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

JAN 2001

OFFICE OF
AIR AND RADIATION

Dr. Ines Triay
Carlsbad Field Office
Department of Energy
P.O. Box 3090
Carlsbad, NM 88221

Dear Dr. Triay:

Thank you for your letter dated February 10, 2000, which informed us of the preliminary results of the WIPP Actinide Source-Term Waste Test Program (STTP) experiments. These results appeared to show the transient existence of plutonium in the +6 oxidation state [Pu (VI)] and the +5 oxidation state [Pu (V)]. These experiments also suggested that magnesium oxide backfill, which is required by EPA's certification of the WIPP, may not perform in the WIPP as expected at least in one instance.

We have reviewed your initial analysis (Enclosure 1), your white paper (Enclosure 2), our related Compliance Application Review Documents (Enclosure 3), and comments and analysis from the Environmental Evaluation Group (EEG) (Enclosures 4 and 8). In addition, we held two meetings with you to discuss the STTP experiments and reviewed numerous documents submitted in response to questions we posed during those meetings.

Our review indicates that the preliminary results of these experiments do not challenge the Agency's conclusions as represented in our certification decision (Enclosures 6, 7 and 9). We previously acknowledged that Pu (VI) and Pu (V) may exist shortly after closure of the WIPP facility (Enclosure 3). As oxygen is removed from the system by corrosion and microbial activity, the higher oxidation states of Pu will be lowered to Pu (IV) and Pu (III) as the repository changes from oxidizing to reducing conditions and the system approaches long-term equilibrium. As we note in Enclosure 6, the STTP experiments did not appear to duplicate the reducing conditions achieved by previous work; therefore, we do not consider the results of the STTP experiments to be directly comparable.

The results of introducing MgO into container L-28 also were not conclusive. MgO appeared to have been effective for a short period of time, but ceased to function. In our analysis, the experiment was not a good test of MgO effectiveness because it did not adequately test MgO under WIPP-like conditions (see Enclosure 7).

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C. Trivelpiece

In summary, the preliminary results of the STTP experiments do not appear to challenge the actinide chemistry models used in the WIPP Compliance Certification Application. There is abundant experimental evidence that supports the conclusion that MgO will be effective and that the repository will have a reducing environment supporting the existence of Pu III and Pu IV over the long term (Enclosure 3).

We will place our report and related materials that you sent in our public docket. Please contact Mary Kruger at (202) 564-9310 if you have questions.

Sincerely,

Frank Marcinowski, Acting Director
Radiation Protection Division

Enclosures

Enclosure 1

Letter from I. Triay to F. Marcinowski
February 10, 2000

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

February 10, 2000

Mr. Frank Marcinowski
Office of Radiation and Indoor Air
U.S. Environmental Protection Agency
401 M. Street, S. W.
Washington, DC 20460

Dear Mr. Marcinowski:

This purpose of this letter is to provide information to the Environmental Protection Agency regarding the status of two activities at the Waste Isolation Pilot Plant (WIPP).

1. The supplier of the magnesium oxide (MgO) used as backfill in the disposal areas has changed. Material provided by the new supplier meets the technical criteria established in the specification for MgO. The change in vendor and MgO material will have no impact on the expected performance of the MgO within the repository environment.

2. Experiments conducted as part of the WIPP Actinide Source-Term Waste Test Program, at the Los Alamos National Laboratory, have confirmed the transient existence of plutonium in the +6 oxidation state [Pu (VI)] in two of the 15 test vessels containing pyrochemical salts. This transitory existence of Pu (VI) was not unexpected, but investigations continue in order to confirm hypotheses regarding the oxidation of the plutonium in these containers. Overall, these experiments continue to support the conclusion that actinide solubility models used in the WIPP Compliance Certification Application are conservative, i.e., they project higher concentrations of actinides than those that were measured in the test containers.

Attachments to this letter provide additional information on these items. If you have any questions, please contact George Basabilvazo at 505-234-7488.

Sincerely,

Inés R. Triay

Dr. Inés R. Triay
Manager

Enclosure(2)A: Magnesium Oxide Supplier Evaluation
B: Plutonium (VI) Analysis

cc w/ enclosures:
D. Huizenga, DOE EM
M. Kruger, EPA-ORIA

FILE COPY

cc w/o enclosures:
G. Basabilvazo, DOE/CAO
B. Lilly, DOE/CAO
N. Elkins, SNL MS 1395
M. Marietta, SNL MS 1395
B. Villarreal, LANL
J. Epstein, WID

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CAO:ORC:GTB:00-0016:UFC 5486.00

Attachment A: Magnesium Oxide Supplier Evaluation

Sandia National Laboratories
Operated for the U.S. Department of Energy by
Sandia Corporation

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Internet: nzelkin@sandia.gov

January 27, 2000

Mr. George T. Basabilvazo, Acting Assistant Manager
Office of Regulatory Compliance
U. S. Department of Energy
Carlsbad Area office
P. O. Box 3090
Carlsbad, NM 88220

Subject: Evaluation of Candidate MgO Materials for use as Backfill at WIPP

Dear Mr. Basabilvazo:

Sandia was requested by DOE/CAO to evaluate two candidate MgO materials for use as backfill at the WIPP. Sandia evaluated materials recommended and supplied by Martin Marietta Magnesia Specialties and by Premier Chemicals. Materials were evaluated on the basis of reactivity, particle size, chemical purity, and density. Based on the evaluation, Sandia considers either material acceptable from a technical perspective.

If you have any questions, please contact Yifeng Wang of my staff at (505) 234-0030.

Sincerely,

Robert H. Walter

for Ned Z. Elkins

UNIQUE #	DOE UFC	DATE REC'VD	ADDRESSEES
0000356	5400.00	JAN 28 2000	G. Basabilvazo D. Mercer Org attachment

To. G. Basabilvazo

Copy to:

DOE/CAO	D. Mercer
MS-0771	M. S. Y. Chu, 6800
MS-1395	M. G. Marietta, 6821
MS-0733	H. W. Papenguth, 6832
MS-0779	K. W. Larson, 6848
MS-1395	B. A. Howard, 6821
MS-1395	M. K. Knowles, 6821
MS-1395	Y. Wang, 6821
6810 Day File	

Attachment A: Magnesium Oxide Supplier Evaluation

Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation

4100 National Parks Highway
Carlsbad, NM 88220
Phone: (505) 234-0030
Fax: (505) 234-0061
E-mail: ywang@sandia.gov

date: January 18, 2000

to: Melvin G. Marietta, MS 1395 (6821)

from: Yifeng Wang, MS 1395 (6821)

subject: Evaluation of Candidate MgO Materials for use as Backfill at WIPP

Sandia was requested by DOE/CAO to evaluate two candidate MgO materials for use as backfill at the WIPP. Hans Papenguth and James Krumhansl conducted the requested evaluation; their detailed report is attached to this memorandum.

The primary purpose of backfill at WIPP is to control chemical conditions, so that actinide solubilities are minimal. Sandia evaluated materials recommended and supplied by Martin Marietta Magnesia Specialties and by Premier Chemicals. Materials were evaluated on the basis of reactivity, particle size, chemical purity, and density. Both candidate materials are acceptable in terms of particle size, reactivity, purity and bulk density.

DOE provided criteria to the manufacturers of the candidate materials. One of these criteria states that the total pounds of MgO emplaced must be the same. The lower net density (MgO plus equivalent CaO) of the Premier Chemicals Gabbs MgO results in a slight (~2%) increase in MgO bulk volume relative to the current supplier sample. While Sandia does not consider the slight decrease in net density of the Premier product significant with respect to the ability of the backfill to fulfil its stated function, adherence to the DOE criteria could require an increase in the volume of MgO emplaced if the Premier product is selected. This can readily be accomplished if the MgO super sacks and min-sacks are filled by weight, rather than by volume.

In summary, Sandia considers either material acceptable from a technical perspective.

Distribution

SWCF-A:1.2.07.1.1:PA:Parameters:MgO
SWCF-A:1.1.01.2.7:DPRP:NF:MgO Research Technical Studies (WPO#49064)

MS-0733	H. W. Papenguth, 6832
MS-0750	J. L. Krumhansl, 6118
MS-0771	M. S. Y. Chu, 6800
MS-0779	K. W. Larson, 6848
MS-1395	B. A. Howard, 6821
MS-1395	M. K. Knowles, 6121
MS-1395	Y. Wang, 6821
MS-1395	M. G. Marietta, 6821
MS-1395	N. Z. Elkins, 6810
MS-0733	J. W. Kelly, 6832
DOE	G. Basabilvazo
DOE	D. Mercer
WID	D. Haar
CTAC	M. B. Gross
CTAC	T. W. Thompson

Plutonium (VI) Analysis

The Waste Isolation Pilot Plant (WIPP) Actinide Source-Term Waste Test Program (STTP) was conducted at the Los Alamos National Laboratory (LANL) to test the hypothesis that: *The Actinide Source Term Solubility Model for dissolved and colloidal actinides used in the Compliance Certification Application (CCA) yields upper bounds on the mobile actinide concentrations from actual TRU waste in contact with WIPP brines.* This hypothesis derives from an expectation that the effect of complex, incompletely known chemical and physical conditions and processes in the disposal area containing actual waste will result in mobile actinide concentrations less than those predicted by the equilibrium solubility and colloid models in the CCA. Those processes include: dissolution and co-precipitation of actinides; occlusion of actinides in mineral phases; sorption on several kinds of waste material substrates and precipitates; and, slow evolution of mineral phase assemblages. Secondary objectives of the STTP were to corroborate the CCA assertion of reducing conditions and oxidation state distributions of the mobile actinides and to study the behavior of soluble actinides in actual wastes. It is expected in the WIPP that reducing conditions will prevail and dissolved and colloidal plutonium (Pu) will be in the +III and +IV oxidation states. Iron was added to the STTP test containers to represent waste drum container material, with the expectation it would maintain reducing conditions.

The STTP, therefore, is an extensive set of experiments designed to provide time-sequential quantitative measurements of mobile actinide (thorium, uranium, plutonium, americium) concentrations in WIPP relevant brines that have been in contact with actual contact-handled (CH) transuranic (TRU) wastes on a long-term basis (five years). In addition, the STTP enables evaluation of the influence of known additive chemical variables and unknown variables inherent in actual wastes on the behavior and concentration of mobile actinides, and on plutonium (Pu) speciation.

The STTP experiments were initiated in 1995 and consist of 39 liter-scale test containers with homogeneous or solidified waste and 15 drum-scale test containers with heterogeneous or debris waste. The CH-TRU waste for these tests was selected from the existing waste inventory at LANL, and for the liter-scale tests included aqueous waste solidified by Portland cement (12 containers), organic, aqueous, and inorganic waste solidified by Envirostone (12 containers), and pyrochemical salts (15 containers). Test vessels were loaded nominally in triplicates with respect to waste, with two containing simulated Salado Formation brine (Brine A) and the third containing simulated Castile Formation brine. A major difference between these brines is a higher magnesium (Mg) concentration in Brine A. Recently, five of the liter-scale test containers, L-1, L-20, L-21, L-31 and L-32, have been dismantled.

A comparison between the maximum predicted actinide concentrations by the CCA models and the measured concentrations in STTP tests shows that for all but one of the comparisons, the maximum predicted actinide concentration was an upper bound. The only exception occurred in liter-scale test container L-3 where the concentrations were very low and near the limit of detection. The results of the STTP confirm that the model

predictions form an upper bound on actinide concentrations. However, two tests have yielded actinide behavior that warrants further investigation. First, although iron mesh was introduced to simulate the reducing conditions expected in the repository, plutonium was identified and quantified in the +6 oxidation state [Pu(VI)] in one ambient pressure pyrochemical test container (L-26) and one pressurized container (L-28). Second, after addition of magnesium oxide (MgO) to the pressurized container (L-28) and re-pressurizing with carbon dioxide (CO_2) to 60 bar (870 psig), concentrations of plutonium initially decreased and subsequently increased. Pu(VI) was identified during this period. Preliminary data indicate that total Pu concentrations and Pu(VI) have now begun to decrease in L-28.

Several possible explanations have been developed for the presence of Pu(VI) in the two test containers based upon an initial review and analysis of preliminary data. While the STTP is a valuable set of experiments because it uses actual CH TRU waste, it is an extremely complex system that includes some waste constituents and additives that may not be present in the WIPP in significant quantities. This makes interpretation of STTP results, in the context of performance of the WIPP repository, quite difficult. For example, the WIPP Project, the Environmental Protection Agency (EPA), and the National Academy of Sciences (NAS) have all concluded that the large amounts of iron and other reductants in the disposal room will create reducing conditions and that the probability of significant quantities of Pu(VI) is unlikely. Investigators at Argonne National Laboratory, LANL, and Pacific Northwest National Laboratory (PNNL) have observed reduction of Pu(VI) in controlled laboratory experiments carried out in the presence of metallic iron. Iron, in the form of iron mesh, was added to the STTP containers to attempt to reproduce the same ratio of iron available to the brine in the repository. However, because Pu(IV) in the test containers was oxidized to Pu(VI), it is apparent that reducing conditions were not achieved and/or maintained in some of the STTP tests. The high plutonium and americium activities in the pyrochemical salt tests are believed to generate peroxide and hypochlorites that, in a basic solution, are strong oxidants that can oxidize Pu(IV) to Pu(VI).

It is believed that contact between brine and the iron mesh might have been delayed or prevented by encapsulation of the iron within a solid mass of pyrochemical salts formed in these containers. This potential for solidification of the pyrochemical salts in Brine A has been observed in L-31 and L-32, which have been dismantled and subjected to post-test analysis. In both instances, the solids in the container formed a solid mass that could not be broken up to determine the condition of the iron-mesh that had been added to the samples. Encapsulation would also be possible in L-28 where the reaction between the brine and hydrated MgO could have formed a solid mass of Sorel cement or brucite [$Mg(OH)_2$]. If the iron was not available for solubilization during the tests because of encapsulation, the expected reducing conditions would not have occurred and soluble Pu(IV) would be available to be oxidized to Pu(V) or Pu(VI) in an oxic environment. The detection of Pu(VI) indicates that oxic conditions were present in these STTP test containers. In fact, Pu(V) was detected in other pyrochemical salt containers, L-27, L-36 and L-39, which attests to the oxic conditions in at least some of the pyrochemical salt tests. However, it is likely that the conditions in most of the test containers are not

representative of the expected redox conditions in the WIPP disposal areas, and that the Pu(VI) results are not significant with respect to repository performance. Post-mortem examinations of the other liter-scale test containers that have been opened show that iron mesh exposed to either Brine A or Castile Brine did not dissolve as expected because of the formation of a protective coating on the surface of the iron. In these cases, the iron mesh in L-1 (Portland cement and Brine A), L-20 (Envirostone and Brine A) and L-21 (Envirostone and Castile brine) had a magnesio-ferrite coating and showed little corrosion.

The Pu concentration in L-26 remained very low for about a year and then increased rather rapidly. Pu(VI) was identified and quantified during this period of higher Pu concentrations. The test conditions and results for L-28, the test container pressurized with 60-bar CO_2 were different than for L-26. After about 17 months under test, the container was depressurized, MgO was added and then the CO_2 pressure re-applied. Immediately after adding the MgO, the Pu concentrations reduced by a factor of about five. However, after re-pressurizing, the Pu concentrations rose to approximately double those before adding the MgO. Preliminary data from the most recent samples indicate the Pu concentrations may have peaked and appear to be decreasing. There are a number of possible explanations for this behavior that relate to possible interactions between the brine, MgO and CO_2 and that are unlikely to be representative of those occurring in the repository.

