EEG-77

PLUTONIUM CHEMISTRY UNDER CONDITIONS RELEVANT FOR WIPP PERFORMANCE ASSESSMENT

Review of Experimental Results and Recommendations for Future Work

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Environmental Evaluation Group
New Mexico

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FOREWORD

The purpose of the New Mexico Environmental Evaluation Group (EEG) is to conduct an independent technical evaluation of the Waste Isolation Pilot Plant (WIPP) Project to ensure the protection of the public health and safety and the environment. The WIPP Project, located in southeastern New Mexico, became operational in March 1999 for the disposal of transuranic (TRU) radioactive wastes generated by the national defense programs. The EEG was established in 1978 with funds provided by the U. S. Department of Energy (DOE) to the State of New Mexico. Public Law 100-456, the National Defense Authorization Act, Fiscal Year 1989, Section 1433, assigned EEG to the New Mexico Institute of Mining and Technology and continued the original contract DE-AC04-79AL10752 through DOE contract DE-ACO4-89AL58309. The National Defense Authorization Act for Fiscal Year 1994, Public Law 103-160, and the National Defense Authorization Act for Fiscal Year 2000, Public Law 106-65, continued the authorization.

EEG performs independent technical analyses of the suitability of the proposed site; the design of the repository, its operation, and its long-term integrity; suitability and safety of the transportation systems; suitability of the Waste Acceptance Criteria and the compliance of the generator sites with them; and related subjects. These analyses include assessments of reports issued by the DOE and its contractors, other federal agencies and organizations, as they relate to the potential health, safety and environmental impacts from WIPP. Another important function of EEG is the independent environmental monitoring of radioactivity in air, water, and soil, both on-site and off-site.

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TABLE OF CONTENTS

ABSTRACT

The Waste Isolation Pilot Plant (WIPP), located at a depth of 650 m in bedded salt at a site approximately 40 km east of Carlsbad, New Mexico, was constructed by the US Department of Energy for the disposal of transuranic wastes arising from defense-related activities. The disposal site is regulated by the US Environmental Protection Agency (EPA). During the process leading to certification of the site for initial emplacement of waste, EEG and their contractors reviewed the DOE Compliance Certification Application (CCA) and raised a number of issues. This report reviews the issues related to the chemistry of plutonium as it will affect the potential for release of radioactivity under WIPP conditions. Emphasis is placed on conditions appropriate for the Human Intrusion scenario(s), since human intrusion has the largest potential for releasing radioactivity to the environment under WIPP conditions. The most significant issues that need to be addressed in relation to plutonium chemistry under WIPP conditions are (1) the effects of heterogeneity in the repository on Pu concentrations in brines introduced under the human intrusion scenario, (2) the redox state of Pu in solution and potential for plutonium in solid phases to have a different redox state from that in the solution phase, (3) the effect of organic ligands on the solubility of Pu in WIPP-relevant brines, and (4) the effects of TRU waste characteristics in determining the solubility of Pu. These issues are reviewed with respect to the treatment they received in the DOE CCA, DOE's response to EEG's comments on the CCA, and EPA's response to those comments as reflected in the final EPA rule that led to the opening of the WIPP. Experimental results obtained in DOE's Actinide Source-Term Test Program (STTP) during the last two years are reviewed and interpreted in the light of other developments in the field of Pu solution chemistry. This analysis is used as the basis for a conceptual model for Pu behavior under WIPP conditions.

This report identifies three issues that can be addressed as part of the five-year re-certification cycles mandated by the WIPP Land Withdrawal Act (U.S. Congress, 1996, '8.(f)(1)) and implemented in the EPA Final Rule (U.S. EPA, 1998a). First, the impact of organic ligands on the complexation of a system with multiple cations could be delineated by some simple experiments with Th (IV), citrate,

EDTA, Ca^{2+} and one or more transition metals. An experiment with Pu (IV) could be designed to determine the lability of Pu oxidation states in the presence of organic ligands. Second, the issue of using analogs for Pu could be addressed with appropriate experiments using U and Pu at redox conditions in the range anticipated at the WIPP. Attention to the published experimental results of U and Pu could make a considerable contribution to this effort. Third, the issue of uncertainty in calculated actinide solubility can be resolved with experimental data for Pu (IV) compounds of appropriate compositions. The report also recommends starting by constructing a data base for U and Pu using the published, peer-reviewed OECD/NEA U and Pu data bases.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) was constructed by the US Department of Energy (DOE) to serve as a disposal site for transuranic radioactive wastes that arose through defense-related activities. The WIPP facility was built in a bedded salt formation at a depth of 650 m and is located approximately 40 km east of Carlsbad, New Mexico. The disposal facility is regulated by the US Environmental Protection Agency (EPA) through their Radiation Protection Standards for disposal of transuranic waste. The regulatory process involves DOE filing with EPA a Compliance Certification Application. (CCA). This was done in October, 1996 (DOE, 1996). The Environmental Evaluation Group (EEG), which conducts independent technical evaluations of the impact of the WIPP project on public health and on the environment, identified a number of concerns arising from the CCA. One of these concerns was a group of issues related to the chemistry of actinide elements, especially plutonium, under conditions that are relevant for assessment of the long term behavior of the WIPP facility (Chaturvedi et al., 1997).

The EPA published its technical review of the DOE WIPP source term program and modeling in October, 1997. EEG then asked Dr. V. Oversby to evaluate the DOE modeling efforts and the EPA review. That review, which was communicated to EEG as a letter report, identified many of the issues that were subsequently summarized in a letter from EEG to EPA (December 31, 1997, contained as Appendix 8.3 in EEG-68, 1998). Detailed reviews of the DOE Chemical Conditions Model, the actinide solubility calculations, and the SOTERM appendix to the CCA were also provided to EEG by Dr. Oversby, and are contained in Appendix 8.4a of EEG-68. Dr. Oversby's review of the EPA technical support document issued in 1997 was reproduced on pages 45-56 of EEG-68.

A meeting was held in Albuquerque, NM, on February 20, 1998, so that EEG, Dr. Oversby, and scientists from Sandia National Laboratories and their contractors could discuss EEG's concerns. Following that meeting, DOE sent a response to the EEG comments to the WIPP Program Manager at

EPA, with a copy to EEG (letter dated February 24, 1998). The relevant technical content of EEG's concerns and DOE responses are discussed in the following section.

On May 18, 1998, EPA issued its final rule certifying the WIPP facility and identifying the requirement for a five-year recertification cycle (EPA, 1998a). EPA also published a separate document that responded to comments that had been received during the public comment period for WIPP certification. The details of the EPA responses, where they are relevant to plutonium chemistry issues, are discussed in the next section.

PLUTONIUM CHEMISTRY ISSUES

There are four major factors that will determine the effective solubility of plutonium in the WIPP environment. These are (1) the redox conditions, (2) the brine composition, (3) the availability of ligands through degradation of the waste, and (4) the effects of slow kinetics of reaction due to lack of lability of species (i.e., persistence of metastable species). The brine composition, itself, will be affected by the persistence of metastable reaction products, especially those formed by backfill materials, such as MgO.

The DOE CCA attempted to predict the solubility of plutonium and other actinides under WIPP conditions by using a chemical modeling code, FMT. The FMT code was developed at Sandia National Laboratory for use in performance assessment exercises for the WIPP project. FMT used the Pitzer formalism for dealing with the corrections to activity of solution species in high ionic strength brines. DOE chose to use an oxidation state analogy for dealing with actinide chemistry. This analogy treated each possible oxidation state in isolation and did not allow for the different oxidation states of a single element to interact in response to other conditions in the reacting system. For the actinide (IV) oxidation state, DOE used thorium data in the model calculations and claimed that this was conservative because thorium would be more soluble than plutonium in the (IV) oxidation state.

In her review of the DOE CCA, Oversby (1997) discussed each of the factors listed above and recommended experimental work to provide data needed to improve the modeling efforts and also recommended improvements to the modeling itself. In particular, a sensitivity analysis to determine the effects of uncertainties in the solubility measurements and stability constants used in the FMT data base as well as the uncertainties in the Pitzer parameters used to estimate activity coefficients in brines was recommended. The appendices to the Oversby (1997) report discussed in detail issues that arose through the review of the DOE CCA and selected supporting documents. These reviews and the review by Oversby of the EPA technical review of the DOE WIPP source term program and modeling led EEG to conclude that the following items were of concern (cited from EEG-68):

“1. The FMT model is unique to WIPP. EEG found that the model predicts differences for actinide sulfate and carbonate solubilities that can not be explained by chemistry, thus leaving the reliability of the calculations suspect. The unexpected results need to be explained or the model needs to be re-examined for possible problems with the code.

