E-mail to Dr. Dave Moody, DOE/CBFO (1/25/10)

Dave,

Attached are follow-up comments and questions related to our initial completeness letter (May 21, 2009) and the chemistry questions 1-23-6a and 1-23-6c.

My staff and contractor staff are continuing to review the responses that you provided to our comments in our various completeness letters, but especially the May 21, 2009 letter. We need clarification on some issues raised by your responses on the effects of borate on the +III actinide solubility in the WIPP repository, the Nd solubility data included in CRA-2009 Appendix SOTERM and Borkowski et al 2008, and possible issues related to the geochemistry conceptual model and FMT modeling calculations for the CRA-2009 PABC. Below are nine potential issues/questions that will need to be settled and additional information that we will require before the related completeness comments can be resolved. These are not in order of potential importance and additional questions and data requirements are likely to arise as we continue the evaluation.

Please ensure that these questions are responded to promptly and clearly. Our questions result, in part, from the lack of clarity in the current responses. We need your documentation to "tell the story" in a straightforward manner. Some of this may be addressed in some documentation that we have been promised but have not yet received (but need to receive in short order). In addition to specific responses to the items below, we will be reviewing the information to understand if it represents a change to the current chemistry model or just the parameterization of the current model. We will be reviewing the responses to 1) make sure that they completely address the issue, and 2) whether they appear to be technically adequate. Also, our understanding of these issues would benefit from the clarification of the relationship between the findings from recent or ongoing experiments and the implementation of the modelling for the current performance assessment.

This email will be placed in the docket. Please consider these comments and questions as part of completeness letter 1, question 1-23-6.

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January 25, 2009 Follow-up questions to issues first raised in EPA's May 21, 2009 letter, comment 1-23-6

1. There seems to be a disconnect between the previous (CRA-2004 PABC) FMT modeling results and the experimental investigation of Nd(III) solubilities. Borkowski et al. (2008) assumed that the stable Nd(III) phase in the carbonate system would be NdOHCO3(s). In the CRA-2004 PABC modeling results, the stable +III phase was predicted to be Am(OH)3(s). I have looked at a few of the CRA-2009 PABC FMT output files that you sent to me, and it appears that the stable +III phase predicted by the FMT model continues to Am(OH)3(s). In Figure 4-8 of Borkowski et al (GWB brine with carbonates), it appears that they were able to get fairly good reproducibility of results from undersaturation (dissolution of NdOHCO3) and oversaturation (precipitation) experiments. There appears to have been limited to no characterization of the post-experiment solid phases. Although precisely what was done to characterize the solids after the experiments was unclear to me after reading the test plan and Borkowski et al. 2008 report, Marion Borkowski stated in our conference call this week that there were insufficient amounts of solids to characterize after the oversaturation (precipitation) experiments. As a result, the identity of the solid phases at the end of the experiments is not certain. The data in Figure 4-8 and the interpretation by Borkowski et al 2008 seem to indicate that the stable phase was NdOHCO3. Consequently, FMT calculations predict that Am(III) solubility for WIPP PA is controlled by Am(OH)3(s) but the experiments seem to indicate the solubility-controlling phase will be AmOHCO3. This raises the question of whether the FMT modeling is accurately predicting the concentrations of Am(III) (and by analogy Pu(III)) in the WIPP brines for PA.

2. The observed differences in the concentrations at similar pcH in GWB and ERDA-6 brine are attributed to borate complexation. GWB has approximately 2.5 times the borate concentration of ERDA-6. The neodymium concentrations measured at pcH 8.7 in ERDA-6 brine (no carbonate) is approximately 5 x 10-8 M (Figure 4-10). In GWB brine at pcH 8.7 (Figure 4-9) is approximately 5 x10-7 M. What is the neodymium-borate speciation that would explain a ten-fold increase in neodymium concentrations with a 2.5-fold increase in borate concentration? If it is a one-to-one complex such as NdB(OH)4++, then one would expect that increasing the borate concentration by a factor of2.5 would increase the Nd(III) concentration by approximately the same factor.

3. The "shoulder" in the Nd concentration in ERDA-6 brine as a function of increasing pcH was attributed by Borkowski et al. 2008 to borate complexation. However, the reason for the decreasing Nd complexation as a function of pcH above about 9.75 was not clear. There is no reason that I know of for borate complexation to cease at higher pcH, and ifhydrolysis species such as Nd(OH)3(aq) became more important at high pcH, these concentrations would be present in addition to the Nd-borate species concentrations. It is unclear whether a different solid might be controlling the Nd(III) solubilities in the high-pcH region. An understanding of the solubility in this pcH region is important because in ERDA-6 the maximum concentration is observed at approximately the repository pcH predicted by FMT calculations (9.6-9.7). [Note: Clarification on this issue was requested in a phone call with LANL staff, but it was not resolved.]