In L-28, MgO was added to Brine A, under normal atmospheric CO_2 conditions, before introduction to the test vessel. The pH of this slurry prior to its introduction to the vessel was approximately 8.4. After addition of the MgO slurry to the vessel, the vessel was re-pressurized and the pH decreased to approximately 7.7 and later to 7.6. This is a clear indication that the system was never in equilibrium with brucite and hydromagnesite (hydrated magnesium carbonate•magnesium hydroxide), the condition anticipated in the WIPP disposal room, since brucite will not form at a pH below approximately 8.4. The pH of the system then decreased to approximately 5, the original pH of the vessel before the MgO addition. This indicates that the buffering capacity of MgO was either overwhelmed by the CO_2 in the vessel or that reaction products formed on the Mg and prevented further reaction.

Calculations and experiments at SNL have shown that a minimum threshold concentration of magnesium chloride in brine is required to form Sorel cement. The source of the Mg for precipitation of Sorel cement in the presence of MgO is from the brine itself and the pyrochemical salt wastes, not the MgO. As CO_2 is introduced to Salado brine containing MgO, calcite ($CaCO_3$) initially precipitates, followed by Sorel cement and finally brucite. Formation of Sorel cement in L-28 may have coated the MgO particles and seriously changed the chemical kinetics of the reaction with carbonate. In addition, there are indications that the MgO-brine slurry may have reacted with the brine and solidified upon entry to the vessel, and the MgO may thus have been restricted to the volume above the protective screen or may have formed a solid mass with a limited surface area for reaction.

It is apparent that the conditions in the tests wherein Pu(VI) was observed may not be representative of those expected for the overall WIPP repository. It should also be noted that the plutonium concentrations in these containers increased and then decreased very quickly (over about four years) in terms of the time frames relevant to the repository (10,000 years), and that the appearance of the +6 oxidation state was even more transitory. Moreover, the total plutonium concentrations in these containers were at all times less than predicted by the models for Pu(III) and Pu(IV). The transitory occurrence of Pu(V) and Pu(VI) in the STTP are not unexpected and are consistent with information presented primarily in Chapter 6 and Appendix SOTERM of the WIPP CCA.

Finally, it is relevant to note that the waste-form in these containers (pyrochemical salts) is expected to constitute only a small fraction of the WIPP inventory. The TRU Waste Baseline Inventory Report estimate of the salt waste volume (final form) is 640 cubic meters. This represents approximately 0.4% of the total waste volume for CH-TRU (about 160,000 cubic meters). With consideration of uncertainties in the data, the salt waste volume is believed to be less than 1% and probably less than 0.5% under all circumstances. Of this 0.4%, about 95% is anticipated to come from the Rocky Flats Environmental Technology Site (RFETS). It should be considered that even though the salt waste volume is very small, the treatment of the RFETS residues involves a large amount of plutonium. The residues have significantly higher concentrations of plutonium than other wastes (up to about 20% or so). Therefore, the amount of plutonium in this salt waste is disproportionately larger than the average plutonium concentration ratio in the total waste inventory volume.

It is important that the specific reasons for the actinide behavior in these two STTP vessels are understood and the WIPP project is continuing its attempts to ascertain the specific reasons for this behavior. Additional analysis and review of the STTP results are currently underway to learn more about the behavior of plutonium under STTP conditions and its relevance to the WIPP repository.

Enclosure 2

DOE White Paper on STTP Experiments

THE OBSERVATION OF PLUTONIUM IN THE +VI OXIDATION STATE IN THE ACTINIDE SOURCE-TERM TEST PROGRAM EXPERIMENTS

1.0 INTRODUCTION

The Actinide Source-Term Waste Test Program (STTP) experiments were intended to support the Actinide Source Term Model (ASTM) used in the Waste Isolation Pilot Plant (WIPP) Compliance Certification Application (CCA). Specifically, the STTP was a series of long-term tests wherein actual contact-handled transuranic (CH-TRU) wastes were immersed in WIPP relevant brines. The tests were intended to confirm that actinides would not be solubilized to a greater degree in brine equilibrated with real waste than projected by the ASTM.

The STTP tests were designed in late 1994 and 1995 and were based on the repository conceptualization at that time. The tests were initiated at the Los Alamos National Laboratory (LANL) in 1995. However, since these tests were being designed while the WIPP Project Technical Baseline was still in development, the design details of individual tests were sometimes different than the final repository conditions. A specific example of these differences was the addition of bentonite as a backfill in some tests. Magnesium oxide (MgO), rather than bentonite, was adopted as the WIPP backfill in late 1995/1996. Because of these differences, care is needed in interpreting the results of the STTP tests, especially in extrapolations to WIPP repository conditions. The results of the STTP were always intended to be confirmatory of levels of actinide solubilities and the results were not used directly in the calculations supporting the CCA. In large part, this was because of the difficulty of interpreting results from the extremely complex systems represented in the tests.

The STTP successfully demonstrated that the ASTM predictions were conservative. Thus, under WIPP relevant conditions and immersion in WIPP formation brines, the actinides in waste solidified with Portland cement and Envirostone and in pyrochemical salt wastes, either were solubilized at concentrations well below the predictions of the ASTM, and/or were not significantly solubilized. However, in two of the liter-scale tests with a pyrochemical salt waste matrix (L-26 and L-28) plutonium in the +VI oxidation state [Pu(VI)] was identified. Pu(V) was detected in other pyrochemical salt containers (L-27, L-36). After addition of MgO to one of these containers (L-28), concentrations of plutonium and americium (Am) initially decreased and then rapidly increased. Following this increase, Pu(VI) was identified in a single sample. The plutonium concentrations in L-26 and L-28 are currently decreasing, and Pu(VI) levels have declined below detectable limits in both containers, even using advanced spectroscopic methods.

The explanation of these results lies in the detailed chemistry of these containers, and as noted above, significant differences exist between STTP test conditions and those expected on a repository scale. The conditions experienced in some of the STTP environments may only occur in the repository as isolated microenvironments, i.e., within drums or localized areas. If these microenvironments occur, they will be transitory in nature , as supported, for example, by the data for L-26 and L-27, and will not be representative of the overall chemical behavior of the repository. Differences between the test conditions and the expected repository environment will be discussed

in this paper. As an example, iron was included in the STTP vessels to simulate the iron available from the waste drums. This iron was included inside the test container as a mesh contained in the waste, and in some cases appears to have been encapsulated by the waste. However, this arrangement is quite different from that which can be expected in the repository where the iron will surround the waste.

It is also important to recognize that the pyrochemical salt waste form does not comprise a major component in the waste inventory. The TRU Waste Baseline Inventory Report (revision 3) estimates that the salt waste represents less than 0.02% of the total waste by weight for CH-TRU waste. About 95% of all pyrochemical salt waste is expected to be from the Rocky Flats Environmental Technology Site. The treatment of these Rocky Flats wastes involves a large relative amount of plutonium, i.e., these wastes have significantly higher concentrations of plutonium than other wastes (up to 20% greater).

This paper presents the results to date for the two liter-scale containers that developed Pu(VI) and provides a preliminary evaluation of results. Section 2 gives background information on the STTP, its purpose, conduct and preliminary results. Section 3 gives more detail on the relevant results from L-26 and L-28, while Section 4 provides a discussion of these results.

2.0 STTP BACKGROUND

2.1 Purpose of STTP

A primary objective of the STTP was to test the hypothesis that: *The Actinide Source Term Model for dissolved and colloidal actinides used in the Compliance Certification Application (CCA) yields upper bounds on the mobile actinide concentrations from actual TRU waste in contact with WIPP brines.* The basis for this hypothesis lies in the knowledge that various processes will tend to reduce the concentration of soluble and colloidal actinides. Those processes include: slow dissolution and co-precipitation of actinides; occlusion of actinides in mineral phases; sorption on several kinds of waste material substrates and precipitates; slow aging of solubility-controlling solids; and, slow evolution of mineral phase assemblages. For simplicity these processes are not included in the ASTM, so that predictions from that model may be expected to give upper bounds, and to be conservative.

A secondary objective of the STTP was to corroborate the CCA assertion of reducing conditions and oxidation state distributions of the mobile actinides. It is expected in the WIPP that reducing conditions will prevail and dissolved and colloidal Pu will be in the +III and +IV oxidation states. Reducing conditions in the STTP were anticipated primarily from the iron (Fe) that was added to represent actual waste drum container material. This will be discussed in relation to L-26 and 28 in a later section.

2.2 STTP Actual TRU Waste Tests

The STTP experiments were initiated at LANL in 1995 to test the above hypothesis by measuring mobile actinide concentrations in simulated WIPP brines mixed with actual CH-TRU waste and

potential backfill materials. These measurements were to be compared with concentrations predicted from dissolved species and colloid solubility models. The hypothesis would be supported by STTP results if measured mobile actinide concentrations were bounded by the source term model predictions. The results from the STTP experiments were not directly used in the CCA, since their function was simply to ensure that under the complex real waste chemical environments the solubility of the actinides was no greater than predicted by the ASTM. Moreover, because of the differences in conditions between the STTP experiments and those expected in the repository with MgO backfill, the results of the STTP do not directly describe the overall processes in the repository.

The STTP experiment consists of 39 liter-scale test containers and 15 drum-scale test containers. The CH-TRU waste for these tests was selected from the existing waste inventory at Los Alamos National Laboratory (LANL). Compromises were necessary in the design of the STTP. These included: a limited sample of waste; potential variability of the waste; chemical complexity of the system; and, the relatively short (compared with the performance assessment period) test duration of approximately 4 years.

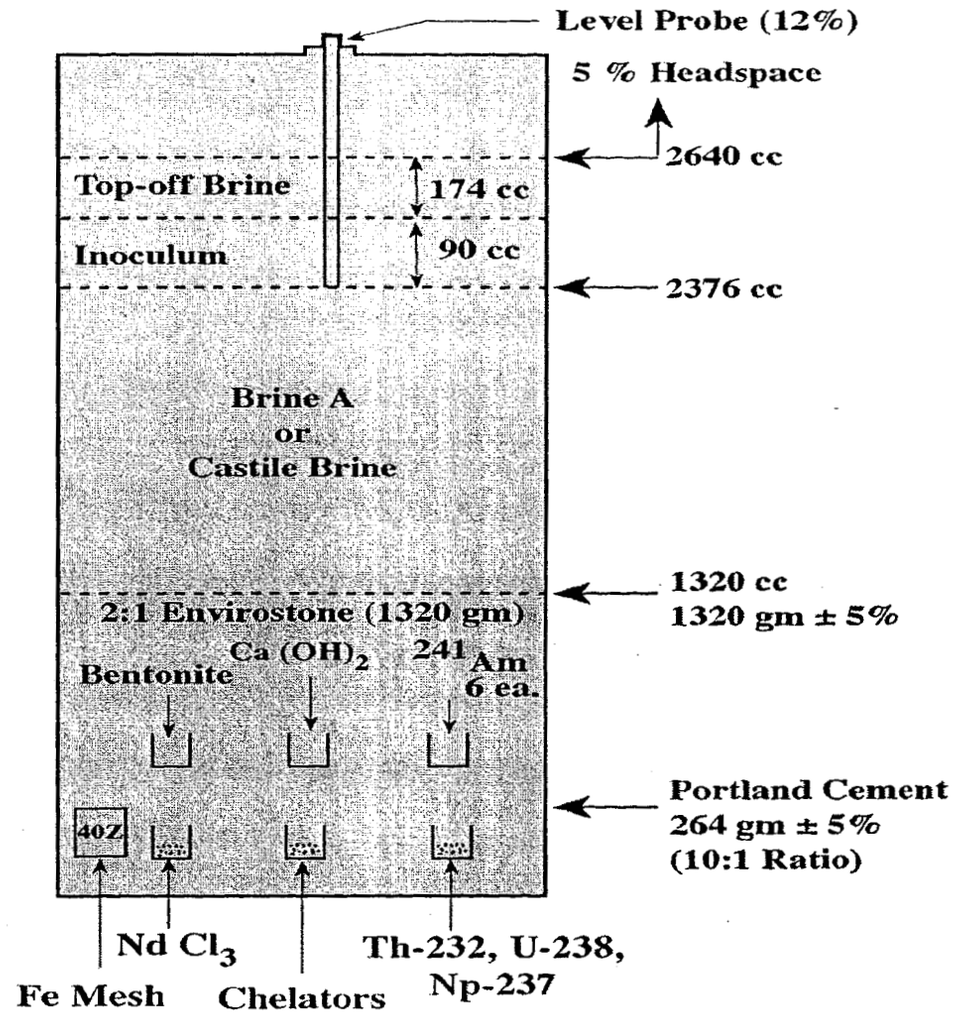
The liter-scale test containers were loaded in the following manner:

1. The test container was loaded with waste, in most cases with nominally 110 grams of Fe mesh, and influencing chemical variables.
2. Brine A or Castile brine and inoculum were added to the test container. The inoculum was obtained from brine obtained at or near the WIPP site. The inoculum added to each test container could be expected to contain organic colloids and organisms.
3. The test container was topped off with brine to leave a headspace volume of about five- percent of the test container volume.
4. The test container was then loaded onto an agitation device that rotated the test containers through 360-degree rotation once a week for 15 minutes.
5. Six of the test containers (L-4 to L-6 and L-28 to L-30) were pressurized with carbon dioxide to 60 bar (870 psig). This was intended to simulate conditions which were considered possible early in the project due to CO_2 production by microbial degradation. At the time that the STTP tests were designed and initiated MgO backfill was not under consideration. MgO will sequester CO_2 produced by the microbial degradation.

A schematic of non-pressurized liter-scale tests is depicted in Figure 2-1. The set-up for pressurized containers is shown in Fig 2-2.

The 39 liter-scale tests include three major compositional types: twelve containers that contain aqueous waste solidified by Portland cement; twelve that contain organic, aqueous, and inorganic waste solidified by Envirostone; and fifteen that contain pyrochemical salts. The wastes for these vessels were taken from portions of solidified waste that was obtained from standard 55-gal drums containing actual waste. This "homogeneous" waste was comminuted to improve contact between the actinides in the solids and the liquid phase. The comminuted waste was placed in the all-titanium liter-scale test containers that each had a volume of three liters.