2. Rather than use an extensive plutonium data base, the FMT predictions relied on thermodynamic data for other elements and an oxidation state analogy argument. EEG recommends that the calculations be performed using data for plutonium and the values for solubility and complex ion formation contained in the peer-reviewed data compilation by OECD/NEA.

3. EEG agrees with EPA’s documentation of the shortcomings of the solubility uncertainty ranges advanced by DOE. However, EPA has accepted the ranges as adequate based on a weak argument. EEG recommends that the uncertainty range needs to be determined with the appropriate plutonium data.

4. In the solubility calculations, the CCA inappropriately discounts the role of organic ligands on plutonium solubility by arguing that EDTA is the strongest complexing agent. But citrate forms very strong complexes with actinides in the +4 oxidation state and very weak complexes with other cations. Thus, the solubility of a stable plutonium-citrate complex in individual waste containers needs to be calculated.

5. There are serious unanswered questions about the impact of magnesium oxide backfill on the solubility of the actinides. It is proposed that magnesium oxide will reduce the solubility of the actinides by controlling pH. But, it is not known how long the early reaction product, nesquehonite, will persist. The FMT model calculates that the presence of nesquehonite drives the solubility of the +4 actinides, such as plutonium, higher than in the no backfill case. This requires further investigation.”

The comments by Oversby concerning the EPA "Technical Support Document 194.24: EPA's Evaluation of DOE's Actinide Source-Term" as reproduced in EEG-68 (1998) included

> "The EPA evaluation of expected redox states, solubility, and speciation of actinides under WIPP disposal conditions was very narrow in its scope. In general, only the references cited by DOE and the work done by the DOE contractors was discussed. The evaluation would be considerably strengthened, and might reach different conclusions, if relevant results published in the open literature of studies conducted by other scientists were discussed.
>
> The EPA has limited their review of the DOE solubility calculations to an exercise in which EPA used the Sandia computers, codes, and databases to determine whether they could get the same numerical values for results if they tried to duplicate the work done by DOE. It would have been very surprising if they had failed to find agreement under those conditions. A more reasonable evaluation would require a comparison of the results of calculations using a code that is used more widely in the modeling community with those obtained by the Sandia FMT code.
>
> There has been no evaluation by EPA of the thermodynamic properties data used in the database for the solubility calculations. There has been no attempt by EPA to assess the degree to which the calculations might represent the conditions expected for WIPP disposal. Both of these tasks are needed in order to determine whether the DOE calculations have any validity.
>
> In evaluation of the effect of organic ligands on the mobilization of actinides, EPA considers only the case of homogeneous equilibrium, in which the entire actinide inventory in the repository is well-mixed with a very large volume of brine that inundates the repository. This is an unrealistic and non-conservative model for evaluation of the effect of organics. In addition, EPA bases their evaluation of the ability of organics to mobilize actinides on an analysis that only considers EDTA. While this analysis gives the correct result for the importance of EDTA, it does not speak to the issue of the importance of citrate in the waste and its ability to increase the mobility of Pu."

The specific comments by Oversby on each section of the EPA evaluation of DOE’s source term were also reproduced in EEG-68 (1998). This EEG report was submitted to EPA as comments on the proposed rule. The limitations of the oxidation state analogy were discussed, and it was noted

> “The oxidation states expected by DOE for Pu in the WIPP repository are III and IV. Any Pu(V) formed is expected to be rapidly reduced by iron. EPA concurs with this conclusion; however, Pu(V) is observed as a long-lived transient in many laboratory experiments. Pu(V) may be formed as a result of radiolysis reactions in the brines and while its total abundance in the repository is likely to be low, it might be significant as a transient species in some waste containers. The release scenarios considered important for WIPP are those involving human intrusion, with drilling through the repository to a brine-containing formation below the repository. Upwelling of brine from this lower layer through the repository might allow rapid transport of brines containing some Pu(V) to the surface.”

The issue of heterogeneity in the repository was raised by Oversby (cited in EEG-68, 1998) during a discussion of section 7 of EPA’s evaluation document, which concerns the effect of complex ion formation on enhancement of solubility. EPA concluded that organic ligands would not increase actinide mobility. In their analysis, EPA used the same assumption used by DOE that the system could be modeled assuming homogeneous equilibrium of brine and actinides. In her discussion of this point, Oversby stated

> “both DOE and EPA assumed that the actinides would be evenly distributed throughout the repository and that the brines would be well-mixed and have a uniform composition throughout the repository. This is unlikely to be the case and is certainly not appropriate for evaluation of the development of dissolved actinides inside a partially destroyed waste container, a scenario that is important with respect to assessment of human intrusion consequences.”
>
> and

> "To model the behavior of Pu with citrate, we must also consider heterogeneous equilibria for organic complexation with the actinides. The main difficulty arises because the Pu in the waste is probably located in the same drums as the citrate, which is the dominant organic ligand. This is because these wastes arise from chemical separations of Pu and are not the type of waste described in the general descriptions of TRU waste as contaminated equipment, clothing, etc. To get an accurate estimate of the effect of organic ligands on Pu solubility, one must calculate the concentration of Pu as citrate complex inside a waste drum that has been breached, but can still provide a hindrance to mixing of the brine inside the drum with a larger pool of brine outside the drum. This will give a high concentration of Pu in solution as the citrate complex. Other ions will not compete with Pu sufficiently to prevent complex formation because the stability for (IV) actinide complexation – as shown by the stability constant for Th(IV) on p. 39 of the SOTERM appendix – is orders of magnitude larger than that for other ion complexes with citrate."

EEG met with EPA WIPP project staff on December 10, 1997, in Albuquerque, NM to discuss some of EEG's concerns with the draft EPA rule on WIPP. A summary of the issues discussed, as well as a summary of several other issues that had been raised previously, was sent to Mr. Frank Marcinowski (EPA Radiation Protection Division, Washington, DC) by letter dated December 31, 1997, with copies to other interested parties including DOE and the EPA Docket for WIPP (A-93-02). DOE arranged a meeting between Sandia staff working on the WIPP project, their contractors, EEG, and their consultants in Albuquerque on February 20, 1998, to discuss the actinide solubility issues in detail. Following that meeting, DOE responded to the comments contained in the EEG letter of December 31, 1997, by letter dated February 24, 1998, to Ms. Mary Kruger (WIPP Program Manager for EPA). The DOE responses contained in the February 24, 1998, letter did not address the substance of the solubility issues raised by EEG in their letter of December 31, 1997, and at the meeting held on February 20, 1998. DOE restated their previously published arguments. An independent observer at the meeting, Prof. R. C. Ewing, who had been a member of the National Research Council's Committee on the Waste Isolation Pilot Plant, sent written comments to EEG after the meeting. These comments, contained in a letter dated February 22, 1998, to Mr. Robert H. Neill, Director of EEG, highlighted the need for further experimental work on actinide chemistry and the need to go beyond the simple Th analog model to actual experiments with plutonium. Prof. Ewing stated in particular (letter reproduced in EEG-68, 1998) that "The project is still not in a position to present and discuss models of the longer term evolution of the chemistry of the WIPP system."

The DOE response concerning the use of the Th(IV) analog for plutonium(IV) behavior did not address the central issue in actinide chemistry where multiple oxidation states are possible. It is the lability between the various oxidation states and the details of the chemical environment that determine the formal oxidation state of actinides such as Pu, U, and Np. It is also well known that the solution species oxidation state may be different from that in the solid (e.g., U(VI) in solutions in contact with air and with uranium(IV) dioxide solid). The use of Th(IV) to model Pu(IV) behavior has the intrinsic limitation that Th can only exist in geologic systems as Th(IV). This point will be discussed in more detail in the section concerning recent experimental results obtained by workers outside the WIPP project.

The other issue raised by EEG was that of homogeneous versus heterogeneous equilibria. DOE maintained the assumption of homogeneity for the chemical conditions in the repository, which was a consequence of mixing of chemical species through the solution phase in a fully saturated brine environment. Further, the CCA stated that no chemical microenvironments that influence the chemical environment are expected to persist, which can be viewed as a tacit recognition that microenvironments could have an impact on the overall chemical environment. The assumption of a repository fully saturated with brine is not the expected condition for the WIPP repository, to which access of brine is expected to be limited under normal geologic conditions.

