium-borate species is represented as $AmB(OH)_4^{2+}$, but on page 46, the neodymium-borate species are represented as $NdB_4O_7^+$ and $Nd(B_4O_7)_2^-$. DOE should address whether there is any basis for assuming the identity of the species (borate or tetraborate) that would form, and the anticipated effects the formation of such a species would have on neodymium solubility in GWB and ERDA-6 brines.

4-C-27. DOE should address whether transformation of the initial $NdOHCO_3(s)$ in their experiments to $Nd(OH)_3(s)$ could have substantially changed the carbonate concentrations during the undersaturation experiments, including whether it was possible that the initial spike addition was relatively unimportant and the total carbonate at the end of the experiments could have been completely controlled by dissolution of the neodymium hydroxycarbonate solid.

4-C-28. Figure 3-4 of Borkowski et al. (2008) shows the solution concentrations of americium(III) as a function of pcH in the absence and presence of CO_2, and the data are attributed to Kim et al. (1984). However, examination of this reference shows that the reported solubility experiments were carried out in a CO_2-free system. DOE should confirm that the data source is Bernkopf and Kim (1984) or otherwise clarify the data source. DOE should also clarify whether other references to Kim et al. (1984), for example in the final paragraph of page 37, should in fact be Bernkopf and Kim (1984).

4-C-29. Figure 4-7 of Borkowski et al. (2008) shows the neodymium concentration as a function of time in the undersaturation experiments with GWB and carbonate. The data in this figure show that

neodymium concentrations increased rapidly after the start of the experiments, then gradually decreased over time toward the final concentrations in the experiments. These data indicate that in the GWB experiments with carbonate, the steady-state concentration was approached from oversaturation in the "undersaturation" experiments as well as in the oversaturation experiments. DOE should address whether this phenomenon was observed in the ERDA-6 and 5 M NaCl undersaturation experiments with carbonate.

4-C-30. On page 46 of Borkowski et al. (2008), it is stated that the addition of carbonate to modeling calculations performed with Geochemists Workbench led to a slight increase in the neodymium concentration because of the formation of the $Nd_2(CO_3)_2^{2+}$ complex at pcH greater than 9. The analogous americium(III) species [$Am_2(CO_3)_2^{2+}$] is not included in the FMT database. DOE should discuss whether the $Am_2(CO_3)_2^{2+}$ species should be included in the FMT database.

4-C-31. The formation of significant actinide(III)-borate species appears to be previously unreported. DOE should investigate whether there are any literature data, for example related to dissolution of borosilicate glasses containing +III actinides, that would support or contradict the formation of such species. A publication that might be considered, among others, is Rai et al. (1992).

4-C-32. On page 29 of Borkowski et al. (2008), it was stated that XRD analysis of $NdOHCO_3(s)$ synthesized for the purpose of the experiments confirmed the "predominance" of a neodymium mixed hydroxy-carbonate phase. DOE should discuss whether any XRD peaks consistent with $Nd(OH)_3(cr)$ or other possible solid phases were observed in the XRD pattern, i.e., whether it is possible that the solids synthesized for the experiments contained a mixture of phases. If the solids in the undersaturation experiments could have been a mixture of phases, DOE should address the expected impact on the solubility results.

4-C-33. On page 35 of Borkowski et al. (2008), it was stated that neodymium solubility was studied in 5 M NaCl at 10^{-2} M total carbonate concentration. DOE should explain why this carbonate concentration was not listed in the test matrices (Tables 4-2 or 4-4).

4-C-34. Because the data in Figure 4-5 (neodymium(III) solubility in 5 M NaCl in the presence of carbonate) were obtained over different time periods and had different initial carbonate concentrations, it is difficult to interpret these data. DOE should provide a table showing whether the experiments were from undersaturation or oversaturation, the initial pcH and carbonate concentration, experiment duration at time of sampling, sample pcH and neodymium concentrations for the data in this figure.