STTP Liter-Scale Test Container
2:1 Ratio

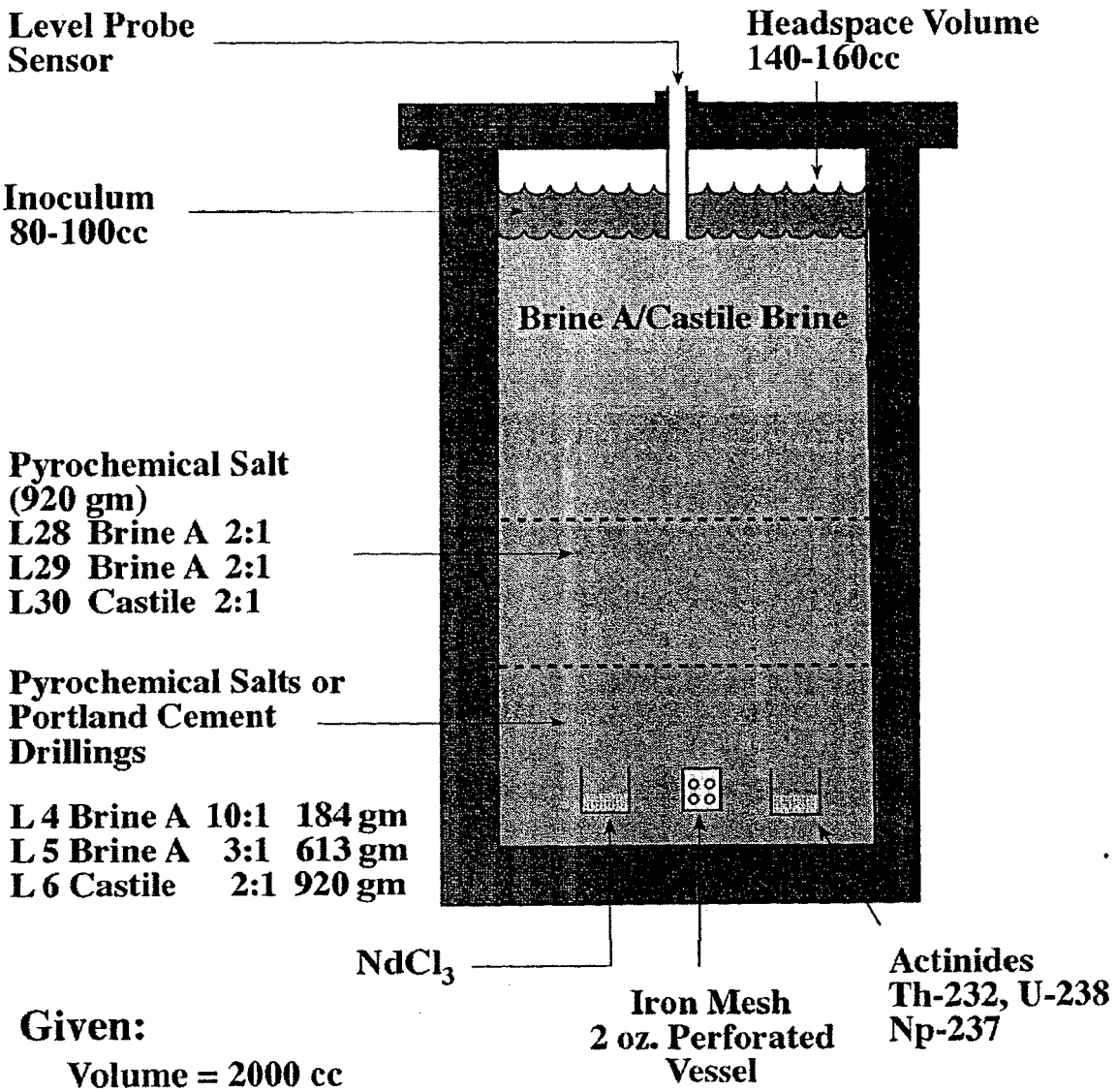


Given:
Volume = 3000 cc
Headspace Volume = < 12% or < 360 cc
Inoculum = 5-10%
Assume Envirostone and Portland Cement = 1.0 gm/cm^3

Los Alamos
CST-94-1985A

Figure 2-1. Loaded non-pressurized liter-scale test container

STTP Pressurized Liter-Scale Test Container



Given:

Volume = 2000 cc

Minimum free brine volume = > 0.5 Liter

Inoculum volume = ~ 4-5% or 80-100 cc

Headspace volume = 240 cc minus inoculum volume

≈ 240-100 cc ≈ 140 cc

Los Alamos
CST-95-079A

Figure 2-2. Loaded pressurized liter-scale container

Iron (Fe), chelators, and hydrated lime ($Ca(OH)_2$) were added to some test containers to simulate the range of some anticipated controlling variables. Bentonite, a potential backfill material at the time the tests were initiated, was added to three of the pyrochemical salt test containers. Table 2-1 shows the type of waste, brine, and other added materials for the liter-scale tests. The tests were nominally loaded in triplicates with the same waste type and other added materials. The waste in two of the waste triplicates was inundated with Brine A and the third was inundated with Castile brine. Brine A simulates Salado Formation brine, and the other brine identified as Castile brine, simulates Castile Formation Brine.

As noted above, and indicated in Table 2-1, six of the test containers (L-4 to L-6 and L-28 to L-30) are high-pressure. These six test containers are pressurized with carbon dioxide to 60 bar (870 psig). A pressure of 60 bars was chosen to simulate the effects of high CO_2 pressure. Higher pressures were expected at the time, but this pressure was considered sufficient to investigate the effects of interest. The increase in fugacity, and thus the increase in pcH, with pressure becomes more gradual above 60 bar. After initiation of the STTP, MgO was selected as a backfill material for the repository to sequester CO_2 and buffer the repository pcH. In the presence of MgO, repository CO_2 pressures are expected to be much less than 60 bars. The L-28 test was modified by adding MgO in February 1997.

The 15 drum-scale tests consisted of the total contents of standard 55-gal drums containing actual waste. The contents were placed in all-titanium drum-scale (65-gal) test containers. The wastes in the drum-scale tests were of two major compositional types: twelve drums contained combustible debris and three contained massive metal. The test containers are periodically rotated to allow all of the solid phase waste to contact brine. Iron mesh was added to each drum. Chelators, nitrate, phosphate and bentonite were each added to three drums. Ten kilograms of brine-equilibrated bentonite were added to D-4 and D-5 and ten kilograms of bentonite that was not equilibrated with brine was added to D-6. The nitrate and phosphate were added as nutrients for microbial activity with the combustible debris waste. Similar to the liter-scale tests, the drums were also nominally loaded in triplicates with the same waste types and added materials. The brine in two of the waste triplicates was Brine A and the third was Castile brine. Table 2-2 shows the waste type, brine, and added materials for the drum tests.

Plutonium and americium were contained in the selected wastes. Uranium (U), thorium (Th) and neptunium (Np) were added as soluble salts to each test container. Additional americium was added as a soluble salt to six of the liter-scale test containers. Simulated WIPP brines were initially added to the waste in all containers. The temperature of the STTP experiments has been maintained at 30°C since the beginning of the liter-scale tests in 1995.

Table 2-1. Liter-scale Test Matrix

Test Container	Waste Type	Brine Type	Fe Added	Am Added	Chelators and $Ca(OH)_2$ Added	Bentonite Added
L-1	PC(2)	Brine A(5)	Yes			
L-2	PC	Brine A	Yes			
L-3	PC	Castile(6)	Yes			
L-4(1)	PC	Brine A	Yes			
L-5(1)	PC	Brine A	Yes			
L-6(1)	PC	Castile	Yes			
L-7	PC	Brine A				
L-8	PC	Brine A				
L-9	PC	Castile				
L-10	PC	Brine A		Yes		
L-11	PC	Brine A		Yes		
L-12	PC	Castile		Yes		
L-13	Enviro(3)	Brine A	Yes			
L-14	Enviro(3)	Brine A	Yes			
L-15	Enviro(3)	Castile	Yes			
L-16	Enviro(4)	Brine A	Yes			
L-17	Enviro(4)	Brine A	Yes			
L-18	Enviro(4)	Castile	Yes			
L-19	Enviro(5)	Brine A	Yes			
L-20	Enviro(5)	Brine A	Yes			
L-21	Enviro(5)	Castile	Yes			
L-22	Enviro(6)	Brine A	Yes			
L-23	Enviro(6)	Brine A	Yes			
L-24	Enviro(6)	Castile	Yes			
L-25	Pyroch(7)	Brine A	Yes			
L-26	Pyroch	Brine A	Yes			
L-27	Pyroch	Castile	Yes			
L-28(1)	Pyroch	Brine A	Yes			
L-29(1)	Pyroch	Brine A	Yes			
L-30(1)	Pyroch	Castile	Yes			
L-31	Pyroch	Brine A	Yes			Yes
L-32	Pyroch	Brine A	Yes			Yes
L-33	Pyroch	Castile	Yes			Yes
L-34	Pyroch	Brine A	Yes		Yes	
L-35	Pyroch	Brine A	Yes		Yes	
L-36	Pyroch	Castile	Yes		Yes	
L-37	Pyroch	Brine A		Yes		
L-38	Pyroch	Brine A		Yes		
L-39	Pyroch	Castile		Yes		

1 High Pressure; 2 Portland Cement
3 Absorbed Organic Liquids in Envirostone; 4 Absorbed Aqueous Laboratory waste in Envirostone
5 Cemented Inorganic Sludge in Envirostone; 6 Cemented Organic Sludge in Envirostone
7 Pyrochemical Salt

Table 2-2. Drum Test Matrix

Test Container	Waste Type	Brine Type	Fe Added	Chelators Added	Nitrate and Phosphate Added	Bentonite Added
D-1	Combust(1)	Brine A(2)	Yes			
D-2	Combust	Brine A	Yes			
D-3	Combust	Castile(3)	Yes			
D-4	Combust	Brine A	Yes			Yes
D-5	Combust	Brine A	Yes			Yes
D-6	Combust	Castile	Yes			Yes
D-7	Combust	Brine A	Yes	Yes		
D-8	Combust	Brine A	Yes	Yes		
D-9	Combust	Castile	Yes	Yes		
D-10	Combust	Brine A	Yes		Yes	
D-11	Combust	Brine A	Yes		Yes	
D-12	Combust	Castile	Yes		Yes	
D-13	Metals	Brine A	Yes			
D-14	Metals	Brine A	Yes			
D-15	Metals	Castile	Yes			

1 Combustibles
2 Simulated Salado Brine
3 Simulated Castile Brine

2.3 STTP Results

All test containers were sampled periodically. After the samples were taken, for all but the pressurized tests the sample volume that had been extracted was replaced with fresh brine to maintain the volume. Brine samples are taken from above a protective screen with a long needle syringe. The protective screen serves to prevent plugging of the needle when taking a sample. A brine sample is taken after the test containers have been rotated and allowed to settle over a weekend, or a minimum of about 32 hours. This time allows particulates and coagulated-immobile colloids to settle to the bottom of the test container or the bottom of the screen and prevent plugging of the syringe and needle used for sampling. Deactivation and Decommissioning (D&D) of two pyrochemical salt containers showed the presence of voluminous suspensions and suspended particles in recently agitated containers.

The brine samples were sequentially filtered with 5μ, 1.2μ, and 0.01μ filters before being distributed for extensive analysis. The analyses included measuring the total alpha activity, pcH, Eh, relevant metals, relevant anions, total inorganic carbon, total organic carbon, and the U, Pu, Am, Th, Np and neodymium (Nd) concentrations. Other less frequent analyses, such as particle size distribution, colloid characterization, and microbial analysis, have also been performed. The headspace gas has also been periodically sampled and analyzed in an effort to detect onset of corrosion, microbial processes and radiolysis. The gases analyzed included: hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide, and nitrous oxide.

During the four years of testing, the brine chemistry of tests with Portland cement and debris wastes, including concentrations of metals and anions, was established early in the test in most containers, and did not significantly change over most of the testing period. The measured pcH in most containers was also established early in the test and did not significantly change over most of the testing period. For the exceptions to this result, the pcH varied from 0.6 to 2.3 pcH units during the test period. In four of the containers the pcH increased (all Castile brine) and in six (all Brine A) the pcH decreased.

For most test containers, the actinide concentrations are relatively low, less than 10^{-5} moles/L, and did not change significantly during the testing period. The Pu and Am concentrations for 42 of the 54 tests are less than 10^{-6} moles/L. Current trends are that the actinide concentrations are either relatively constant or decreasing. The only additives that significantly increased actinide concentrations were the chelators. The chelators, as expected, increased the dissolved concentration of Pu, but the liter-scale tests with chelators were not the tests with the highest measured Pu concentrations. The drum-scale tests with chelators had the highest actinide concentrations for these tests. The addition of Fe, Am and nitrate did not appear to have a pronounced effect on the measured actinide concentrations. Tests with added phosphate and bentonite exhibited significantly lower concentrations of actinides. Evaluation of the ratio of the total alpha activity of the coarse- (>1.2 μ) and fine- (0.01μ – 1.2μ) filtered brines, indicates that no measurable contribution of colloidal actinides to the total actinide concentrations in the STTP brines was observed.

3.0 OCCURRENCES OF PU(VI) IN THE PYROCHEMICAL SALT LITER-SCALE CONTAINERS

Pu(VI) has been detected in brine samples from L-26 and L-28. The plutonium concentrations in L-26 and L-28 are currently decreasing, and Pu(VI) levels have declined below detectable limits in both containers, even using advanced spectroscopic methods. The total plutonium concentrations at all times have been well below model predictions in these containers. Following addition of MgO to L-28, an initial decrease in actinide concentration was followed by a relatively rapid increase in concentrations, especially of Pu. After reaching a maximum concentration, which was less than that predicted using the CCA model, all actinide concentrations began to decline. The results from these containers are summarized in the following sections.

3.1 Background

In the CCA, it is assumed that plutonium will persist only in the +III and +IV oxidation states, with 50% of the cases (vectors) assumed to be Pu(III) and 50% Pu(IV). It is believed that the presence of large quantities of Fe will produce reducing conditions in the repository, and prevent Pu speciation in either the V or the VI state. This assumption is significant because the solubility of Pu(VI) is higher than Pu(III) or Pu(IV). This assumption was presented to a Conceptual Model Peer Review Panel (CMPRP) and the National Academy of Sciences (NAS) WIPP review panel. Both of these expert review panels, as well as the EPA, accepted that this is a reasonable assumption for WIPP. After initiation of the STTP, but before submission of the CCA, MgO was selected as a

backfill for the WIPP because of its ability to sequester CO_2 and to buffer the pcH to a range between 9-10, where actinide solubilities are lower. MgO also reduces carbonates in solution, which can form highly soluble compounds with actinides. This predicted behavior has also been reviewed and accepted by the CMPRP, the NAS review panel and EPA.

Pu(VI) was detected in two of the 15 liter-scale containers containing pyrochemical salt wastes from TA-55 (a LANL technical area where nuclear materials are handled) waste drums. Pu(V) was detected in two of the other containers (Table 3-6). The pyrochemical salt waste streams were from two major processes, direct oxide reduction and oxygen sparging of electrorefined plutonium metal and salts. The pyrochemical salt waste contained refractory MgO crucibles used for direct oxide reduction. For the STTP, the crucibles and any salt lumps were comminuted, as was all solidified and sludge wastes. It was expected that the pyrochemical salt waste would be high in sodium chloride, potassium chloride, calcium chloride, magnesium oxide, magnesium chloride, fluorides, and some residual unreacted calcium metal and calcium oxide. The pyrochemical salts used for STTP contained the highest concentrations of ^{239}Pu and ^{241}Am relative to tests with any other waste forms (Table 3-1).

The pyrochemical salt tests were integrated into the STTP test matrix to determine the effect of high alpha activity waste, which could increase brine radiolysis. Radiolysis can produce oxygen, peroxide, and hypochlorite and result in a more oxic system. The effect of radiolytically produced oxidants was expected to dominate the Eh of the experiments as discussed in the Test Plan for the STTP.

The liter-scale test containers were formulated to contain approximately 1320 gm of comminuted pyrochemical salt wastes with a nominal 110 gm of Fe mesh in a flow-through plastic container added to most containers. Most of the test containers had brine added in a 2:1 brine to solid ratio (except L-34, 35, and 36 with a 3:1 ratio). The non-pressurized liter-scale test containers have a volume of about 3 liters with about 5% (150 cc) of the volume for gas headspace. This would leave about 2850 cc for waste and brine. Assuming the waste takes up 1320 to 1350 cc of space, the brine volume in each test container is about 1500 to 1530 cc.