When EPA issued its Final Rule concerning the certification of the WIPP facility, they also published a response-to-comments document (EPA 1998b) to provide a record of the comments received and their disposition. The EPA response to issues related to actinide solubility (other than those associated with MgO) are discussed below. Of the issues that EEG raised, EPA discussed the effect of organic ligands on solubility (Issue V, pp. 6-60 to 6-66), the oxidation state analogy (Issue Y, pp. 6-71 to 6-76), solubility uncertainty range problems (Issue Z, pp. 6-76 to 6-80), and plutonium (VI) (Issue CC, pp. 6-84 to 6-86). In addition, EPA discussed issues raised that involved the long-term behavior of the MgO backfill and its effects on brine chemistry and actinide solubility, as well as issues related to the FMT computer code and its data base. In this report, we will focus on the issues related to actinide solubility for which we have recommendations for further experimental work and limit our discussion of issues related specifically to the MgO backfill and the FMT computer code.

We recognize that MgO is a key component of the repository chemistry, but there are limited data from the WIPP Source Term Program for MgO Backfill. At the time the STTP experiments were begun in 1995, other material, such as bentonite, was considered a leading backfill candidate and was included in the test matrix. The idea to use MgO as the only backfill in the WIPP repository came as a late development in the application process (NEA/ IAEA, 1997). MgO was added to only one of the liter-scale tests in the Source Term Program in February 1997. The waste was a pyrochemical salt immersed in brine and maintained under 60 bar of CO_2 pressure. Prior to adding MgO, that container had exhibited a very high actinide solubility. The results of the MgO addition are discussed briefly in this report; the observations do not change the recommendations for further experimental work to resolve the identified actinide solubility issues. Moreover, the behavior of MgO in brines has far-reaching implications and merits its own investigation.

As discussed above, concerns about the use of the FMT computer code have been documented previously. Rather than revisit that conceptual model and computer code, this report promotes two approaches to address our documented concerns. First, directly tackle the issue of model uncertainty by generating experimental data for plutonium in brines of appropriate chemical composition. Second, starting with a peer-reviewed database for plutonium and uranium, adjust solution species activity as a function of ionic strength using Specific Ion Interaction Theory, rather than try to determine Pitzer parameters, which can have very large uncertainties for highly charged species, for use in the FMT code. Details can be found in the final section of this report.

In their discussion of the effect of organic ligands, EPA echoed the argument DOE had used in the CCA. They assumed a well-mixed, homogeneous repository and calculated average concentrations of organics and actinides in the case of brine saturation of the repository. They also cited a calculation showing that EDTA formed the strongest complexes of all organic ligands with actinide(IV) species and, further, that other divalent cations in the brine, such as Fe(II) and Ni(II) would be able to use up most of the EDTA, so there would not be much left for the actinides. EPA then concluded that since EDTA formed the strongest An(IV) complexes and would not significantly increase An(IV) mobility, then no other organic complex would either. This reasoning does not accommodate the observation that citrate forms strong complexes with An(IV) cations and not with divalent cations, so there is no competitive reaction that eliminates citrate from the brine. We believe that the issue of the effect of organic ligands, especially citrate, on the mobility of plutonium under the Human Intrusion scenario remains unresolved. We will, therefore, recommend in the final section of this report some simple experiments that could resolve the issue.

The EPA addressed comments on the limitations of the use of Th(IV) as an analog for Pu(IV) chemistry by confining their comments to the behavior of the An(IV) oxidation state. They did not consider the possibility for Pu(IV) in the solid waste forms to coexist with a Pu(V) or Pu(VI) solution species in the brines. Work conducted during the last two years, both within and outside the WIPP program, indicates that dealing with the Pu(IV) oxidation state in isolation is an oversimplification of the actual chemistry of Pu-bearing systems (see next two sections). We believe that the issue of description of the behavior of Pu under scenarios relevant to Human Intrusion at WIPP must be addressed by relevant experiments using Pu-bearing wastes that are representative of those that may be disposed of at WIPP. Particular attention should be paid to experiments using wastes such as pyrochemical salts, since these may contain high percentages of Pu as discussed in the section on the WIPP Source Term Program. An outline of some appropriate experiments is given in the final section of this report.

The uncertainty range used by DOE for solubility estimates attracted several criticisms that were discussed in the EPA response to comments. (Note: In the Response to Comments document EPA used the terms “Am(VI)” and “Am(IV)”. These should be An(VI) and An(IV), where An stands for any actinide element.) EPA stated (p. 6-77) that in the uncertainty analysis “solubility data for actinides in the +6 oxidation state were not used. This decision seems appropriate in view of the fact that the CCA source term was unable to develop a solubility model for U(VI), which is the only hexavalent actinide species expected under WIPP conditions." In view of recent experimental results that strengthen the possibilities that Pu(VI) as well as U(VI) may be important species in WIPP-related brines, EPA is urged to reconsider this position. Exclusion of An(IV) data from the uncertainty analysis because of difficulties that DOE contractors had with extrapolation of such data, including (apparently) data for Th(IV), exposes the weakness of both the uncertainty estimates for An(IV) species as well as the potential unreliability of the solubility calculations for these species. For these reasons, we recommend that appropriate experiments be conducted that can give an estimate of the range of solution concentrations and solution species identities that might exist in WIPP brines under potential Human Intrusion scenario conditions.

The EPA response to comments concerning the potential for Pu(V) or Pu(VI) to exist in the WIPP repository was two-fold. They argued first that the cited experimental observations were not relevant to WIPP because of the use of non-representative experimental conditions. They further argued that the presence of organic ligands in the repository would make Pu(V) and Pu(VI) unstable relative to Pu(IV). In light of recent experimental results (discussed below), this issue needs to be revisited. Work to address the possibility for Pu(V) and Pu(VI) species to exist in WIPP brines under conditions relevant to the Human Intrusion scenario and the effects of organic ligands are discussed in the final section of this report.

WIPP SOURCE-TERM PROGRAM

The DOE has sponsored an “Actinide Source-Term Waste Test Program” (STTP), conducted at the Los Alamos National Laboratory. The purpose of this testing program is to provide quantitative measurements of the mobile actinide concentrations in WIPP brines in continual contact with actual Contact-Handled Transuranic (CH-TRU) wastes. Additional objectives of the tests are to determine the influence of chemical additives on actinide concentrations and speciation and to measure the rate of gas generation in the test systems. Results from this test program, which included the detection of Pu(V) and Pu(VI) in four liter-scale containers, were presented to EEG at a briefing in Albuquerque on November 23, 1999, by Robert Villarreal (Los Alamos). EEG was given copies of viewgraphs used at the presentation; these viewgraph materials form the basis of the discussion that follows. Eight of the viewgraphs referenced in this report are reproduced in the Appendix.

This report was drafted prior to meetings held with EEG, EPA and DOE in April and June, 2000. The author has had an opportunity to ask the principal investigator of the STTP tests clarifying questions about the materials from the November meeting and has chosen to limit specific discussion to those materials. The discussions and materials presented at the subsequent meetings in April and June do not change the interpretations and recommendations in this report. Moreover, we have also been advised that some of the references cited in these subsequent discussions are in various stages of review prior to publication. For example, the material presented by L. Brush at the April and June meetings included reference to the work of Clark et al., LANL, for which the text is not available because it is still in internal review at Los Alamos. Other investigators at Los Alamos are also in the process of completing their analyses of the complex STTP systems. It would be more appropriate to reserve comment on the materials presented at the April and June meetings until after that work has been finalized, published, and is available for a detailed review.

The STTP program includes 15 drum-scale tests with heterogeneous wastes (combustibles, lab wastes, metals, etc.), 33 liter-scale tests with homogeneous wastes (sludges, cemented or solidified wastes, pyrochemical salts), and 6 pressurized liter-scale tests with homogeneous wastes. We will focus discussion on the 33 liter-scale tests, of which 22 used Brine A (Salado formation brine) and 11 used Castile brine. [Note: In the Human Intrusion scenario, it is penetration of the Castile anhydrite formation accompanied by penetration of a brine pocket in the Castile that would cause brine to be brought up to the repository level and, through interaction with waste, potentially lead to releases of radioactivity at the surface via transport up the drill hole. For this scenario, it is actinide concentrations in the Castile formation brines that are most important, rather than the Salado formation brines.] All STTP tests were conducted in titanium vessels. The tests began in 1995 and had been running for at least 4 years at the time of the presentation in November, 1999.

The Castile brine, which is most relevant for the Human Intrusion scenario is a sodium chloride brine with minor sulfate and borate and small amounts of magnesium and bromine. The Salado Brine is a magnesium chloride brine with lesser amounts of sodium and potassium chloride and minor amounts of sulfate, borate, calcium, bicarbonate, and bromide.