4. If the trend in Nd concentrations in GWB (Figure 4-8) is simply extrapolated up to pcH 9.4 (the pcH predicted by FMT modeling for GWB brine in the repository), the Nd concentration could be as high as 4 x 10-5 M, which is much higher than the concentrations predicted for the CRA-2004 PABC (GWB no ligands) of 2 x 10-7 M. In our discussion, LANL staff said that the solubility at the pcH of 9.4 would be best represented by the solubility of Nd(III) in ERDA-6, because as pcH is increased, Mg precipitates and the composition of GWB approaches that of ERDA-6. However, if one compares the predicted Mg concentration of GWB at pcH 9.4 based on FMT modeling for the CRA-2004 PABC to the composition of ERDA-6, the Mg concentration in the higher-pcH GWB is still 0.55 M, which is 29 times the Mg concentration in ERDA-6. Even if one accepts that the solubility in ERDA-6 is a perfect way to estimate the concentration of Nd in pcH 9.4 GWB (1 x 10-6 M or higher), then the concentration is still, at a minimum, 5 times what was predicted by FMT (2 x 10-7 M). There is a lot of uncertainty in such a prediction, because the higher-pcH GWB is not the same composition as ERDA-6 and the results with carbonate in ERDA-6 (Figure 4-11) were only approached from undersaturation in this pcH region. Consequently, the concentration of Nd(III) in pcH 9.4 GWB could be higher than 10-6 M.

5. When discussing possible effects of increased +III actinide solubilities on PA during our call, a LANL staff member said that he thought the increased ligands concentrations predicted for the CRA-2009 PABC FMT calculations might have increased the +III actinide solubilities to the extent that americium was inventory limited. Although he did not think Pu would be inventory-limited, he suggested that high EDTA concentrations might result in sufficient EDTA complexation that the effects of borate would be relatively unimportant. I have only looked at what I believe are the ERDA-6 results for the CRA-2009 PABC calculations. This output file (FMT_PABC09_E6_HMAG_ORGS_013.OUT) is for ERDA-6 brine, with organics, and was run on July 8 2009. The total concentration of Am(III) was predicted to be 1.51 x 10-6 M at pcH 9.7. This concentration does not dwarf the concentration observed in Figure 4-11 (about 1 x 10-6 M), so it does not appear that EDTA complexation of the +III actinides will be so high that the potential effects of borate complexation described bythe results of Borkowski et al. 2008 can be neglected.

6. Figure 4-9 presents Nd(III) solubility data in GWB as a function of pcH in the absence of carbonate. At pcH values of approximately 7.3 and 8.0, the concentrations measured in experiments approached from undersaturation are higher by approximately an order of magnitude than the concentrations measured in experiments approached fromoversaturation. Does DOE have an explanation for this?

7. DOE's response to 1-23-6c dated November 25, 2009 statement that "For the III actinides, the complexation of borate effectively substitutes for the calculated effect of carbonate presently in the WIPP model." Is inconsistent with the modeling results from the CRA-2004 PABC. These results, both with and without ligands present in the brine, showed that aqueous americium-carbonate complexes constituted negligible proportions of the total americium in solution in all four solution compositions (GWB and ERDA-6 with and without ligands). In addition, because there is an assumed excess of Am(OH)3(s) in the WIPP repository, "competition" between

borate and carbonate for americium in the system will not occur. Americium-borate aqueous complexes, if formed, will form in addition to americium-carbonate complexes. However, under WIPP conditions, current FMT modeling does not predict significant carbonate complexation of the +III actinides.

8. DOE should perform FMT calculations to predict the concentrations of Nd(III) under the conditions of the Nd(III) solubility experiments in the NaCl, GWB, and ERDA-6 brines. These calculations would provide direct evidence of the extent of the differences between the experimental results and the FMT calculated solubilities, which will be useful even though experimental data are unavailable at higher pcH in GWB. For the carbonate experiments, it may be useful to perform calculations using $Am(OH)_3(s)$ as the solubility-controlling solid as well as calculations using $AmOHCO_3(s)$ as the solubilty controlling solid, to indicate potential solution composition changes that might be caused by a change in the stable phase or mixed solid phase formation.

9. Another question is related to the carbonate concentrations in the experiments that they conducted. I understand that they spiked an initial carbonate concentration into the solutions and used "gas-tight polypropylene bottles" for the experiments. Did they measure carbonate concentrations in solution at the end of any of the experiments to confirm that there was no loss of CO_2? It is my understanding that all of the experiments were performed in a CO_2-free glove box, so gain of CO_2 should not have occurred. Do they assume that the amounts of $NdOHCO_3$ precipitated in their experiments were so small that it did not affect the total carbonate in the solutions?