Table 3-1: STTP Pyrochemical Salt Matrix

Test Container Number	Brine	Brine /Solid Ratio	Fe Mesh	Waste weight (gm)	Origin*	Pu µg/g of waste	Am µg/g of waste	Influencing Variables
25	Brine A	2:1	Yes	1,338	DOR	244	0.3	
26	Brine A	2:1	Yes	1,315	DOR	2,352	1.71	
27	Castile	2:1	Yes	1,315	DOR	2,716	1.18	
28	Brine A	2:1	Yes	907	DOR	11,530	0.634	60 Bar CO_2
29	Brine A	2:1	Yes	907	DOR	4,715	2.131	60 Bar CO_2
30	Castile	2:1	Yes	930	DOR	2,185	0.651	60 Bar CO_2
31	Brine A	2:1	Yes	1,315	OS	950	0.49	Bentonite
32	Brine A	2:1	Yes	1,315	OS	2,950	2.21	Bentonite
33	Castile	2:1	Yes	1,338	OS	380	0.83	Bentonite
34	Brine A	3:1	Yes	862	OS	2,630	3.06	$Ca(OH)_2$ & Chelators
35	Brine A	3:1	Yes	885	DOR	404	0.79	$Ca(OH)_2$ & Chelators
36	Castile	3:1	Yes	885	DOR	13,437	5.61	$Ca(OH)_2$ & Chelators
37	Brine A	2:1	No	1,315	DOR	1,624	0.83	^{241}Am added
38	Brine A	2:1	No	1,338	OS	1,695	5.55	^{241}Am added
39	Castile	2:1	No	1,338	OS	2,912	8.70	^{241}Am added

* DOR = Direct Oxide Reduction
OS = Oxygen Sparging

Two brines were used in these tests. The first two test containers in a triplicate contained Brine A and the third test container had Castile Brine. The chemistry of Salado brine (Brine A) is considerably different from Castile Brine (Table 3-2). The high $MgCl_2$ concentration in Brine A is expected to have a significant role in the solidification of pyrochemical salts. The high Na and Cl, and the low Mg concentration in Castile Brine is projected to have a solubilizing role in the pyrochemical salt tests. Also, because of the high Mg concentration, Brine A has a buffering capacity that maintains the pcH in pyrochemical salts in the range of 8 to 9, while Castile Brine has little buffering capacity and the pcH measurements of these containers are more alkaline, in the 10 to 11 range.

Table 3-2: Composition of Salado (Brine A) and Castile Brines

Compound	Brine A (g/l)	Castile Brine (g/l)
$MgCl_2 \cdot 6H_2O$	292.10	3.86
NaCl	100.10	261.64
KCl	57.20	7.23
Na_2SO_4	6.20	23.70
$Na_2B_4O_7 \cdot 10H_2O$	1.95	6.00
$CaCl_2$	1.66	1.33
$NaHCO_3$	0.96	0.00
NaBr	0.52	1.13
LiCl	0.125	0.00
RbCl	0.027	0.00
$SrCl_2 \cdot 6H_2O$	0.015	0.00
KI	0.013	0.00
$FeCl_2 \cdot 6H_2O$	0.0125	0.00
CsCl	0.00125	0.00

3.2 Results

3.2.1 Observations of pcH of Pyrochemical Salt Tests

The initial pcH of the brine in all 15 pyrochemical salt tests was basic, presumably from the solubilization of Ca, CaO, and $CaCO_3$. The test containers with Brine A displayed a buffering effect from the high Mg content in the brine resulting in pcH of 8-9 while the tests with Castile brine were generally in the pcH 10-11 range. Liter-scale tests L-28, L-29, and L-30, which were pressurized with CO_2, became acidic, and the pcH values shortly after pressurization were 5.4, 5.7, and 6.2, respectively. The pcH trends are summarized in Table 3-3.

3.2.2 Dissolution of Pu in STTP Pyrochemical Salt Wastes

Table 3-4 shows the initial Pu loading of the pyrochemical salt containers, and the percentage that dissolved and for a time remained in solution after contact with brine. Table 3-4 includes the concentrations of Pu in units of ppb. Table 3-5 gives conversions to molarity and molality. Table 3-4 indicates that most of the pyrochemical salt containers showed very low soluble Pu levels. With the exception of L-26, L-27 and L-28, Pu solubilized was less than 1% and was less than 0.1% in many containers. Table 3-4 also shows that the percent solubilized in L-26 and L-27 has declined considerably from the peak values. The same is indicated in Figure 3-1, which shows the Pu concentrations for the three replicates L-25, L-26 and L-27, and for the three pressurized containers, L-28, L-29 and L-30.

Table 3-3: pcH Trends of Liter-Scale Pyrochemical Salt Tests

Test Container	Initial pcH	Peak pcH	Low pcH	Final pcH
25	8.4	8.4	7.6	7.9
26	8.4	8.4	7.6	7.9
27	11.1	11.5	10.7	11.8
28	5.4	7.7	5.2	5.2
29	5.7	5.7	4.8	5.1
30	6.2	6.4	5.9	6.4
31	9.0	9.1	8.6	8.8
32	8.9	9.0	8.6	8.7
33	9.8	9.9	9.6	9.6
34	9.0	9.0	8.6	8.8
35	8.3	8.3	8.2	8.3
36	11.2	11.4	11.0	11.3
37	8.8	8.8	7.5	7.8
38	8.6	8.6	7.4	7.8
39	9.9	9.9	9.4	9.5

Table 3-4: Pu Concentration & Activity in Pyrochemical Salt Test Containers

Test Container	Weight of Waste (gm)	Maximum Calculated Pu Conc.[1] (ppb)	Measured (Most Recent) Pu Conc. (ppb)	% Pu Solubilized in Brine (Most Recent)	Highest Measured Pu Conc. (ppb)	% Pu Solubilized in Brine (Highest Measured)
L-25	1,338	163,250	61	0.04	170	0.1
L-26	1,315	1,546,450	6,127	0.4	70,826	4.6
L-27	1,315	1,785,770	27,324	1.5	243,438	13.6
L-28	907	5,228,850	197,984	3.8	197,984	3.8
L-29	907	2,321,900	6,865	0.3	8,446	0.4
L-30	930	452,900	1,011	0.2	2,226	0.5
L-31	1,315	624,650	209	0.03	209	0.03
L-32	1,315	1,939,650	171	0.009	697	0.04
L-33	1,318	254,254	121	0.05	196	0.1
L-34	862	1,113,550	20	0.02	50	0.004
L-35	885	178,770	111	0.06	1,458	0.8
L-36	885	5,945,850	4,650	0.08	19,963	0.3
L-37	1,315	1,067,800	79	0.007	139	0.01
L-38	1,338	1,113,950	8	0.0007	19	0.002
L-39	1,338	1,948,128	1,251	0.06	2,599	0.1

1 Maximum calculated Pu concentration is the concentration which would result if all the available Pu were dissolved in the available brine.

Table 3-5: Equivalency of Units for ^{239}Pu Concentrations in STTP Tests

ppb (1)	ppm (2)	Molarity (3)	Molality (4)
1	1×10^{-3}	4.18×10^{-9}	3.42×10^{-9}
10	1×10^{-2}	4.18×10^{-8}	3.42×10^{-8}
100	1×10^{-1}	4.18×10^{-7}	3.42×10^{-7}
500	5×10^{-1}	2.1×10^{-6}	1.72×10^{-6}
1,000	1	4.18×10^{-6}	3.42×10^{-6}
5,000	5	2.1×10^{-5}	1.72×10^{-5}
10,000	10	4.18×10^{-5}	3.42×10^{-5}
50,000	50	2.1×10^{-4}	1.72×10^{-4}
100,000	100	4.18×10^{-4}	3.42×10^{-4}
200,000	200	8.37×10^{-4}	6.86×10^{-4}

(1) ppb = parts per billion; μg/L
(2) ppm = parts per million; mg/L
(3) molarity = mole of solute/L; solute = ^{239}Pu = 239 gm/mol
(4) molality = mole of solute/kg; density of brine assumed to be 1.22 gm/ml for all test containers

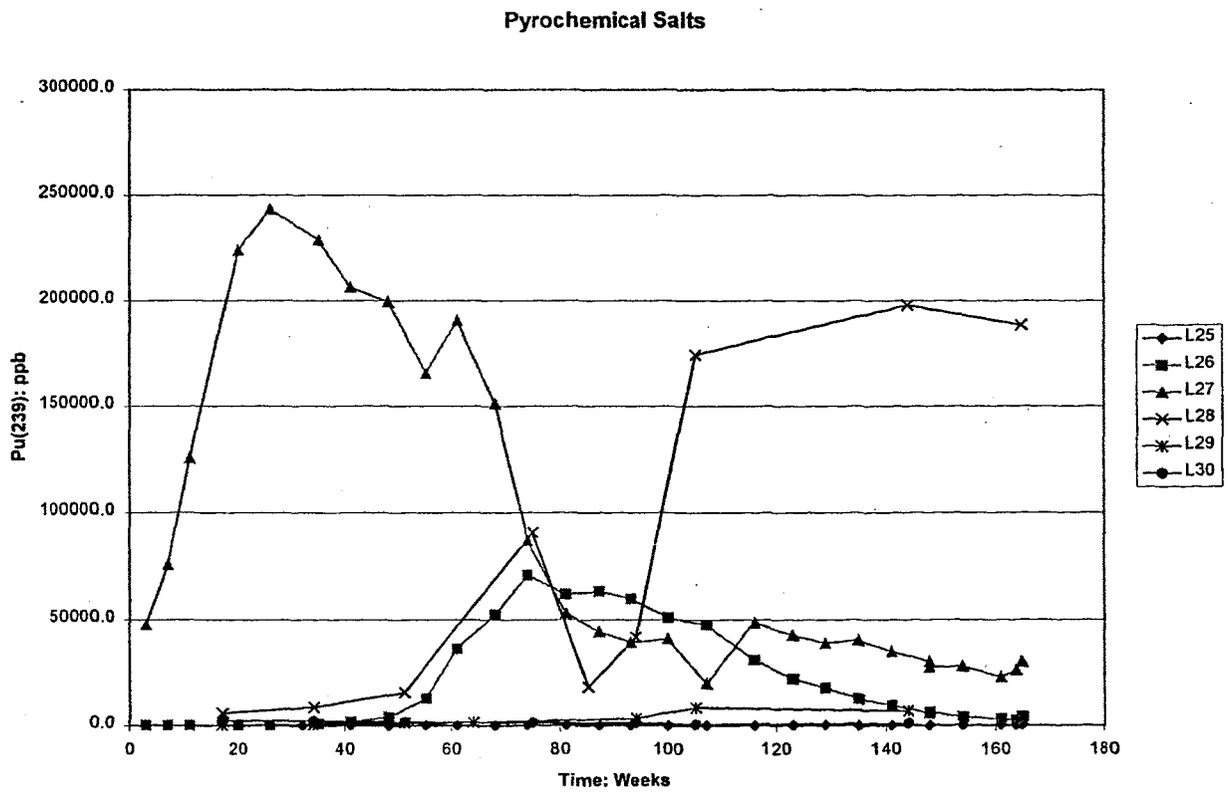


Figure 3-1: Plutonium Concentrations for Pyrochemical Salt Containers L-25 through L-30

Table 3-6: Concentration of Fe and Pu in L-26, L-27, and L-36, and in Pressurized Containers: L-28, 29, and 30

Test Container	Date	Fe (ppm)	Pu (ppb)[2]	pcH	Pu(V)[1]	Pu(VI)[1]
26	05/08/95	0.4	43	8.42		
26	06/12/95	< 0.1	61	8.18		
26	07/17/95	< 0.1	17	8.11		
26	09/18/95	1.4	187	8.11		
26	10/30/95	3.3	180	7.95		
26	01/29/96	1.9	903	6.78		
26	03/18/96	1.3	1,675	7.68		
26	05/06/96	29	3,996	7.63		
26	07/08/96	1.5	12,775	7.69		
26	08/19/96	1.9	36,161	7.81		
26	10/15/96	3.4	52,507	7.82		
26	12/02/96	1.8	70,826	7.74		
26	02/03/97	3.7	61,920	7.74		
26	03/24/97	< 0.1	63,413	7.64	No	Yes
26	05/06/97	0.7	59,729	7.80	No	Yes
26	07/07/97	<0.1	50,970	7.72	No	Yes
26	08/25/97	1.9	47,587	7.81	No	Yes
26	02/16/98	< 0.1	30,893	7.77	No	Yes
26	04/06/98	< 1.0	21,929	7.77	No	Yes
26	05/18/98	1.0	17,607	7.85	No	Yes
26	07/13/98	< 1.0	12,566	7.87	No	Yes
26	08/24/98	< 1.0	9,557	7.88	No	Yes
26	11/02/98	4.1	5,642	7.88	No	No
26	11/02/98	1.7	6,127	7.85	No	No
26	1/4/99	3.7	4,029	7.89	No	No
26	3/1/99	1.1	3,138	7.96	No	No
26	4/5/99	<1.0	2,496	7.99	No	No
26	5/17/99		4,141	7.50	No	No
27	5/8/95	43	47,672	11.08		
27	6/12/95	63	75,828	10.94		
27	7/17/95	125	125,602	10.72		
27	9/18/95	131	224,024	10.73		
27	10/30/95	169	243,438	10.74		
27	1/29/96	219	228,974	10.65		
27	3/18/96	206	206,253	10.72		

Test Container	Date	Fe (ppm)	Pu (ppb)[2]	pcH	Pu(V)[1]	Pu(VI)[1]
27	5/6/96	243	199,254	10.74		
27	7/8/96	206	165,474	10.75		
27	8/19/96	185	190,511	10.84		
27	10/15/96	183	151,097	10.84		
27	12/2/96	169	87,162	10.87	Yes	No
27	2/3/97	161	52,994	10.93		
27	3/24/97	174	44,265	10.92	Yes	No
27	5/6/97	156	39,175	10.9		
27	7/7/97		40,784	10.92	Yes	No
27	8/25/97	82	19,717	10.96	Yes	No
27	2/16/98	145	48,611	10.98	Yes	No
27	4/6/98	104	42,564	11		
27	5/18/98	102	38,916	11.11	Yes	No
27	7/13/98	82	40,267	11.18	Yes	No
27	8/24/98	98	34,880	11.05	Yes	No
27	11/2/98	71	30,127	11.07	Yes	No
27	1/4/99	101	27,905	11.08	Yes	No
27	3/1/99		22,799	11.14	Yes	No
27	4/5/99	47	26,053	11.15	Yes	No
27	5/17/99		29,683	11.03	No	No
28	8/28/95	19	5,989	5.4		
28	1/22/96	29	8,731	4.9		
28	6/3/96	62	15,678	4.7		
28	12/9/96	165	90,942	4.5		
28	2/3/97 (MgO)			-		
28	3/3/97	3	18,098			
28	5/12/97	-	41,822	-		
28	6/2/97	1	-	7.6		
28	8/11/97	101	174,367	5.2		
28	9/21/98	15	197,984	5.0		
28	5/17/99	49	188,463	5.1	No	Yes
28	12/6/99				No	No
29	8/28/95	58	161	5.7		
29	1/22/96	634	440	5.0		
29	6/3/96	1,468	1,326	5.0		
29	9/9/96	773	1,514	4.8		

Test Container	Date	Fe (ppm)	Pu (ppb)[2]	pcH	Pu(V)[1]	Pu(VI)[1]
29	5/12/97	94	3,384	4.9		
29	8/11/97	225	8,446	5.1		
29	9/21/98	34	6,865	4.7	No	No
30	8/28/95	<1	2,166	6.2		
30	1/22/96	1,967	2,226	5.9		
30	6/3/96	1,515	1,750	5.9		
30	12/9/96	454	1,297	-		
30	5/12/97	256	1,243	6.1		
30	8/11/97	52	555	6.4		
30	9/21/98	9	1,011	6.6		
36	05/15/95	24	19,844	11.20		
36	06/19/95	43	19,963	11.04		
36	07/24/95	64	14,997	11.09		
36	09/25/95	103	6,704	11.06		
36	11/06/95	74	8,077	11.11		
36	02/05/96	94	2,446	10.58		
36	03/25/96	83	3,426	11.14		
36	05/13/96	68	3,193	11.13		
36	07/15/96	66	2,773	11.17		
36	09/03/96	57	3,798	11.19		
36	10/21/96	59	7,618	11.21	No	No
36	12/16/96	55	19,342	11.24		
36	02/10/97	55	18,179	11.22		
36	03/31/97	53	6,513	11.20	No	No
36	05/26/96	30	9,915	11.17	No	No
36	07/14/97		10,918	11.10		
36	12/08/97	43	17,493	11.22		
36	02/23/98	40	16,841	11.28	Yes	No
36	04/13/98	59	10,536	11.28		
36	06/01/98	33	9,198	11.37	Yes	No
36	07/20/98	24	7,112	11.30		
36	08/31/98	34	2,475	11.44	No	No
36	11/09/98		4,650	11.28	No	No
36	01/11/99		700	11.29	No	No
36	03/08/99		1,439	11.38	No	No

1 "Yes" indicates that Pu was found in this oxidation state, "No" that it was not found, blank that no determination of oxidation states was made.