Liter-scale tests L01-L12 were conducted with Portland Cement and solidified aqueous inorganic sludges. In addition to these components, L04-L06 were pressurized to 60 bars with carbon dioxide, and L10-L12 contained ^{241}Am as an additive. The Am would increase the total radioactivity in the test and enhance any effects due to radiolysis in the solution. The concentrations of actinides in the waste were not given in the presentation materials; however, the amount of Pu present can be calculated using a "Theoretical Pu Conc. (ng/ml)" value. We estimate a total Pu amount in the tests ranging from 30 to 200 mg in 0.25 to 1.3 kg of waste, implying a Pu concentration in the vicinity of 0.01%.

The results from non-pressurized tests with Portland cement showed that Th concentrations were uniformly less than 1 ppb in the brines, U concentration ranged from < 1 ppb to 8 ppb with no obvious correlation with test conditions, Pu had 2 results at <0.5 ppb, one at 0.5 ppb, 3 results at 1.0 to 1.1 ppb, one at 1.6 ppb, one at 7.8 ppb and one at 11.3 ppb. The two highest results for Pu occurred in the tests with Am added conducted in Salado brine, and may be due to enhanced solubility resulting from oxidation of Pu by radiolysis products and higher solubility of Pu at the pH found in tests with

Salado as compared to Castile brines (pH 9 versus pH 13). Results for Np concentration were erratic, with 6 values less than 1 ppb and one each at 9, 33, and 264 ppb. All of the high values for Np were found in Salado brine tests; however, since 3 other, nominally equivalent tests (except for a higher solution to solid ratio in the tests with high Np concentrations) gave results of < 1 ppb, it is hard to postulate a rational explanation for the results. Am concentrations were uniformly less than 1 ppb, even in the tests where Am was added to the system.

Th concentrations in the non-pressurized Portland cement tests were, with one exception, lower to much lower than concentrations found for U and Pu. This provides strong evidence that Th "solubility" is unlikely to be a realistic or conservative analog for Pu and U under WIPP disposal conditions.

Tests in Portland cement with carbon dioxide pressure at 60 bars gave much higher concentrations of U and Pu, but Th concentrations remained below 10 ppb. The U results showed extreme variability between the 3 different pressurized tests, but were more consistent within a given test as a function of time. Results for U were 9 to 15 ppm for the L04 test (i.e., about 10,000 times higher than Th concentrations for the same test), 0.3 to 0.7 ppm for the L05 test, and 3 to 5 ppm for the L06 test. Concentrations of Pu were also higher in the pressurized tests as compared with the non-pressurized tests, but the results were very erratic. The L04 test showed values for Pu starting at about 2 ppb and climbing (exponentially) to 255 ppb. The L05 test started at 2 ppb, reached 184 ppb by the second reported result, and then dropped to 5 to 25 ppb (in random order) for the last 4 sampling periods. The L06 test started at 25 ppb, peaked at 638 ppb at the 4th sampling period, and ended at 319 ppb at the 7th sampling. Results for Np were, with two exceptions, lower than those for U and Pu, and showed similar irregularities in solution concentration with time as did Pu. Again, the results show that Th concentrations are lower to very much lower than Np, Pu, and U concentrations and argue strongly against the use of Th as an analog for the chemistry of Np, Pu, and U.

Envirostone is a mixture of 80 to 90 % calcium sulfate with 10 to 20 % melamine-formaldehyde resin and about 0.1 % ammonium chloride. Results of tests using aqueous wastes absorbed onto Envirostone gave high to very high solution concentrations for U, very erratic concentrations for Pu, ranging from low (2.4 ppb) to high (1013 ppb), and also very erratic results for Np and Th, but with concentrations for those elements generally less than found for Pu. There was no obvious pattern to the results. Tests using cemented wastes with Envirostone showed lower concentrations, probably due to the beneficial effects of the cement. Uranium concentrations, however, were still rather high, ranging from 0.3 to 0.8 ppm.

Fifteen tests were conducted using pyrochemical salts. These tests are particularly important since the amount of plutonium in pyrochemical salts is not a trivial fraction of the WIPP inventory and may be present in high concentrations in some cases. Estimates for the total amount of plutonium to be disposed of at the WIPP range between 13 and 16 metric tons (see, for example, Table 4, page 14 in Rechard et al., 2000). The pyrochemical salt residues to be sent from Rocky Flats contain about 1 metric ton of plutonium contained in 14.9 metric tons of pyrochemical salts (U.S. DOE, 1998a). The material falls into three categories; (1) electrorefining salts, (2) molten salt extraction salts, and (3) low-Pu and high-Pu-concentration direct oxide reduction salts. In two records of decision, the DOE has stated its intentions to;

1) repackage the low plutonium concentration direct oxide reduction salt residues to prepare them for disposal at WIPP (U.S. DOE, 1998b),
2) repackage the molten salt extraction/electrorefining salt residues, with possible blending at Rocky Flats to get below the 10 percent plutonium safeguards termination limit, for disposal at WIPP (U.S. DOE, 1999),
3) pyro-oxidize as much of the high plutonium concentration direct oxide reduction salt residues as possible, and probably all, and then repackage, with possible blending at Rocky Flats to get below the 10 percent plutonium safeguards termination limit, for disposal at WIPP (U.S. DOE, 1999).

Because the Pu concentration in pyrochemical salts that might be sent from Rocky Flats to WIPP could be very high, we believe that particular importance should be placed on the results of STTP tests that used pyrochemical salts. In the STTP series, all tests with pyrochemical salts were done using 2 parts liquid to 1 part solid, with the exception of tests using $Ca(OH)_2$ with chelating agents, which used a 3:1

ratio. General observations are that Pu concentrations for these tests are very much higher than for tests with the other waste types. The highest solution concentration of Pu was reported for the L27 test with Castile brine and pyrochemical salts (no additives) and was 30 ppm Pu. This is 30,000 times higher than for tests using cemented sludges. It should also be noted that the pH of this test was 11.1, so the result is far from easy to explain using equilibrium concentration calculations for Pu(IV) in Castile brine. Results for other actinides are also higher in these tests as compared to cemented waste tests, but the differences are no where near as large as for Pu. [Note: The tests using pyrochemical salts began in May, 1995, and (at least for some tests) continued through November, 1998, or later.]

Tests using pyrochemical salts in brine equilibrated with bentonite (L31-L33) produced lower Pu concentrations (0.12 to 0.21 ppm), but higher U concentrations in 2 cases. [The higher U may be due to complexation with carbonate released from the bentonite on equilibration with the brine. No chemical composition of the solution analyzed is given, so this hypothesis cannot be checked with the presently available information.]

Tests using pyrochemical salts with $Ca(OH)_2$ and chelating agents (L34-L36) gave relatively low concentrations of Pu in the Salado brine (0.1 ppm at pH 8.3 and 0.01 ppm at 8.8), but a very high concentration in the Castile brine (4.6 ppm at pH 11.3). Concentrations of Np, on the other hand, were higher in the Salado brine (1.25 ppm at pH 8.3 and 0.15 ppm at pH 8.8) than in the Castile (0.02 ppm at pH 11.3). Concentrations of Pu in these tests were always higher than those of Th and, in the case of the Castile brine, the difference was a factor of 65.

Tests of pyrochemical salts with Am added were also conducted. It is not clear whether these tests contained other additives. These tests gave the lowest concentrations of Th, Np, and U of all the pyrochemical salt tests, and among the lowest results for Pu. The highest Pu concentration was, again, in the Castile brine, with Pu = 1.25 ppm at pH 9.5. There is certainly no evidence from these tests of an enhancement of solubility due to radiolysis effects.

Tests of pyrochemical salts in brines pressurized with carbon dioxide to 60 bars (L28-L30) have generally high concentrations of Pu and U, and of Np in Salado brine. The highest Pu concentrations were found in one of two nominally identical tests in Salado brine. Test L28 had [Pu] = 6 ppm at the first reported point, while test L29 had [Pu] = 0.16 ppm at the same point. Similar differences persisted through the test period. Tests with Castile brine pressurized with carbon dioxide resulted in Pu concentrations of 1 to 2 ppm, uranium concentrations of 3 to 8 ppm, while Th concentrations were very much lower (0.01 to 0.05 ppm). Magnesium oxide was added to test L28 after the 4th sampling period, which had a [Pu] = 91 ppm. The next sampling period showed a lower Pu result (18 ppm), but subsequent samplings showed increasing Pu concentrations, rising to 42 ppm at the next sampling and then to 174 and 198 ppm at the two final reported sampling points.