4-C-35. A review of the recent literature regarding aqueous thorium speciation in carbonate solutions indicates that the speciation selected by the OECD critical review (Rand et al. 2009) is the most consistent with the available data. The thorium-carbonate and -hydroxycarbonate speciation and stability constants in the FMT database differ from the Rand et al. (2009) review and compilation and should be revised. However, such a revision of the FMT database will involve a significant effort because Pitzer parameters are unavailable for the thorium-hydroxycarbonate species identified by Rand et al. (2009) as the most likely significant species, including $ThOH(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4CO_3^{2-}$. Because of the low CO_2 fugacities established

by the brucite-hydromagnesite buffer in the WIPP repository, it is uncertain whether replacing the current thorium-hydroxycarbonate and -carbonate speciation and stability constants in FMT with the revised thorium-hydroxycarbonate and -carbonate species from Rand et al. (2009) would significantly affect calculated thorium concentrations under WIPP repository conditions. In DOE's response to Completeness Comment 1-23-3, Borkowski and Richmann (2009) indicated that the FMT-calculated thorium concentrations remain conservative. However, no quantitative evaluation was presented to support this assertion.

As part of their evaluation of actinide solubility uncertainties for the CRA-2009 PABC, DOE has presumably used FMT to calculate expected thorium concentrations in carbonate-bearing solutions in the experiments reported by Ősthols et al. (1994), Rai et al. (1995), Felmy et al. (1997), Altmaier et al. (2005) and Altmaier et al. (2006). DOE should examine whether the thorium concentrations predicted by FMT modeling consistently differ from the reported experimentally measured thorium concentrations in carbonate-bearing solutions. Realistic or conservative predicted +IV actinide solubilities would be indicated if the FMT-predicted concentrations are consistently the same or higher than the concentrations measured in the experiments with carbonate. For the CRA-2014 PA, DOE should evaluate the available data in an effort to derive Pitzer parameters for the thorium-hydroxycarbonate species $ThOH(CO_3)_4^{5-}$ $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4CO_3^{2-}$ and update the thorium aqueous speciation data in the FMT database.

4-C-36. An experimental investigation reported by Altmaier et al. (2004) has indicated that intrinsic thorium colloids (eigencolloids) can form and remain stable at high ionic strength (up to 5 M NaCl or 4.5 M $MgCl_2$). The resulting total mobilized thorium concentrations (dissolved plus intrinsic colloids) appear to be independent of ionic strength, with a mean $\log[Th]_{total} \approx \log[Th]_{colloidal} = -6.3 \pm 0.5$. This reported intrinsic colloid concentration exceeds the PABC 2009-calculated dissolved thorium concentration of $\log[Th]_{dissolved} = -7.2$ by approximately an order of magnitude. The colloidal thorium concentration reported by Altmaier et al. (2004) is not accounted for in the implementation of the colloidal actinide source term model in PA because intrinsic thorium(IV) colloids were assumed not to be present, based on an evaluation of the literature for the Compliance Certification Application and the colloidal actinide source term conceptual model peer review.

Altmaier et al. (2004) also observed the formation of colloidal $Mg_2(OH)_3Cl{\bullet}4H_2O$ that sorbed thorium (producing thorium pseudocolloids or mineral fragment colloids) in 4.5 M $MgCl_2$. In solutions saturated with respect to $Mg_2(OH)_3Cl{\bullet}4H_2O$, the thorium concentration was reported to be $\log [Th]_{total} = -4.8 \pm 0.2$. In comparison, the mineral fragment colloid concentration used in PA for thorium(IV) is much lower, with $\log[Th]_{mineral\ fragment\ colloids} = -7.6$. Altmaier et al. (2004) noted that at lower magnesium concentrations, $Mg_2(OH)_3Cl{\bullet}4H_2O(cr)$ is not stable and these colloids would not form. However, PABC-2009 calculations with GWB brine indicate that $Mg_2(OH)_3Cl{\bullet}4H_2O(cr)$ is stable under WIPP repository conditions, so formation of these pseudocolloids in Salado brines cannot be ruled out on this basis. Altmaier et al. (2004) stated that the relatively small solid to solution ratios in their experiments are not applicable to a repository environment where sorption of thorium on the large amounts of solid $Mg_2(OH)_3Cl{\bullet}4H_2O(cr)$ would prevail over sorption onto the mobile colloids. However, it is not clear that such an argument is consistent with the existing WIPP colloidal actinide source term conceptual model.

DOE should address whether significant thorium intrinsic colloids and pseudocolloids could form in

the WIPP repository. Unless the formation of such colloids can be ruled out by the available data, DOE should address the possible effects of such colloid formation on repository performance.

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Rand et al. (2009) - Rand, M., J. Fuger, I. Grenthe, V. Neck and D. Rai. 2009. *Chemical Thermodynamics of Thorium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development, Chemical Thermodynamic Series Volume 11,