2 For conversion of ppb to molarity or molality see table 3-5

Plutonium concentrations, the concentrations of soluble Fe, and the pcH for containers L-26 and L-28 are shown as a function of time in Figures 3-2 and 3-4. Concentrations for L-27 are shown in Figure 3-3 for comparison. Note that L-25, which is nominally similar to L-26, has a much lower Pu content in the waste, and consequently shows small soluble concentrations. The concentrations of soluble Fe in the non-pressurized pyrochemical salt tests were typically less than 1 ppm except for the Castile brine tests, L-27 and 36. The concentration of soluble Fe in the pressurized test containers was relatively high at certain times as shown in Figure 3-4 and Table 3-6. The data in Figure 3-4 and Table 3-6 indicate that the soluble Pu and Fe concentrations in L-28 were highest at the lowest pcH (4.5). Concentrations of Pu and Fe both decreased significantly upon addition of MgO but increased as the system was repressurized with CO_2 and the pcH began to drop again. Note that the Fe concentration in L-28 was relatively low compared with L-29 and 30 (Figure 3-5).

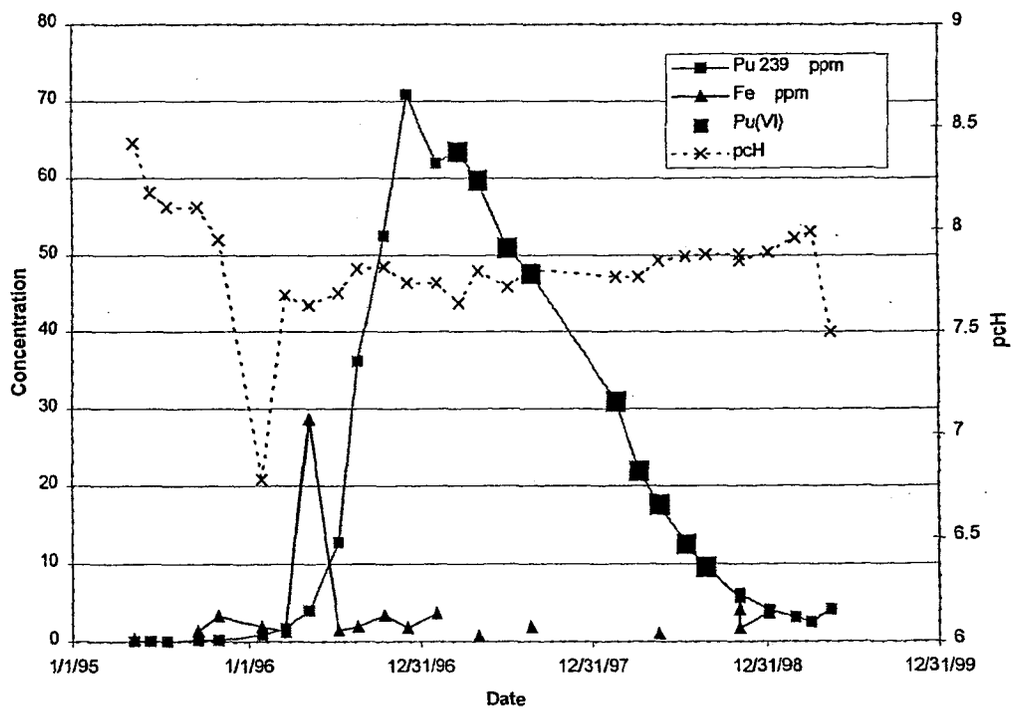


Figure 3-2: Pu and Fe Concentrations and pcH for L-26

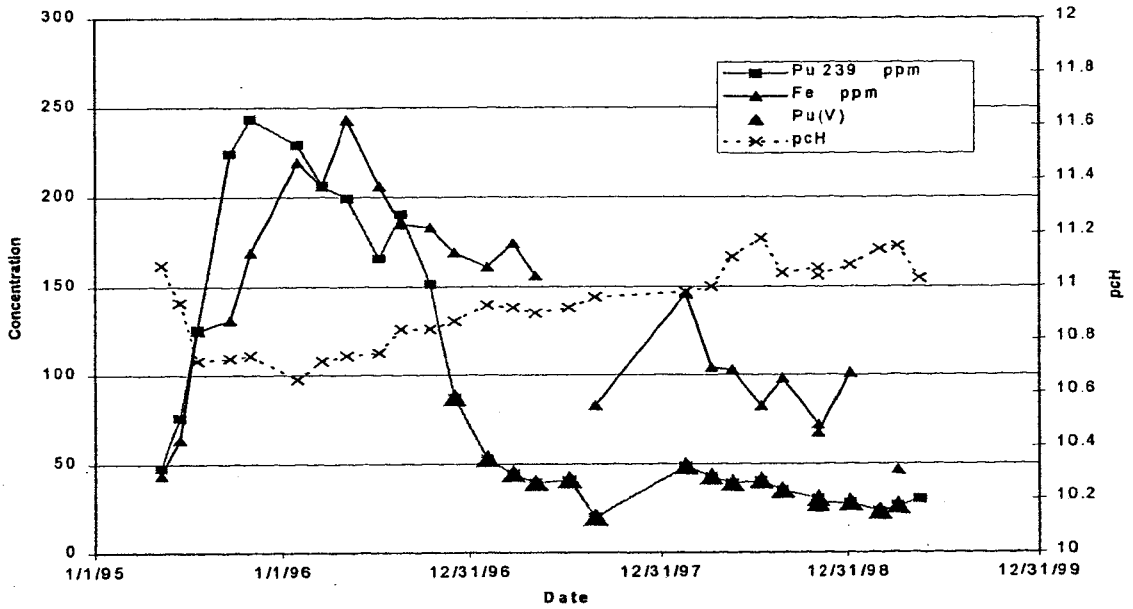


Figure 3-3: Pu and Fe Concentrations and pcH for L-27

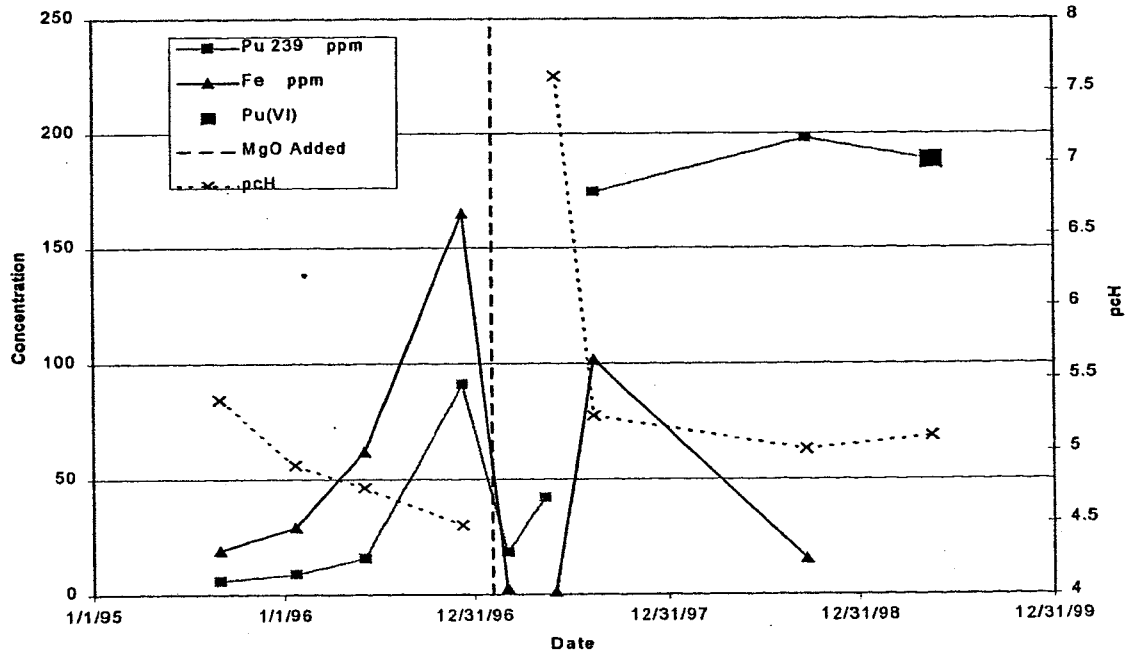


Figure 3-4: Pu and Fe Concentrations and pcH for L-28

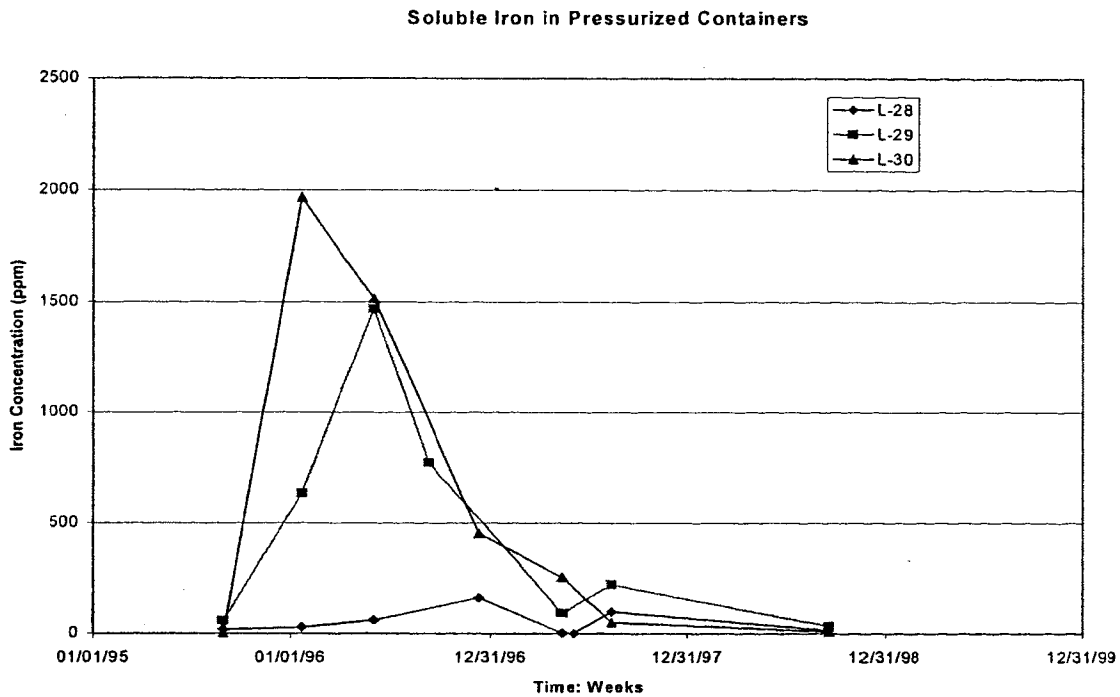


Figure 3-5: Fe Concentrations in the Pressurized Containers

3.2.3 Pu(VI) in Pyrochemical Salt Tests

To date, two containers have UV/VIS evidence of Pu(VI); L-26 and L-28. Liter-scale 26 is a Brine A experiment that showed very low concentrations of actinides for over one year, when concentrations of Pu and Am began to increase rapidly (Figures 3-1, 3-2). After showing the presence of Pu(VI) for about 1½ years, the levels of plutonium during the subsequent (most recent) 1½ years have continued to decline and Pu(VI) has not been detectable.

L-28 is a Brine A experiment that had a high loading of Pu and Am and the headspace of the test container was pressurized with 60 bar (870 psig) of CO_2. The pcH of the test container was initially 8.4 but the continued source of CO_2 dropped the pcH to the acid side of neutral after a few months and continued to drop to pcH 4.5 (Table 3-6, Fig 3-4). Subsequently, a decision was made to add MgO to the test container. Prior to addition of MgO, the Pu and Am concentrations had increased significantly.

MgO powder (76.4 gm) was added to Brine A as a slurry and the test container vessel was immediately agitated (rotated). The addition of MgO as a slurry was difficult because combining MgO with Brine A resulted in immediate formation of a suspended precipitate (slurry) that became more pronounced with time. The slurry had to be injected very rapidly after mixing or it would become too viscous to inject into the test container through the small-bore tubing used to inject the slurry.

Once the MgO slurry was added to the test container, the pcH increased from 4.5 to 7.7 and the concentration of all actinides decreased by a factor of 5 to 10. The Pu concentration decreased from about 91,000 ppb to 18,000 ppb. The headspace volume in L-28 after addition of MgO slurry is estimated to be about 50 ml. After repressurizing with CO_2 to 60 bar, the pcH decreased and the concentration of all actinides, especially Pu, increased dramatically over the next two months and continued to increase to about 200,000 ppb (Table 3-7). Pu(VI) was identified in one sample taken after the rapid increase in Pu concentration. A preliminary result from the next sample taken from L-28 did not show Pu(VI).

Container L-27 shows high early Pu concentrations which decrease after about eighteen months. This vessel contained Castile brine which has less magnesium than Brine A, and which therefore is not expected to engender formation of an impenetrable mass of the pyrochemical salts as occurs in Brine A containers. Pu(VI) was not detected in L-27, but Pu(V) was found, appearing after total concentrations started to decrease. Pu(V) was also found in two samples from L-36. However, in more recent samples from both containers Pu concentrations have declined, and Pu(V) has not been detected (Table 3-6).