For some tests that had high Pu concentrations, spectroscopy was done to determine speciation of the Pu. Pu(VI) was positively identified in tests L26 and L28. The Pu(VI) appears to have been present after the MgO was added to L-28. Pu(VI) is suspected, but was not positively identified, in test L27. All of these tests contained fresh Fe mesh and were found to have hydrogen gas in the head space over the brine, indicating actively reducing conditions. This is clear evidence that thermodynamic equilibrium has not been achieved in these systems, and should raise a cautionary flag concerning the use of equilibrium thermodynamic calculations to predict the potential for releases under the dynamic conditions expected for the Human Intrusion scenario.

The drum scale tests produced relatively low actinide concentrations in the brines, except for the tests using combustible materials with chelating agents. The results for D07-D09 were [Pu] between 1 and 3 ppm, [Th] between 7 and 14 ppm, [U] between 12 and 17 ppm, and [Np] between 15 and 18 ppm. In this case, concentrations of Th are higher than those of Pu and similar to those of U and Np. The chelating agents used were acetamide, acetate, citrate, oxalate, and thiocyanate at 160 ppm each. Similar tests without chelating agents gave [Pu] between 1.7 and 2.0 ppb, indicating that the presence of chelating agents increased the solubility of Pu by a factor of about 1000. This is in direct contradiction to the claims made by DOE in the CCA that chelating agents would not increase the solubility of actinides (U.S. DOE, 1996, SOTERM.5).

Some general conclusions can be drawn from the results of the STTP tests.

1. Solution concentrations of actinides in the presence of pyrochemical salts can be rather high.

2. Thorium is not a conservative analog for the behavior of Pu.

3. Concentrations of Pu in brines increase if chelating agents are present.

4. The addition of MgO to a test that contained a high concentration of both Pu(VI) and carbon dioxide gas did not produce a long-term decrease in plutonium concentration in the test system, provided a level of Pu(VI) that could be detected by spectroscopy, and appeared to raise questions about the arguments that MgO would lower plutonium solubility.

5. It can not be assumed that equilibrium will be achieved rapidly, even in the relatively homogeneous conditions that pertained in the STTP tests.

6. Pu(VI) can exist, at least as a long-term transient species, in brines that are held under actively reducing conditions (i.e., redox conditions buffered by the corrosion of metallic iron to produce hydrogen gas).

ADVANCES IN PLUTONIUM AND URANIUM CHEMISTRY OUTSIDE THE WIPP PROGRAM

The chemistry of plutonium has been studied most extensively because of the use of plutonium in nuclear weapons. Research has focused on the production of weapons grade Pu in nuclear reactors, separation of the Pu from the much larger quantity of matrix (target) material, and subsequent purification of the Pu prior to conversion to metal. Studies of plutonium chemistry under conditions that are relevant for natural, geologic systems have been conducted only in recent years. Some of the results obtained at high temperatures or in acid solutions that constitute the "conventional wisdom" concerning plutonium chemistry may not be appropriate to the near neutral pH conditions and lower temperatures that pertain under geologic disposal conditions.

Studies of the reaction of plutonium dioxide with water by Haschke et al. (2000) have recently shown that a PuO_{2+x} phase is formed, where $x \leq 0.27$. This phase, which is analogous to the UO_{2+x} phase, where $x \leq 0.25$, has been synthesized at temperatures between 25°C and 350°C. The PuO_{2+x} phase decomposed in vacuum if heated at 500°C. As x increases from 0 to 0.27, the lattice constant of the solid phase of plutonium increases only very slightly. Given the difficulty of working with highly radioactive solids, it is not surprising that earlier work failed to identify the PuO_{2+x} phase by x-ray diffraction analysis. One method of identification that is simple, once one has the proof of existence of the PuO_{2+x} phase, is color. High-fired Pu-oxide, which is the stoichiometric PuO_2 phase, is yellow to buff colored, while the PuO_{2+x} phase has an intense green color. Haschke et al. (2000) also note that the existence of the PuO_{2+x} phase also explains one of the "mysteries" of Pu chemistry. It has long been known that so-called low-fired oxides, which are Pu-oxides prepared at relatively low temperatures, dissolved quite easily, while high-fired oxides that had been heated to high temperatures were nearly impossible to dissolve. Haschke et al. (2000) postulate that the PuO_{2+x} phase releases Pu(VI) to solution, especially in cases where aqueous solutions are in contact with air, which can continue the formation of the PuO_{2+x} phase. This accounts for the predominant species in water coexisting with PuO_2 being Pu(VI) for solutions where air is present. Given the difficulties of eliminating all oxygen from experimental systems, it may be that some PuO_{2+x} phase is always present, either due to residual air in the experimental system or to autoradiolysis of the plutonium oxide.

The mechanisms discussed by Haschke et al. (2000) for the formation and dissolution of PuO_{2+x} would also be possible in brines. Thus, the observations of Pu(VI) in the STTP tests may be explained by the presence of the PuO_{2+x} phase in these tests. For tests with lower concentrations of Pu than those for the pyrochemical salts, the chemical form of the plutonium may not be Pu-oxide, but rather some other chemical compound in which Pu exists as a trace constituent. In that case, one might expect quite different behavior, dominated by the chemistry of the host phase in which Pu plays a minor role.

Until recently, positive identification of Pu(V) and Pu(VI) in solution has been limited to cases where the concentration of Pu has been rather high. During the last few years Stefan Röllin, working at Studsvik Nuclear (Nyköping, Sweden) has developed a method for chemical separation by ion chromatography as a pretreatment to analysis by ICP-MS. The method was developed for use with spent fuel leaching experiments conducted at Studsvik for the Swedish Nuclear Fuel and Waste Management Company (SKB) (Röllin, 1999). The ion chromatography step provided clear separation of Pu(III), Pu(IV), Pu(V) and Pu(VI); the ICP-MS detection of the separated valence states of plutonium can then be done at sub-ppb levels. If valence states are changed during the ion chromatography column separation step, the peak positions and shapes are affected. This allows detection of alterations of the chemistry due to analytical methods to be detected. This method, if adapted for use with WIPP brines, could be used to determine speciation of Pu in all of the STTP tests.

Advances have been made in the understanding of uranium chemistry under reducing conditions, both in solutions of low ionic strength and in brines. Experiments were conducted at Finland's VTT Technical Research Centre by Kaija Ollila as part of the European Union's Nuclear Fission Safety R&D Programme (1996-1998) under the project "Source term for performance assessment of spent fuel as a waste form". Ollila (1999) found that the solubility of uranium dioxide under reducing conditions (Eh -0.2 to -0.3 V) and pH about 9 was approximately 1×10^{-9} M, both in saline solutions without carbonate present and in dilute solutions with 0.003 M bicarbonate content. Experiments in dilute groundwater solutions were conducted both from oversaturation and from undersaturation. Results obtained from oversaturation gave [U] in solution that was about a factor of 2 lower than that obtained by dissolution of uranium dioxide pellets that most likely had an outer layer of UO_{2+x} phase. Speciation of U in solution showed that for experiments conducted under anaerobic, but not actively reducing, conditions the U was present as U(VI) to the extent of 85% or more. For actively reducing conditions, the speciation was 60-70% U(VI) in dilute groundwaters and 20-37% U(VI) in saline solutions. The "solubility" measured for anaerobic conditions was one order of magnitude higher than that measured for actively reducing conditions.

Ollila (1999) concluded that the presence of U(VI) in solution, caused by dissolution of the outer layer of the uranium dioxide pellets, had more effect on the measured "solubility" than the chemistry of the solutions used in the experiments (dilute synthetic groundwater or saline solution). Ollila's results, showing the limited effect of salinity on solubility for uranium dioxide, suggest that the WIPP project should reconsider the use of the OECD/NEA data bases for U and Pu and the relatively simple methods suggested in these data bases for correction of ion activities as a function of ionic strength. This would eliminate the need for Pitzer parameters for complex actinide solution species and eliminate a number of uncertainties in the chemical calculations used by DOE to support the performance assessment estimates for WIPP.

A CONCEPTUAL MODEL FOR PU BEHAVIOR UNDER WIPP DISPOSAL CONDITIONS

The work of Haschke et al. (2000) documenting the existence of PuO_{2+x} for $x \leq 0.27$ highlights the similarities between the chemistry of U and Pu and can be used together with the data obtained by several national high level waste disposal programs to construct a conceptual model for the behavior of Pu under WIPP disposal conditions. The PuO_{2+x} phase is not stable at temperatures above 500^oC, so would not be present initially on high-fired PuO_2. It may, however, form slowly on the surface of high-fired oxides that are exposed to air atmosphere before disposal, or may form due to radiation effects even in the absence of air. We will, therefore, assume that all Pu-oxides contain some excess oxygen in their structure after disposal at WIPP.

The PuO_{2+x} phase releases Pu (VI) to solution when it is contacted with an aqueous phase, either dilute groundwater or brine. This is a direct analogy to the behavior of UO_2 solid, which forms a UO_{2+x} phase on its outer surface when exposed to an air atmosphere or to an aqueous solution that is in contact with air, and then releases U(VI) to the solution phase, even though the predominant redox state in the solid is U(IV). This behavior explains the higher than expected Pu concentrations found in SKB tests of spent fuel conducted under anaerobic or reducing conditions. Some level of PuO_{2+x} phase may be expected on any Pu-oxide in the repository, even if the general conditions are reducing through the corrosion of metallic iron. This is because the PuO_{2+x} phase could form by autoradiolysis effects in the Pu-oxide and will not encounter the general reducing conditions until it is formed. The general reducing environment may not be sufficiently powerful to reduce the PuO_{2+x} phase once it has formed. Likewise, Pu(VI) in solution may not reduce directly to Pu(IV) in solution, but may require an active surface to assist in the electron transfer operations.

The PuO_{2+x} phase would be expected to occur in pyrochemical salt wastes, where the concentration of Pu is high and the Pu would be present in relatively pure oxide form. Other waste types, such as solidified aqueous wastes, might have Pu present in dilute solid solution in a matrix of non-radioactive oxides. In this case, the predominant redox state of Pu may be Pu(IV), without any tendency to form the higher mixed oxide phase. The conceptual model for Pu behavior in WIPP should consist, therefore, of two types of Pu-oxides: (1) waste containing rather high purity PuO_{2+x} phase as the main Pu-bearing component in the waste, and (2) waste containing low levels of Pu dispersed in a matrix that is capable of dominating the chemistry of the Pu. Type 1 wastes would be likely to release Pu(VI) directly to solution, while type 2 wastes may not.

RECOMMENDATIONS FOR FUTURE WORK TO IMPROVE PLUTONIUM RELEASE ESTIMATES AND RESOLVE OUTSTANDING ISSUES

Results of experiments and tests within the WIPP program and by other, independent research workers during the past several years have provided evidence that the issues raised by EEG during the period prior to certification of the WIPP facility have basis in fact. These issues should be addressed during recertification of the WIPP facility. To assist in planning a program to address these issues, we summarize below the original basis for EEG's concerns and a brief outline of experiments or activities that could resolve these issues.

(I) ISSUE: EFFECT OF ORGANIC LIGANDS

There are two underlying issues that are important for the consideration of organic ligands and their effect on the solubility of actinides. The first issue is whether a scenario that provides a potentially higher release from the repository has been overlooked in the analysis of "features, events, and processes" for the PA calculations. The second issue is whether the ligand chosen for the "bounding calculations" is appropriate for estimation of the largest potential effect on actinide solubilities.

The DOE and EPA assume that the repository contents are well mixed in a brine solution. The EPA response to comments states that "consideration of every possible combination of potential events for chemical mixture in specific drums would present an impossible number of hypothetical situations to represent in a performance assessment". We agree with that statement, but disagree that DOE actually performed the correct bounding calculation. The appropriate bounding calculation would use the organic ligand for which the An(IV) species have the highest ratio of stability constant as compared with other cations in solution.

The appropriate bounding calculation must also consider the type of waste that produces the largest amount of Pu and citrate together in a single waste container. Selection of this scenario should have occurred during the required "features, events, and processes" (FEPs) analysis that is intended to identify FEPs that can have an impact on total calculated releases. The feature of Pu and citrate being collocated in a waste drum is highly probable and the penetration of such a drum during a drilling event under the human intrusion scenarios would be proportional to the potential number of such drums. Thus, the calculation could easily be included in the potential scenarios used to construct the CCDF without considering an impossibly large number of individual cases.

The DOE and EPA have assumed that the organic ligand that has the largest complexation constant with actinides, especially An(IV), will be the most important in changing solubilities of these actinides. They then calculate the competition between other cations in solution and the dissolved actinides for EDTA, the ligand with the largest An(IV) complexation constant, and conclude that almost all of the EDTA will be bound to transition metal ions and, therefore, will not affect An(IV) solubility.

The conclusion for EDTA is correct. The $\log_{10}$ of the stability constant for EDTA with Th(IV) at 0.3 molal NaCl is given in SOTERM as 15.56, while that for Fe(II) is given as 14.3 at 0.1 molal total ionic strength. While the slight differences in ionic strength will give some changes in the complex stabilities, it is the ratio of the stability constants that is important. The affinity of Th(IV) for EDTA is only a bit over 10 times that of Fe(II) for EDTA. Since the concentration of dissolved Fe(II) in the WIPP site is expected to be much higher than that of Th(IV), the EDTA will be consumed in complexing the Fe(II) and will not have a large effect on the Th(IV) solubility.

The conclusion reached by DOE and EPA that complexation will not have a significant effect on An(IV) solubility if the ligand is citrate should be revisited in light of the following observations. The $\log_{10}$ of the stability constant for Th(IV) with citrate at 0.1 molal NaCl is given in SOTERM at 9.31, while that for Fe(II) with citrate is given as 4.4 at 0.1 molal total ionic strength. The ratio of the strength of the complex ions in this case is approximately 100,000 in favor of Th(IV). It should be noted that the EEG assessment of the potential importance of organic ligands in enhancing the mobility of actinides is in keeping with the experimental results found recently under the DOE STTP testing with organic ligands present. Moreover, the WIPP inventory contains 140 metric tons of citrate in comparison to 23 kg of EDTA.

It is also important to remember that for the calculation of competition for organic ligands between two cations in solution, it is only the concentrations of the cations in solution that comes into play – not the total amount of the element present in the repository. If we consider the competition between Th(IV) and Fe(II) for citrate ligands, it cannot be assumed that there is a readily available supply of soluble Fe(II) to replace any ions that are tied up in complexes. The bulk of the iron in the repository will be there as elemental Fe and must first oxidize before it can dissolve.

ISSUE RESOLUTION

Some rather simple experiments involving Th(IV), citrate, EDTA, Ca^{2+} and one or more transition metals dissolved in brine could demonstrate the extent of complexation of each type of cation in the presence of other cations. Additional experiments using Pu(IV) as the starting actinide could also address the lability of Pu oxidation states in the presence of organic ligands. The results of these experiments could be used in tests of the validity of calculations of solution equilibria done by the chemical modeling codes used in performance assessment calculations.

(II) ISSUE: USE OF TH(IV) AS AN ANALOG FOR U(IV) AND PU(IV) CHEMISTRY

The key issue is whether the chemistry of an element that can assume many different valence states can be adequately represented by considering the solution state of each possible valence state in isolation. The possibility of self-oxidation of an actinide element through the effects of radiolysis induced in the environment is particularly important in this respect.

EPA states that “A peer review panel of scientists found that the use of solubility data for Am(III) solids for representing Pu(III) and solubility data for Th(IV) solids for representing Pu(IV) was a reasonable approach” (p. 6-69 in EPA Response to comments). This position contrasts with that taken by a

National Research Council review team, who stated in their report (Appendix E, p. 129) "Although the oxidation state model (the assumption that the chemistry of a given oxidation state is similar for all of the actinides) is an appropriate beginning to a difficult problem, deviations from the oxidation state analogy are well known in natural and experimental systems. Substantial experimental verification will be needed to establish the limits of this analogy." (NRC, 1996).

The solubility of freshly prepared Th(IV) amorphous hydrous oxide in NaCl and $MgCl_2$ brines has been shown to be higher than that of the equivalent U(IV) amorphous hydrous oxide under conditions of equal hydrogen ion concentration (Rai et al., 1997). The issue for solubility in the WIPP case is whether the U species in solution will be (IV) and whether the Pu species in solution will be Pu(IV). In order to measure the "solubility" of amorphous U(IV), extreme precautions had to be taken to avoid oxidation of the U from (IV) to (VI). The experimental systems included metallic iron powder (325 mesh) and 70 mg/l $EuCl_2$ (approximately 3×10^{-4} moles/liter). Even with these extreme measures, some of the U solutions seemed to show evidence for the presence of U(VI). Conditions in the WIPP will include metallic iron in the form of solid waste containers. That form of iron will be much less reactive than 325 mesh Fe powder. The solid metal pieces in the WIPP will be likely to form a layer of corrosion products on their surfaces, which will further decrease their reactivity. Thus, while the precautions taken in the experiments of Rai et al. (1997) were appropriate for the purpose of determining the thermodynamic properties of the amorphous U(IV) material, the conditions used may not be appropriate for evaluation of WIPP. It is possible that under the ambient conditions at the WIPP the solubility of U in solution will be more similar to that measured by other scientist for amorphous U(IV) solids, where less extreme measures were taken to ensure extremely reducing and reactive conditions.