Table 3-7: Actinide Concentrations following MgO Addition to L-28

Critical Parameters:

- CO_2 headspace at 870 psig
- Initial pcH 8.4
- Maximum calculated Pu 5,300,000 ppb
- Brine/Solid = 2:1

Added 76.4 gm MgO as slurry in Brine A (2/97)

Date	Nd[1] (ppb)	Th (ppb)	Np (ppb)	U (ppb)	Pu (ppb)	Am (ppb)	PcH	TIC (ppm)	TOC (ppm)
08/95	15	178	3,549	5,230	5,989	35	5.4	108	22
01/96	10	248	8,150	7,099	8,731	59	4.9	280	28
06/96	10	312	8,179	6,290	15,678	80	4.7	263	39
12/96	32	1,359	13,931	10,833	90,942	352	4.5		
2/97					MgO Added				
03/97	9	151	351	106	18,097	40		14	40
05/97	5	36	166	155	41,822	69		20	40
08/97	54	368	2,049	4,520	174,367	330	5.2	315	34
09/98	57	531	1,528	1,550	197,984	392	5.0	171	56
05/99	49	519	744	668	188,463	347	5.1		

[1] For conversion of ppb to molarity or molality see table 3-5

3.2.4 Deactivation and Decommissioning (D&D) of STTP Pyrochemical Salt Test Containers

Two test containers containing pyrochemical salts in Brine A (L-31 and L-32) were terminated and processed through a D&D procedure. It was found that the pyrochemical salts had formed a hard solid several inches thick at the bottom of the test container, and that the perforated plastic

container that contained the Fe mesh was totally encompassed by the solidified mass. In the STTP tests the iron has been added as a unit of the waste inside the test vessel. This configuration (with the iron surrounded by the waste form) is quite different from that which can be expected in the repository where the iron will surround the waste.

4.0 DISCUSSION OF THE PU(VI) RESULTS

In this section a brief summary of the chemical conditions expected in the repository precedes a discussion of the L-26 and L-28 results. The discussion on these STTP results is followed by an evaluation of the relevance of L-26 and L-28 results to the overall WIPP repository conditions.

4.1 Chemical Conditions in the Repository

Actinide solubility, speciation, and complexation in WIPP brine are controlled by several factors including brine composition, pcH, carbonate concentrations, and the concentration (if present) of organic ligands and colloids. The STTP experiments were initiated prior to the decision to place MgO as a backfill in the disposal areas. Because of this, chemical conditions in most STTP vessels differ from those expected at WIPP, particularly with respect to brine pcH. These differing conditions do not reduce the value of the STTP experiments, but do require careful evaluation of the results in applying them to the WIPP repository.

One of the drivers in the selection of MgO as a backfill for WIPP was the potential for CO_2 generation resulting from microbial degradation of organics, plastics and rubbers present in the waste. The MgO emplaced in the repository will hydrate to form $Mg(OH)_2$, or brucite (Figure 4-1). Note that conversion to brucite assumes brine inflow is sufficient to hydrate the MgO. In the absence of sufficient brine inflow, actinide solubility is a moot point, since no fluids exist to transport them. As microbial degradation proceeds, brucite is converted first to hydromagnesite, then to magnesite. Solubility calculations for WIPP (Appendix SOTERM, USDOE, 1996) assumed that brine was in equilibrium with magnesite. However, it has been demonstrated that conversion of brucite to magnesite is inhibited at high CO_2 fugacity, such as those experienced in the STTP (Figure 4-2). This topic was discussed during the CMPRP review of the conceptual model for chemical conditions at WIPP. It was concluded by the CMPRP and the EPA that the fugacity of CO_2 in the disposal areas will always be in the range of 10^{-6} atmospheres, and that the assumed chemical conditions represent a reasonable approximation of future states of the repository.
In addition to its capacity to sequester CO_2, MgO buffers the pcH, such that it will remain between 8.5 and 10. Brucite does not form at a pcH below 8.5. The ability of MgO to buffer the brine pcH in the repository is well established, since the rate of CO_2 production is slow, relative to predicted brine inflow rates. This must be considered for the interpretation of results of the L-28 experiment following addition of MgO when the pcH initially increased only to 7.6, then fell to the range of 5 to 5.2. This topic is further discussed in Section 4-3.

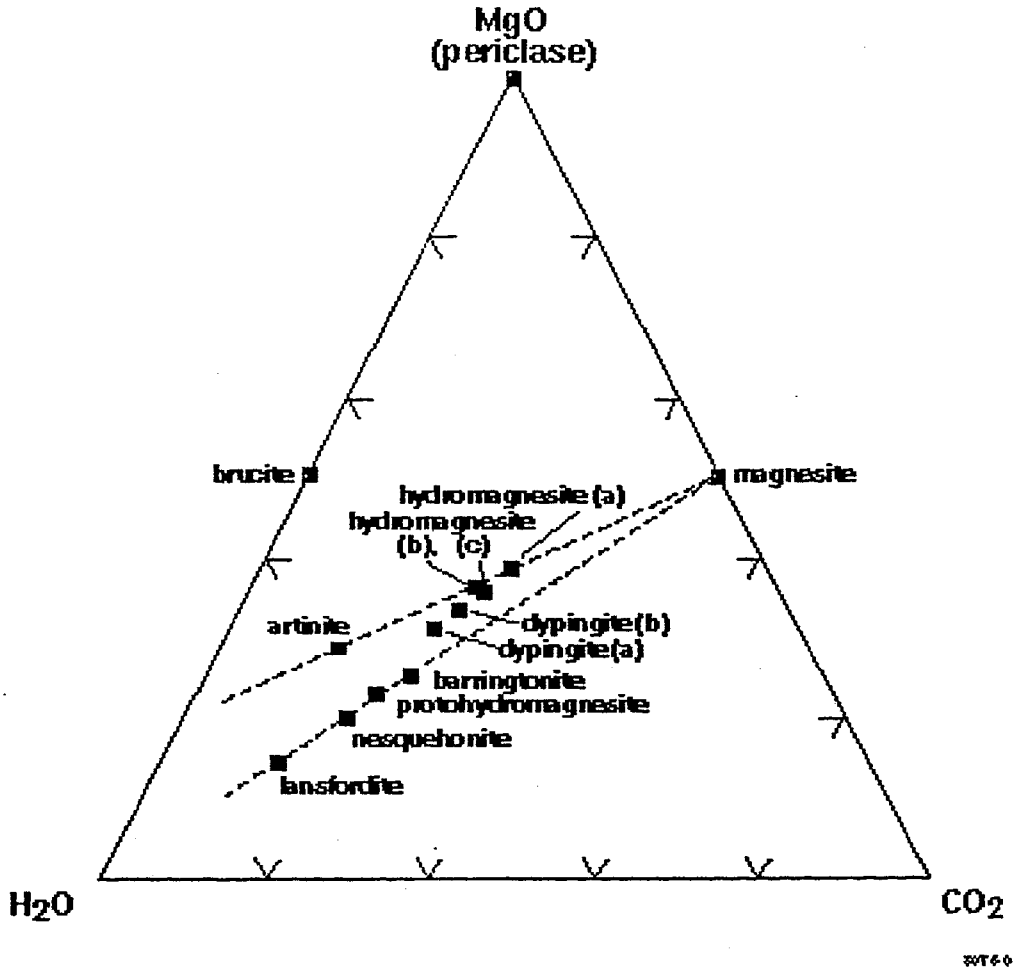


Figure 4-1. Ternary diagram in MgO-CO_2-H_2O space. Magnesium carbonate minerals occupying the interior of the diagram are metastable with respect to magnesite. The upper dashed line is defined by minerals containing two hydroxide anions per formula unit. The lower dashed line is defined by minerals containing waters of hydration but no hydroxide anions.

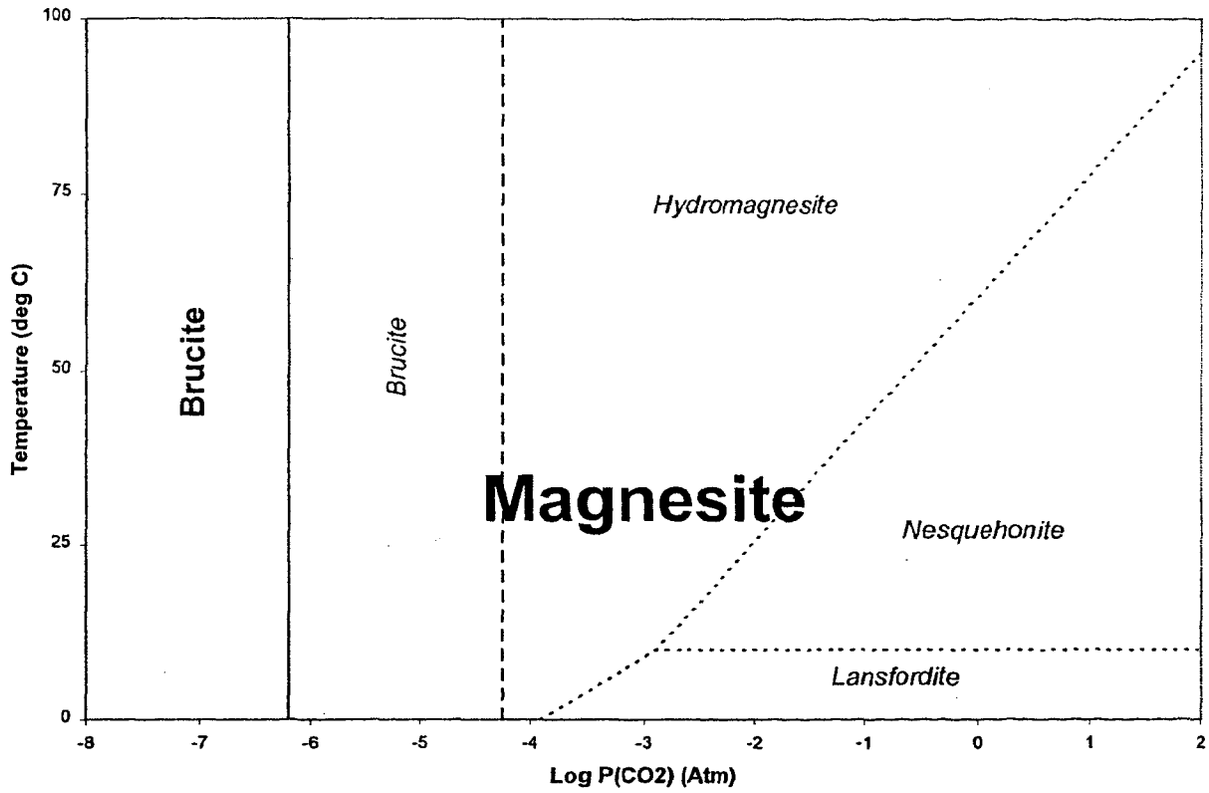


Figure 4-2. Phase diagrams for the magnesium carbonate system; dashed lines indicate boundaries for metastable phases and solid lines represent stable phase boundaries. This diagram, like most equilibrium phase diagrams for magnesium carbonate minerals, represents metastable mineral phases at steady state; the only stable phase in the right side of the diagram is magnesite. At the WIPP, temperature is fixed at about 28°C. Note that the details of the mineral assemblages in the short-term will depend on the starting P_{CO2}.

Metal corrosion and possible microbial activity, both of which will consume O_2 will force the chemical conditions in the repository to quickly become reducing after room closure. This behavior is expected with or without MgO.

In summary, expected chemical conditions in the presence of brine in the repository will exhibit: 1) reducing conditions with respect to actinide speciation; 2) CO_2 fugacity on the order of 10^{-6}, and 3) brine pcH in the range of 8.5 to 10.

4.2 STTP L-26

As described in Section 4.1, the presence of a large quantity of iron in WIPP disposal rooms underlies the assumption of reducing conditions in the repository. These conditions support the CCA assumption that Pu(III) and Pu(IV) will be the dominant, stable species of plutonium in WIPP.

Iron mesh was included in many of the STTP containers as a surrogate for Fe present in the repository. The fact that Pu(VI) was identified in L-26 demonstrates that reducing conditions were not maintained in this experiment. Interpretation of this result requires considerations of test conditions, and the relatively high alpha activity of pyrochemical salt wastes.

As described in Section 3.2.4, the iron mesh in two pyrochemical salt tests (L-31 and L-32) was isolated from the container brine, such that corrosion of this material was inhibited. Examination of the iron mesh from other STTP containers (L-1 and L-21) showed a coating of magnesio-ferrite, which also could have slowed the corrosion process. On the basis of these D&D results, it is reasonable to assume that the iron mesh in container L-26 was segregated from the brine such that Fe corrosion did not proceed normally, if at all.

The high alpha activity in container L-26 could cause brine radiolysis. Radiolysis will produce oxygen, peroxide, and hypochlorite which lead to an oxidizing environment. The effect of radiolytically produced oxidants was expected to dominate the Eh of the experiments as discussed in the Test Plan for the STTP.

The behavior of L-26 therefore appears to be a result of the time-varying oxidizing potential of the brines. If radiolysis generated peroxides or hypochlorites, these oxidants would be depleted early in the experiment because of the reducing effects of the inoculum organisms and any dissolved Fe. Note that the increase in Pu concentrations was delayed for about one year after the start of both L-26 and L-28. If the iron was effectively removed from the system due to encapsulation, or formation of a protective layer on the mesh, oxic conditions could have occurred leading to the oxidation of Pu to the +VI state and increases in dissolved Pu concentrations.

4.3 STTP L-28

Conditions in L-28 prior to addition of MgO are expected to be somewhat similar to those in L-26. No further discussion is necessary for possible scenarios leading to oxidizing conditions in L-28 prior to addition of MgO. The behavior in L-28 following addition of MgO requires consideration of two effects: 1) the absence of stable pcH buffering in the vessel, and 2) the transient decrease, followed by rapid increase in Pu concentrations.

As noted in Section 3, L-28 was initially pressurized with CO_2. After about 18 months, a slurry of MgO mixed with Brine A was added and the container was repressurized. Following this addition, the pcH initially increased to 7.6, then fell again to the 5 to 5.2 range. The absence of pcH buffering in L-28 demonstrates that the MgO hydration products were not available to the system. A likely explanation for this behavior lies in the nature of the MgO after its addition to the vessel. It was noted that mixing of MgO and Brine A resulted in a slurry which solidified rapidly. Several attempts were made before a slurry was successfully injected into the vessel. Further solidification of the material immediately upon introduction to the container would result in formation of a solid mass. The MgO hydration products would, in this case, have been unavailable to the system. Although it is not clear that the slurry hardened into a solid mass, it is certain that the bulk of the MgO was not in contact with the brine in L-28. The significance of this is discussed in Section 4.4.

The second issue in the L-28 vessel relates to the actinide concentrations. After the addition of MgO, actinide concentrations initially decreased, consistent with the expectation that solubilities are reduced in the presence of MgO hydration products. The subsequent, rapid increase in actinide concentrations to values on the trend observed before addition of MgO are associated with identification of Pu(VI). However, since the conditions in L-28 differ significantly from those expected for the repository, it is difficult to relate the experimental results to WIPP-relevant conditions.

4.4 Conclusions

As discussed in Section 2.1, the primary purpose of the STTP was to demonstrate that actinide solubilities in complex conditions would be less than the solubilities predicted using the Actinide Source Term Model. Although the measured concentrations of Pu in L-26 and L-28 are relatively high with respect to other liter-scale experiments in the STTP, the maximum measured concentrations in this experiment, regardless of Pu speciation, remained below that predicted using the ASTM. The conditions in these containers differ from those expected for the overall repository, especially with respect to brine pcH and the radiolyis resulting from the high actinide loading.