For plutonium, the use of Th(IV) to estimate the solubility of Pu(IV) solids neglects the contribution of radiolysis to the local redox conditions surrounding the waste materials. Oxidative conditions can be produced in the immediate vicinity of the Pu solids, leading to production of Pu(V) and/or Pu(VI) solution species. If there are chelating agents, such as citrate, in the waste, these will form ligands for the Pu and reduce the Pu to (IV). In the absence of chelating agents, the Pu(V) and Pu(VI) in solution may be rather long-lived. Thus, the use of Th(IV), for which changes in oxidation state are not possible, as an analog for Pu(IV) excludes relevant chemical processes from consideration.

Rai et al. (1997) noted that “thermodynamic predictions are reliable when interpolated, but questionable when extrapolated”. The use of a different chemical element (e.g., Th) to predict the chemistry of Pu in brines under WIPP conditions must be seen as an even larger extrapolation than that of estimation of expected solubilities of Pu or U in WIPP using data obtained by scientists for brines of somewhat different composition than those expected for WIPP. An indication of significant difference in solution chemistry of Th(IV) and U(IV) can be found in the large differences in treatment needed for the Pitzer parameters for U(IV) and Th(IV) in chloride media. (A large, negative β^2 value was needed for Th^{+4}-Cl^- interactions, while no such value was needed for U^{+4}-Cl^- interactions.)

The new experimental results cited above for Pu-bearing solutions and for the possible oxidation states of Pu in solids reinforce the need for experimental data for systems that contain Pu. These results also underline the dangers in using an chemical analog for Pu that does not have the same range of valance states available for responding to changes in environmental conditions.

ISSUE RESOLUTION

This issue could be resolved if appropriate experiments were done using U and Pu at redox conditions that were in the range of those possible for WIPP. A significant contribution to resolution of this issue could be made by consideration of the published experimental results of U and Pu studies – including studies of leaching of spent nuclear fuel and radioactive waste glasses – that have been conducted in brines.

The specific scenario of Human Intrusion should be investigated by conducting tests using pyrochemical salt wastes together with materials to represent corroding waste drums. An injection of Castille brine together with some air to represent a sudden influx of brine via a drill hole that penetrates a brine pocket below the repository could be added to a vessel containing the pyrochemical salt wastes and the corroding metal pieces. The evolution of the solution chemistry, especially Pu concentration and speciation, should then be monitored. Measurements using the sensitive analytical method developed by Röllin (1999) would be most informative.

(III) ISSUE: UNCERTAINTY RANGE FOR SOLUBILITY ESTIMATES

The basic issue here is whether the uncertainty in calculated solubility/solution concentrations of Pu(IV) and U(VI) and the possible existence of Pu(V) and Pu(VI) solution species can be estimated without examination of actual data for these species.

There are two components for this problem. The first is what is the uncertainty in the chemical environment in the repository. This includes, among other things, determination of the phase assemblage relevant to MgO (or other backfill material) alteration in the presence of brines and the influence of heterogeneous distribution of waste materials, such as citrate complexes in the repository. The second component is the uncertainty in the thermodynamic data and in the Pitzer parameters used in the DOE calculations and the propagation of those uncertainties through the calculations of solubility and solution concentrations.

The estimation of uncertainty in solubility estimates as described in SOTERM addressed only the second factor and only the An(III) and An(V) oxidation states. It is stated that An(VI) was not included in the uncertainty analysis because “the CCA source term was unable to develop a solubility model for U(VI), which is the only hexavalent actinide species expected under WIPP conditions.” (p. 6-77, EPA Response to Comments). This position was taken by DOE despite the fact that work had been funded by WIPP on the topic of a U(VI) model, there is a peer-reviewed thermodynamic database for U species (Grenthe et al., 1992, issued by the Nuclear Energy Agency), and that the work accomplished by early 1996 under contract to WIPP appears to have at least as sound a footing as the database for Th(IV) used as a model for all An(IV) species.

The An(IV) species were eliminated from the uncertainty analysis because “The data available for the +4 model were found to have significant problems in the extrapolated regions and were thus determined to be inadequate for use in this analysis.” (Quoted from a reference cited as “Bynum [1996b]” on p. 6-78 of Response to Comments. Reference not included in references under issue Z). EPA correctly notes that this position seems to be inconsistent with the statements made in SOTERM that data for Th(IV) were available and that these data were used for describing the speciation and solubility of Th(IV) in brines.

It is, basically, very difficult to justify the use of data to form a model for safety analysis purposes and then claim that the data are so poor that you cannot estimate from the data themselves the uncertainties associated with their use. It is, further, very difficult to understand how one can then claim that the uncertainty in a well-studied population – in this case the lanthanides [Ln(III)] and An(III) actinides – can be used as the value for the uncertainty for calculations of An(IV) solubility, when the An(IV) data have just been stated to have “significant problems”. In most technical circles, the term “significant problems” as applied to data has a direct correspondence with “significant uncertainties”.

While EPA seems to have understood the limitations of the uncertainty analysis conducted by DOE, they conclude that “the experimental procedures for determining the solublities of +IV actinide solids are not substantially different from those used to determine the solubilites of +III and +V actinide solids, hence EPA concludes that the uncertainties determined for the +III and +V actinide solids would be inclusive of those that would be obtained for the +IV actinide solids.” (p. 6-79, Response to Comments). If the only problem were the attempt to use the same methods to measure solubilities, we would not have the need for statements concerning “significant problems” with data. Unfortunately, it is the solution chemistry of the An(IV) elements that presents the difficulties, not the methods used in the analysis.

The complexities of the solution chemistry carries forward into the attempts to calculate solubilities using computer models. In the case of the FMT calculations used by DOE, the use of Pitzer parameters for calculation was selected. This method requires the estimation of the Pitzer parameters from existing experimental data on the solubility of appropriate An(IV) species. For highly charged solution species, such as are frequently encountered with the An(IV) elements, there are significant uncertainties in the estimation of the Pitzer parameters. This was encountered in speciation calculations for $Th(CO_3)_5^{-6}$, which forms under high carbon dioxide conditions. Even after "correction" of the Pitzer parameters, which lowered the calculated Th(IV) solubility by many orders of magnitude - i.e., a lot more than +1.4/-2.0 log units - the speciation calculated still indicates that the Pitzer parameters have not been correctly and completely determined for the Th(IV) systems.

ISSUE RESOLUTION

The uncertainty in Pu(IV) solubility for safety analysis of the WIPP repository can only be assessed if there are appropriate experimental data for Pu(IV) compounds in brines of appropriate compositions. If such experimental data were available, a direct analysis of expected Pu solubility under WIPP conditions could be conducted, thereby avoiding the uncertainties of extrapolations of Th(IV) data to the polyvalent element, Pu. In addition to the experiments suggested for resolution of issues in previous sections, we would recommend that DOE construct a data base for U and Pu using the published, peer-reviewed OECD/NEA U and draft, peer-reviewed Pu databases as a starting point. The method for correction of activities of solution species as a function of ionic strength recommended by the OECD/NEA review teams is much simpler to use than the Pitzer parameter method used by DOE in the CCA. Considering the small differences in measured solubility for uranium dioxide found by Ollila (1999) for solutions ranging from very dilute synthetic groundwaters to saline solutions, it would seem that the OECD/NEA method should be sufficient. Predictive calculations could then by done by DOE to simulate the conditions for the STTP tests that showed high Pu and U concentrations. This would provide information that could be used to either validate the data base used or provide guidance for improvement of the data base.

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APPENDIX

Selected Overheads from November 23, 1999 Presentation by Robert Villareal

The Actinide Source-Term Waste Test Program Experimental Results & Status

Presented to:
DOE - Carlsbad Area Office
NM Environmental Evaluation Group

Presented by: Robert Villarreal
Los Alamos National Laboratory

November 23, 1999
Albuquerque, NM

Results of Portland Cement - LS

Liter #	Nd	Th	Np	U	Pu	Am	pcH
L01	<0.5	<0.2	8.6	1.4	<0.5	<0.1	8.79
L02	< 0.8	0.6	0.5	1.9	1.0	0.6	10.22
L03	< 0.5	0.6	0.5	5.5	1.1	0.5	12.89
L07	0.9	0.6	264.0	8.3	1.0	0.5	8.72
L08	1.0	0.3	0.5	<0.3	1.6	0.3	9.13
L09	0.9	0.3	0.6	3.1	0.5	0.4	12.96
L10	1.7	0.6	33.0	7.3	11.3	0.9	8.72
L11	1.9	0.9	<0.3	1.9	7.8	0.4	9.54
L12	1.0	0.3	0.4	0.4	<0.5	0.3	12.97

Portland Cement-Pressurized

Liter #	Nd	Th	Np	U	Pu	Am	pcH
L04	<0.9	1.2	421.0	9999.0	1.6	<0.2	7.34
	<0.9	0.4	8.1	10632.0	2.0	<0.2	7.34
	<0.3	1.4	8.6	10268.0	6.0	0.2	7.32
	<0.4	1.4	12.9	11160.0	17.2	0.1	7.43
	1.1	7.9	21.0	15390.0	66.0	0.5	7.39
	<0.5	6.3	15.9	8507.0	255.0	0.7	7.34
L05	<0.9	<0.3	1.5	696.0	1.7	<0.2	7.44
	<0.9	5.1	26.3	560.7	184.0	0.8	7.12
	<0.3	3.7	15.8	398.0	75.0	0.4	7.34
	<0.4	0.6	1.7	319.0	8.5	<0.1	7.27
	<0.2	0.7	2.5	374.0	24.1	0.3	7.08
	<0.7	2.0	4.2	546.0	5.3	0.1	7.00
	<0.5	0.6	1.7	479.0	13.9	<0.1	7.35
L06	<0.9	<0.3	11.1	2934.0	25.0	<0.2	7.87
	<0.9	2.1	7.4	3680.7	23.6	<0.2	7.49
	0.5	1.5	5.7	3988.0	22.9	0.2	7.69
	<0.4	2.9	13.3	4872.0	638.0	1.4	7.70
	3.9	1.8	3.2	4477.0	57.0	0.5	7.57
	2.7	1.9	7.0	4660.0	281.0	0.9	7.81
	2.7	3.0	11.4	3675.0	319.0	0.9	7.56

Results of Envirostone - LS

Liter #	Nd	Th	Np	U	Pu	Am	pcH
L13	1.0	8.4	0.8	1367.0	13.0	0.2	6.99
L14	5.0	7.6	1.2	1019.0	32.0	0.4	6.99
L15	28.0	8.8	174.3	3454.0	165.7	1.3	6.95
L16	45.0	261.9	179.0	168.0	1013.0	2.3	7.46
L17	1.2	0.6	0.9	271.0	2.4	0.3	7.83
L18	<0.5	0.4	21.0	11027.0	4.0	0.3	7.83
L19	3.5	0.5	20.5	659.0	8.9	0.5	7.88
L20	2.0	1.2	1.1	241.0	1.6	0.3	7.60
L21	<0.5	0.2	4.9	668.0	1.2	0.1	8.10
L22	2.4	0.9	0.9	841.0	1.6	0.3	7.20
L23	<0.7	<0.4	0.7	731.0	<0.5	0.3	7.18
L24	<0.4	0.6	1.1	273.0	3.0	0.5	7.78

Envirostone = 80-90% $CaSO_4$ + 10-20% $C_4H_8N_6O.CH_2O$
(melamine-formaldehyde resin) + ~0.1% NH_4Cl

Results of Pyrochemical Salts

Liter #	Nd	Th	Np	U	Pu	Am	pcH
L25	2.8	0.6	273.0	3.5	61.0	0.6	7.86
L26	1.7	1.4	2.0	2.4	5642.0	33.0	7.88
L27	208.0	307.0	70.0	47.0	30127.0	76.0	11.07
L31	4.0	2.4	138.0	728.0	209.0	0.6	8.75
L32	5.0	1.1	73.0	400.0	171.0	0.6	8.72
L33	0.6	0.4	5.7	2.4	121.0	0.7	9.65
L34	0.6	4.8	152.0	46.0	10.0	0.4	8.77
L35	0.7	85.0	1251.0	51.0	111.0	0.8	8.30
L36	<0.5	71.0	18.0	11.0	4650.0	17.0	11.28
L37	1.1	0.6	0.6	<0.3	79.0	0.7	7.67
L38	1.0	0.6	0.5	0.7	8.3	0.3	7.84
L39	1.0	0.8	8.3	28.4	1251.0	1.9	9.48

Pyrochemical Salt-Pressurized

Liter #	Nd	Th	Np	U	Pu	Am	pcH
L28	15.4	178.0	3549.0	5230.0	5989.0	34.8	5.35
	10.1	248.0	8150.0	7099.0	8731.0	58.7	4.90
	10.3	312.0	8179.0	6290.0	15678.0	80.0	4.74
	31.5	1359.0	13931.0	10833.0	90942.0	352.0	4.48
MgO Add	8.9	151.4	350.7	106.4	18097.5	40.1	
	5.3	36.0	166.0	155.0	41822.0	69.0	
	53.8	368.0	2049.0	4520.0	174367.0	330.0	5.24
	57.0	531.0	1528.0	1550.0	197984.0	392.0	5.01
L29	<0.9	2.8	17.5	54.0	161.0	1.1	5.68
	2.1	124.0	392.0	4840.0	440.0	11.2	5.04
	3.1	183.0	882.0	6194.0	1326.0	17.6	4.98
	3.0	193.0	1127.0	6706.0	1514.0	19.8	4.77
	5.9	360.0	2838.0	6850.0	3384.0	22.0	4.88
	6.1	437.0	3666.0	6152.0	8446.0	37.0	5.06
	6.9	377.0	8179.0	9513.0	6865.0	36.6	4.73
L30	69.0	8.8	34.8	5663.0	2166.0	12.4	6.16
	20.6	46.5	143.0	8134.0	2226.0	12.6	5.94
	11.7	25.5	72.5	8069.0	1750.0	7.7	5.90
	10.2	55.0	90.0	5748.0	1297.0	4.8	6.32
	11.0	26.0	74.0	3030.0	1243.0	4.1	6.08
	1.6	8.6	31.9	4989.0	555.0	1.3	6.38
	6.0	32.9	135.0	2787.0	1011.0	2.8	6.59

Test Containers with Potential Pu(VI)

- L26 (Pyrochemical Salt Waste)

  Pu^{6+} developed slowly - Peaked - Declined

- L27 (Pyrochemical Salt Waste)

  Soluble Pu concentration increased Rapidly - Peaked - Declined
  Pu^{6+} was not identified

- L28 (Pyrochemical Salt Waste; CO_2; MgO

  Pu precipitated with MgO - Increased - Rapid Increase
  Pu^{6+} Identified

- All three test containers: Contain Fe mesh
  Have H_2 Headspace >50%

- Potential Oxidation Mechanisms
  - Basic Solution
  - H_2O_2; NaOCl

Latest Drum-Scale Results

Drum #	Nd	Th	Np	U	Pu	Am	pcH	Remarks:
D01	5.5	10.2	45.0	70.0	2.0	0.2	7.67	-
D02	2.6	16.0	54.0	260.0	1.7	0.3	7.68	-
D03	1.1	0.9	0.8	166.0	1.7	0.4	6.88	-
D04	1.5	2.6	4.4	25.0	2.1	0.3	7.39	bentonite
D05	0.7	0.7	1.2	35.8	0.8	0.3	7.11	bentonite
D06	0.7	0.4	4.8	12.5	0.8	0.1	7.17	bentonite
D07	1841.0	9598.0	17841.0	16985.0	1138.0	4.6	7.37	chelators
D08	1881.0	13916.0	15078.0	12360.0	3228.0	17.3	7.19	chelators
D09	2713.0	7012.0	16081.0	15482.0	2302.0	13.0	7.16	chelators
D10	<2.0	18.6	330.0	76.0	15.0	<0.4	7.52	NO_3/PO_4
D11	<2.0	<1.2	<0.9	17.0	<1.3	<0.4	7.47	NO_3/PO_4
D12	<2.0	<1.2	<0.9	18.0	16.0	<0.4	6.57	NO_3/PO_4
D13	31.0	<1.2	1.2	3.3	<1.3	<0.4	5.78	Fe
D14	10.0	<1.2	1.4	54.0	<1.3	<0.4	6.76	Fe
D15	<2.0	<1.2	3.5	19.0	<1.3	<0.4	7.79	Fe

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