The lack of reducing conditions in some of the STTP vessels is likely a direct consequence of the segregation of Fe from the brine in these experiments. However, as described in Section 1.0, pyrochemical salts comprise only a small fraction of the waste. The ability of this waste to encapsulate the large quantity of Fe present in the disposal areas would not be possible on a repository-scale. Note also in this context, that the configuration in these tests, with the iron surrounded by the waste form, is quite different from that which can be expected in the repository where the iron will surround the waste. Overall, reducing conditions in the repository are still expected.

The MgO slurry was added to the L-28 vessel in February 1997. Since that time, numerous studies have documented the sensitivity of MgO hydration to brine composition and fugacity of CO_2. The relevant points regarding the observed Pu behavior in L-28 are: 1)the method of addition of MgO into the test vessel is inconsistent with the hydration behavior described in Section 4.1, 2) CO_2 fugacity exceeds that expected in the repository by several orders of magnitude, and 3) the MgO may well have formed a solid mass after introduction, thereby inhibiting its reaction with the brine. Therefore, it is difficult to relate these results to WIPP-relevant conditions.

The STTP results substantiate the conservatism inherent in calculations which support WIPP certification. Note that only two of the 54 liter-scale tests did not show actinide concentrations lower than predicted. These two tests, L-3 and L-12, showed concentrations the same as (L-12) or slightly higher than (L-3) predicted. However, in both cases the measured and predicted values were very low, much less than any values which might impact repository performance, and low enough to be at the limits of detection where relative uncertainties would be quite high.

Enclosure 3

Selected Pages from EPA Certification Documents (Docket A-93-02, Items V-B-17 and V-C-1)

TECHNICAL SUPPORT DOCUMENT FOR SECTION 194.24: EPA's EVALUATION OF DOE'S ACTINIDE SOURCE TERM

2.0 Solubility and Actinide Oxidation States (Selected Pages 2 to 5)

A conceptualization of the redox environment within the repository is important to predicting the solubilities of probable solids incorporating actinide species. Actinides can exist in oxidation states ranging from +3 to +6, depending on the specific actinide under consideration and prevailing redox conditions. After closure, the repository is expected to become anoxic relatively rapidly because of reactions between any available oxygen and iron metal and aerobic biodegradation of organic material (SOTERM 2.2.3). Both organic materials and iron metal are expected to be major components of the waste inventory. According to DOE (SOTERM 4.6) "each drum contains about 170 moles of iron in the container... The reaction rate of iron with the brine is very fast (Appendix PAR, Parameter 1). Therefore, as any brine moves into the repository it will react with the iron and establish a highly reducing environment." Additionally, the production of hydrogen by metal corrosion reactions is expected to contribute to creating reducing conditions in the repository. The assumption of reducing conditions after closure is reasonable because of the interaction of the iron and brine. Because of these reactions, oxidizing conditions are expected to last only a short while after closure. EPA therefore concurs with DOE that reducing conditions will prevail in the repository after closure.

The FMT model (A-93-02, II-G-3, Volume 6--FMT Quality Assurance Package), which was used by DOE to calculate solubilities of actinide solids, does not include representations of redox processes, hence actinides must be designated as being present entirely in a single oxidation state. This treatment requires that a conceptualization of the redox conditions in the repository be developed based on available information on the inventory and knowledge of relevant redox reactions. The FMT code is discussed in this document (section 4) and in the Technical Support Document for Section 194.23: Models and Computer Codes (A-93-02, V-B-6, Appendix A).

DOE presents the experimental and chemical reasoning for the determination of the specific oxidation states for each actinide expected to be predominant in the repository (Appendix SOTERM 4; CCA Reference 479). DOE provides a summary of the literature and a discussion of experimental results for thorium, uranium, neptunium, americium, curium, and plutonium. Consideration of actinide chemistry indicates that specific oxidation states can be expected under reducing conditions (CCA Chapter 6.4.3.5; Appendix SOTERM 4). Thorium will be present in the +4 oxidation state, which is the only one stable in the natural environment. Americium is expected to be present in primarily the +3 oxidation state. Higher oxidation of Am(+5) and Am(+6) can occur under oxidizing conditions, but are rapidly reduced by naturally occurring reductants and in brines at pH greater than 9 (Felmy et al. 1990). Plutonium is expected to be present as either Pu(+3) or Pu(+4). Higher oxidation states of Pu (i.e., +5 and +6) can exist under oxidizing conditions, but have been reported to be reduced rapidly by metallic iron (presentation by Ruth Weiner, Technical Exchange Meeting, SNL, June 27, 1996, in Bynum, 1996). Consequently, Pu(+5) and Pu(+6) are not expected to be dominant oxidation states for Pu

under the reducing conditions of the repository and abundance of metallic iron. Uranium is expected to exist in both the +4 and +6 oxidation states; the predominance of which could not be ascertained based on current knowledge or uranium chemistry. The predominance of U(+4) requires extremely reducing conditions, that while possible for the repository, cannot be predicted with certainty. Consequently, for the PA, uranium is designated as being present as U(+4) in 50% of the runs and as U(+6) in the other 50%. Likewise, neptunium is expected to be present as either Np(+4) and/or Np(+5), because the designation of a predominant form could not be made with complete certainty for the repository conditions.

Questions have been raised by stakeholders who believe that PuVI will be present in the WIPP repository. In their description of the actinide source in Appendix SOTERM of the CCA, DOE determined that the any plutonium that might be dissolved in brines that infiltrate into the repository would exist as either Pu(III) or Pu(IV). As described in Appendix SOTERM of the CCA, Pu(V) and Pu(VI) are not expected to be important oxidation state for plutonium under the expected repository conditions. The issue is potentially important because the solids that incorporate Pu(V) and Pu(VI) tend to have higher solubilities than the solids that incorporate Pu(III) and Pu(IV).. Experiments by Reed et al. (1996) indicated that Pu(+6) is stable at a pH of 8 to 10 under oxidizing conditions and in the presence of high carbonate concentrations.

Stakeholders imply that the dominant oxidation for plutonium will be Pu(VI) based on an interpretation of some experimental work conducted by Reed et al. (1996) that were conducted at a pH of 8 to 10 under oxidizing conditions and in the presence of high carbonate concentrations. However, this interpretation of the Reed et al. (1996), as applied to the respository is incorrect because the experimental conditions used by Reed et al. (1996) are not representative of these expected for the repository. The repository inventory includes large quantities of reducing agents in the form of metallic iron, organic matter, and organic chemicals. These reductants are expected to rapidly consume any available oxygen present in the repository atmosphere shortly after closure, producing anaeorobic or reducing conditions. Under reducing conditions, plutonium is expected to be stable in either the +3 or +4 oxidation states based on both experimental studies and chemical equilibrium calculations.

The experimental studies considered by DOE in developing their conceptual model for plutonium includes those conducted at SNL by R. Weiner and coworkers (Weiner, 1996). These studies clearly show that Pu(VI) is reduced by iron in both soluble (i.e., Fe^{2+}) and metallic (i.e., iron powder) forms. In experimental studies of the solubilities of plutonium and other actinides, iron powder is used to maintain reducing conditions, thereby preventing Pu(III) and Pu(IV) from oxidizing to Pu(V) and Pu(VI) (Felmy et al. 1989, p. 30; Rai and Ryan, 1985, p. 248). Other studies have shown that Pu(VI) and Pu(V) are reduced by humic acids even under the oxidizing conditions of seawater (Choppin, 1991, p. 113, 114). Humic acids and other organic acids are expected to be present in the repository from the degradation of cellulosic waste materials. These empirical observations show that Pu(VI) and Pu(V) will not persist in the presence of reductants, such as iron and organics, that will be present in the repository environment.

Also, it is important to note that the conceptual model that was developed to describe the actinide source term is based on conditions of chemical equilibrium. Under the reducing

conditions that will be created by the presence of metallic iron, the stable oxidation states for plutonium are Pu(III) and/or Pu(IV). This conclusion is based on a comparison of the redox conditions (i.e., the Eh or pe) imposed by equilibrium between Fe^{2+} and $Fe(OH)_3(s)$ and the Eh-pH conditions relevant to aqueous plutonium species (Brookins, 1988, p. 73-76, 144-145; Choppin, 1991, p. 110; Rai et al. 1980, p. 417). The $Fe^{2+}/Fe(OH)_3$ stability line in Eh-pH space intersects the Pu(III) and Pu(IV) fields, indicating these are the stable oxidation states for plutonium in the presence of iron. The redox conditions imposed by organic materials are lower than for the iron species (Scott and Morgan, 1990, p. 371-374; Stumm and Morgan, 1996, p. 467-477), providing more information that leads to the conclusion that Pu(VI) will not persist under the expected repository conditions.

In consideration of the extensive empirical and theoretical information that indicates that Pu(III) and Pu(IV) are the stable oxidation states of dissolved plutonium under reducing conditions, the EPA concludes that it would be unreasonable to expect that the higher oxidation states of plutonium [i.e., Pu(V) and Pu(VI)] would persist in the repository environment. EPA agrees with DOE's approach of including Pu(III) and Pu(IV) as the predominant oxidation states for plutonium in actinide source term modeling and PA calculations.

The thermodynamic database for the FMT model contains information for three actinides oxidation states, i.e., Am(III), Th(IV), and Np(V). The solubilities predicted for the Th(IV) solids were used in the CCA also to represent soluble U(IV), Np(IV), and Pu(IV); an approach referred to in Appendix SOTERM as the oxidation state analogy. The oxidation state analogy is based on standard inorganic chemistry principles. In short, the actinide oxidation analogy means that actinides of the same oxidation state tend to have similar chemical properties under similar conditions. This generalization can be made because chemical reactions involving ionic species are related primarily to the charge densities of the reacting species (CCA, Appendix SOTERM). Actinides with the same oxidation state have the same core electronic structure (Silva and Nitsche, 1995, p. 379); hence have similar ionic radii and charge densities, which in turn leads to analogous chemical behavior in solubility and aqueous speciation reactions. Also, as stated by (Silva and Nitsche, 1995, p. 379): "Because of the similarities and the fact that actinide ions in the same oxidation state have essentially the same core structure, actinides ions in the same oxidation state will tend to have similar chemical properties". A similar phenomenon occurs for the lanthanide group elements (i.e., rare-earth elements of atomic numbers 57 through 71), which have the same core electronic structure for ionic species. (Silva and Nitsche, 1995, p. 379). In addition to the theoretical basis, DOE conducted experimental studies and analyses that confirmed the validity of the oxidation state analogy, and subsequently employed it in their representation of the solubilities of actinides (CCA, Appendix SOTERM).

This approach is reasonable in that it is recognized that actinides with the same oxidation state have similar chemical properties (Allard, 1981; Allard et. al., 1980; Jensen,1980). Also, $ThO_2(am)$, which was used to represent Th(+4), is generally expected to be more soluble than solid forms of U(+4), Np(+4), and Pu(+4), that might be expected to form under repository conditions, (Felmy et al. 1996; Novak and Moore, 1996; Novak et al. 1996a, Novak et al. 1996b), making it a conservative choice as the basis for the +4 actinide analogy.

The application of the actinide analogy to the +IV actinides is a good example of its appropriate application to the actinide source term. Besides the oxidation state analogy, another generalization that can be made is that there is an decreasing trend in the solubilities of actinide solid phases across the actinide series (DOE, 1998, p. 5). This generalization is based on the fact that ionic radii of the lanthanides and actinides decrease with increasing atomic number. With decreasing radii, the stabilities of actinide-oxide and actinide-hydroxide bonds are increased, leading to decreased solubility products, which is a direct indication of solubility, for similar compounds (DOE, 1998, p. 5). This effect is exemplified by the decrease in the solubility products of both hydrous actinide dioxides and crystalline actinide dioxides with increasing atomic number as shown by Rai et al. (1987, p.40). The data from Rai et al. (1987, p.40) show that the solubility product for Th(IV) dioxides, which is the actinide with the lowest atomic number, is about 8 orders of magnitude greater than for U(IV) dioxides, about 9 orders of magnitude greater than for Np(IV) dioxides, and about 10 orders of magnitude greater than for Pu(IV) dioxides. These experiments confirm the validity of the actinide analogy for the +IV actinides in that Th(IV) solids are more soluble than U(IV), Np(IV), and Pu(IV) oxide solids. The data compiled by Rai et al. (1987, p.40) are most relevant to low ionic strength conditions. However, more recent experimental data from Rai et al. (1997, pp. 242-243,245) show that the actinide analogy for the order of solubilities of +IV actinides is also relevant to high ionic strength conditions expected for the WIPP. Rai et al. (1997, p. 239) indicate that the solubility products for ThO_2(am) is about 8 orders of magnitude greater than for UO_2(am) in concentrated NaCl and $MgCl_2$ solutions, consistent with the earlier data discussed above. Based on these established trends for the +IV actinides, DOE used the solubility of ThO_2(am) to represent the concentrations of the other +IV actinides [i.e., U(IV), Np(IV), and Pu(IV)] under the expected repository conditions. The experimental evidence provided by Rai et al. (1997, p. 239) and Rai et al. (1987, p.40) clearly indicate that ThO_2(am) is more soluble than the other +IV actinides as indicated by the solubility products determined for the various solids in the following table (Note: higher solubility products indicate higher solubilities for the same chemical conditions).

The FMT model contains no data for U(+6), hence, it was estimated by an alternative method. Table 2-1 lists the actinides and their expected oxidation states which were used in the CCA performance assessment calculations.

In summary, EPA concurred that repository conditions will likely be reducing, and consideration of two oxidation states for Pu (+3 and +4) and U (+6 and +4) is appropriate. The oxidation state analogy approach to assigning solubilites is a reasonable methodology for the purposes of PA, and EPA also agrees that chemical equilibrium models are appropriate for predicting the solubilities and subsequent concentrations of actinides in WIPP brines.

Table 2-1
Predominant oxidation states for actinides expected to exist in the repository
(from Table SOTERM-3)

Actinide	Expected Oxidation State
Thorium	+IV
Neptunium	+IV, +V
Americium	+III
Uranium	+IV, +VI
Plutonium	+III, +IV

EPA 402-R-98-004 **Docket No: A-93-02 V-C-1**

RESPONSE TO COMMENTS: Criteria for the Certification and Recertification of the Waste Isolation Pilot Plant's Compliance with 40 CFR Part 191 Disposal Regulations: Certification Decision

Issue W: MgO chemical processes (Selected Pages 6-66 to 6-69)

1. Concerning the chemistry of the disposal rooms, DOE has assumed that the MgO backfill will react instantly and completely with the waste, gas, and brine in the repository, reacting with CO_2, reducing gas pressure and also reducing the solubility of the radionuclides. However, DOE has not shown that these processes will in fact take place. DOE's peer review panel has rejected DOE's PA assumption in this respect also. (140)

2. The analytical results of these experiments has [allowed] comparison to WIPP and affirms the results of actinide source term solubility models developed by Sandia National Laboratories that have conclusively shown that release of actinides in the accessible environment will not exceed EPA standards. (597)(888)

3. It has been demonstrated in the memorandum by Wang (1998) included as Attachment 7 that, even if all waste drums are fully filled with CRP, the amount of MgO emplaced in the repository will still be enough to control repository chemistry. Consequently, there is no need for imposing a upper limit on CRP inventory and therefore for accurately quantifying the uncertainty in determining weight parameters of those materials. (925)

Response to Comments 6.W.1 through 6.W.3:

DOE provided additional information on MgO processes and the Peer Review Panel later amended its conclusion to find that MgO processes will indeed take place as initially postulated by DOE. The use of an MgO backfill in the repository offers the potential for limiting the chemical conditions (i.e., pH and CO_2(g) partial pressure) in the repository to a relatively narrow range, as described in Appendix SOTERM of the CCA. This process was described in DOE's Chemical Conditions Conceptual Model. While the peer panel initially rejected DOE's conceptualization of the Chemical Conditions Model, the CMPRP accepted the Conceptual Models Third Supplementary Peer Review Report. [Docket: A-93-02, II-G-22] Thus, the panel concluded that the Chemical Conditions Model: Results of the MgO Backfill Efficacy Investigation [Docket: A-93-02, II-A-39] provided "satisfactory evidence that the laboratory phases produced by DOE will in fact transform well within the time constraints needed for the Chemical Conditions Model." Conceptual Models Third Supplementary Peer Review Report, at p.15-16. [Docket: A-93-02, II-G-22] The report concludes [p.16], "Based on the information presented to the Panel in the written material and in oral discussion, the Panel concludes that the results available provide an adequate basis to determine that the MgO backfill will function according to the Chemical Conditions Conceptual Model, as used in the CCA, with respect to reaction with generated CO_2 gas."

4. It has been demonstrated in the memorandum by Wang (1998) included as Attachment 7 that, even if all waste drums are fully filled with CRP, the amount of MgO emplaced in the repository will still be enough to control repository chemistry. Consequently, there is no need for imposing a upper limit on CRP inventory and therefore for accurately quantifying the uncertainty in determining weight parameters of those materials. (925)

5. Confidence has not been developed that wastes within individual drums or the brines entering those drums will undergo the rapid chemical conditioning effect assumed, and insufficient attention has been given to the volumetric expansion and other effects due to MgO reactions (at 21). (1061)

Response to Comments 6.W.4 and 6.W.5:

Experiments conducted by DOE, which are described in SNL [1997], show that reactions between MgO and carbonated brines are rapid. Solution pH values were found to increase in a matter of hours, indicating that the MgO backfill-type material is very reactive. [SNL, 1997, p. 8, 11] Also, significant amounts (a few weight percentages) of uptake of carbon were observed to take place after only days to weeks, indicating that the rates of formation of magnesium carbonates are also rapid. [SNL, 1997, p. 10, 12, 15] These rapid rates of reaction are consistent with experimental results of the transformation of nesquehonite to hydromagnesite after three to seven days of reaction at 52°C. [Davies and Bubela, 1973, p. 290, 291] Also observed, the formation of protohydromagnesite from nesquehonite after 10 months at 10 to 28°C in a simulated sedimentary column indicates that the formation and recrystallization reactions involving magnesium carbonates occur rapidly. [Davies et al.,1977, p. 188, 189, 197,198] The results of these experiments provide adequate information to conclude that reactions involving the MgO backfill material, brines, and carbon dioxide will be rapid and will produce the geochemical conditions expected for chemical equilibrium between brucite and hydromagnesite and/or magnesite.

As noted in this comment, the conversion of MgO to hydrated products can be expected to result in a volumetric expansion of the materials. For example, the increase in volume of the solids involved in the initial reaction between MgO and water, i.e.,

$$MgO + H_2O = Mg(OH)_2$$

can be estimated from the difference in molar volumes of $Mg(OH)_2$ (molar volume = 24.63 cm^3/mol) [Robie et al.1978, p. 20] and MgO (molar volume = 11.248 cm^3/mol) [Robie et al.1978, p. 20], to give a potential increase with reaction of 13.38 cm^3/mol. Similarly, the conversion of $Mg(OH)_2$ to hydromagnesite (molar volume = 211.1 cm^3/mol) [Robie et al.1978, p. 25], i.e.,

$$5Mg(OH)_2 + 4CO_2(g) = Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O \text{ (hydromagnesite)}$$

might be expected to produce an increase in molar volume of 87.95 cm^3/mol (= 211.1 cm^3/mol -

5*24.63 cm^3/mol), if the reaction were to proceed to 100% completion.

However, the combined potential effects of the removal of water by the backfill material and volumetric expansion of reaction products relative to the original MgO are expected to be beneficial to the backfill performance. Clearly, the removal of water, as in the first reaction above, would limit the amount of water available for transporting actinides downgradient. Also, any volume expansion that might occur may result in the formation of dense layers of cementitious material in and around the waste containers, which will also limit the ability of water to contact wastes and solubilize actinides.

In summary, experimental evidence indicates that the MgO backfill material will produce the desired chemical conditions in a rapid time frame. Secondly, the effects of the backfill reactions with carbonated brines can be expected to reduce the potential for actinide transport relative to a system with no backfill. Based on these considerations, EPA concludes that the emplacement of the MgO backfill material will be beneficial to repository performance.

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Issue CC: Plutonium (VI) (Selected Pages 6-84 to 6-87)

1. Regarding the oxidation states that will be present in the repository, it has been noted that Pu(VI) dominates at steady-state conditions. (See Letter, Neill to EPA, Feb. 7, 1997, enclosure re plutonium solubility) (II-H-12). Solubility values should therefore be based on the presence of Pu(VI). (976)

Response to Comment 6.CC.1:

In their description of the actinide source in Appendix SOTERM of the CCA, DOE determined that any plutonium that might be dissolved in brines that infiltrate into the repository would exist

as either Pu(III) or Pu(IV). As described in Appendix SOTERM of the CCA, Pu(V) and Pu(VI) are not expected to be important oxidation states for plutonium under the expected repository conditions. The issue is potentially important because the solids that incorporate Pu(V) and Pu(VI) tend to have higher solubilities than the solids that incorporate Pu(III) and Pu(IV). Experiments by Reed et al. [1996] indicated that Pu(+6) is stable at a pH of 8 to 10 under oxidizing conditions and in the presence of high carbonate concentrations. Comment No. 6.CC.1 implies that the dominant oxidation for plutonium will be Pu(VI) based on an interpretation of some experimental work conducted by Reed et al. [1996] that was conducted at a pH of 8 to 10 under oxidizing conditions and in the presence of high carbonate concentrations.

However, application of Reed et al. [1996], to the repository is incorrect because the experimental conditions used by Reed et al. [1996] are not representative of what is expected for the repository. The repository inventory includes large quantities of reducing agents in the form of metallic iron, organic matter, and organic chemicals. These reductants are expected to rapidly consume any available oxygen present in the repository atmosphere shortly after closure, producing anaerobic or reducing conditions. Under reducing conditions, plutonium is expected to be stable in either the +3 or +4 oxidation states based on both experimental studies and chemical equilibrium calculations.

The experimental studies considered by DOE in developing their conceptual model for plutonium includes those conducted at SNL by R. Weiner and coworkers. [Weiner, 1996] These studies clearly show that Pu(VI) is reduced by iron in both soluble (i.e., Fe^{2+}) and metallic (i.e., iron powder) forms. In experimental studies of the solubilities of plutonium and other actinides, iron powder is used to maintain reducing conditions, thereby preventing Pu(III) and Pu(IV) from oxidizing to Pu(V) and Pu(VI). [Felmy et al. 1989, p. 30; Rai and Ryan, 1985, p. 248] Other studies have shown that Pu(V) and Pu(VI) are reduced by humic acids even under the oxidizing conditions of seawater. [Choppin, 1991, p. 113, 114] Humic acids and other organic acids are expected to be present in the repository from the degradation of cellulosic waste materials. These empirical observations show that Pu(V) and Pu(VI) will not persist in the presence of reductants, such as iron and organics, that will be present in the repository environment.

Also, it is important to note that the conceptual model that was developed to describe the actinide source term is based on conditions of chemical equilibrium. Under the reducing conditions that will be created by the presence of metallic iron, the stable oxidation states for plutonium are Pu(III) and/or Pu(IV). This conclusion is based on a comparison of the redox conditions (i.e., the Eh or pe) imposed by equilibrium between Fe^{2+} and $Fe(OH)_3(s)$ and the Eh-pH conditions relevant to aqueous plutonium species. [Brookins, 1988, p. 73-76, 144-145; Choppin, 1991, p. 110; Rai et al. 1980, p. 417] The $Fe^{2+}/Fe(OH)_3$ stability line in Eh-pH space intersects the Pu(III) and Pu(IV) fields, indicating these are the stable oxidation states for plutonium in the presence of iron. The redox conditions imposed by organic materials are lower than for the iron species [Scott and Morgan, 1990, p. 371-374; Stumm and Morgan, 1996, p. 467-477], providing more information that leads to the conclusion that Pu(VI) will not persist under the expected repository conditions.

In consideration of the extensive empirical and theoretical information that indicates that Pu(III) and Pu(IV) are the stable oxidation states of dissolved plutonium under reducing conditions, EPA

concludes that it would be unreasonable to expect that the higher oxidation states of plutonium [i.e., Pu(V) and Pu(VI)] would persist in the repository environment. EPA agrees with DOE's approach of including Pu(III) and Pu(IV) as the predominant oxidation states for plutonium in actinide source term modeling and PA calculations.

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Enclosure 4

Letters From EEG to DOE

ENVIRONMENTAL EVALUATION GROUP

AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOYER

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December 9, 1999

Dr. Inés Triay, Manager
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P.O. Box 3090
Carlsbad, NM 88221-3090

Dear Dr. Triay, Inés

Thank you for arranging the November 23 and December 7, 1999 presentations by Dr. Robert Villarreal of Los Alamos National Laboratories on the results and status of the Source Term Test Program and the proposed initiatives for future experimental work. The experiments with actual waste substantiate some of our previously published concerns.

Specifically, the experimental results show the presence of plutonium in its highly soluble oxidation state, Pu^{VI}, even in the presence of iron mesh. The MgO backfill does not appear to maintain the system at a pH of 10 as assumed in the CCA calculations. The experiments strongly suggest that other materials such as Portland cement, bentonite, and phosphate merit further investigation as an additive or a backfill.

As to the specific initiatives, we would certainly encourage an experimental program that leads to the successful modeling of plutonium in oxidation states IV, V, and VI. There also appears to be a need for definitive data on the efficacy of MgO in controlling solubility and possible alternatives for the MgO as an engineered barrier. We also see merit in delineating how well the experiments represent the various waste streams to be emplaced in WIPP including the new 65,000 m^3 waste stream that will be generated by the INEEL Advanced Mixed Waste Treatment facility. These efforts should begin as soon as possible, in close coordination with Sandia, so that the results will be available for inclusion in the re-certification PA.

We look forward to providing a technical review of the detailed experimental plans and model development as soon as they are available.

Sincerely,

Robert H. Neill
Director

RHN:js

cc: R. Villareal, LANL
G. Basabilvazo, DOE/CAO

ENVIRONMENTAL EVALUATION GROUP

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March 22, 2000

Dr. Inés Triay
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Dear Dr. Triay: Inés

Recently completed experiments at the Los Alamos National Laboratory (LANL) have raised issues regarding the long-term performance of the Waste Isolation Pilot Plant (WIPP) that should be addressed by the WIPP project. These include indications that the MgO backfill may not behave as anticipated in the WIPP compliance certification application (CCA) and the solubility of actinides assumed in the CCA may be incorrect. As you know, Dr. Villareal and his colleagues from LANL presented the results of their experiments to the EEG on November 23 and December 7, 1999. My letter of December 9, 1999 to you outlined our initial thoughts on these presentations. We were hoping to review the results more thoroughly in a document that is in preparation at LANL. However, we believe the results as presented to us have such important implications for the projected long-term performance of the WIPP repository, that we have decided to bring this matter to your attention at this time without waiting for LANL's publication of the details.

Magnesium oxide backfill was selected with the anticipation that it would maintain the pH of the repository at about 10 by chemically scavenging the carbon dioxide expected to be generated in the repository due to microbial action on the organic material in the waste. At a pH of 10, the solubility of actinides is reduced by several orders of magnitude and these projected solubility values were used in the CCA. In addition, there were many other benefits ascribed to the MgO backfill which helped in the demonstration of the WIPP's compliance with the EPA's long-term radiation protection standards (40 CFR 191 and 40 CFR 194). The CCA also claimed that the MgO backfill satisfies the engineered barrier requirement (40 CFR 191.14.d) of the EPA standards.

An experiment at LANL has indicated that the assumption of the repository pH being maintained at 10 may not be correct. In this experiment, MgO and brine were added to a container of transuranic (TRU) waste to study its effect on the pH. The pH remained close to 5, i.e., at a

chemical state in which the solubility of actinides is much higher than that used in the CCA. Eventually, the plutonium concentration in solution in this experiment was more than twice the concentration prior to the addition of MgO (See Table 1, attached). It is necessary to understand this phenomenon. A potential explanation may lie in the results of another series of experiments conducted by Jim Krumhansl of Sandia National Laboratories, who presented his results at the ICEM'99 Conference in Nagoya, Japan, in September 1999. The Sandia experiments using both the Salado and the Castile brines found no evidence of formation of the hydrous oxide of magnesium, the mineral Brucite [$Mg(OH)_2$], even after 443 days. With de-ionized water, however, the reaction was observed. Could it be that the reactions assumed in the CCA occur only in the presence of fresh water and not brine? These limited experiments cast doubts on the CCA assumption that the reaction between brine and MgO to produce brucite would be relatively rapid, on the order of hours to days.

Experiments conducted at Los Alamos National Laboratories with TRU waste have also shown that Pu (VI) is found in brine in some cases. The results indicate that both Pu (IV) solid and Pu (VI) solution species may coexist under WIPP conditions. The possibility of the presence of plutonium in oxidation state VI was dismissed in the CCA and the solubilities of only Pu (III) and Pu (IV) were assumed. Since the solubility of Pu (VI) is several orders of magnitude higher than that of Pu (IV), this particular experimental observation raises questions about the validity of the CCA assumption, and should be investigated.

Two articles in the January 14, 2000 issue of Science (one by John Haschke et al. and the other by Charles Madic) discuss the issue of Pu (VI). Haschke et al. provide a review of the evidence for formation of $PuO_{2+\chi}$ ($\chi \leq 0.27$), which can explain the Pu results obtained in LANL tests. The $PuO_{2+\chi}$ phase is analogous to $UO_{2-\chi}$, which has been studied extensively in relation to spent fuel testing to support geologic disposal programs. Our understanding developed from spent fuel and UO_2 studies can be used to develop a testable model for the $PuO_{2-\chi}$ behavior at WIPP. This model can be used as the basis to design a focused experimental program to test and validate the model. An experimentally validated model for Pu solubility in WIPP brines would also remove the difficulties associated with the previous PA calculations that attempted to estimate Pu solubility using an analogy to Th chemistry.

According to Charles Madic (in Science, 1/14/2000 issue):

> The new results will also have great consequences for the underground disposal of nuclear wastes. Until now, it was assumed that plutonium would not be very mobile in the underground geological environment because of the solubility of Pu (IV) compounds. But Haschke *et al.* demonstrate that water can oxidize PuO_2 into PuO_{2+x}, in which more than 25% of the plutonium ions exist as Pu (VI), an ion that is far more water soluble, and thus mobile, than Pu (IV). This new property will have important implications for the long-term storage of plutonium.

In summary, we urge DOE to give a high priority to formulation and execution of an experimental program to test (1) the long-term behavior of the MgO backfill under the anticipated WIPP repository conditions in controlling the pH, solubility, and all the other functions ascribed to it in the CCA, and (2) the role of PuO_{2+x} in relation to the solubility of Pu in WIPP brines. We also urge you to develop a model to accommodate the experimental observations and the possibility of existence of Pu in four different oxidation states under the WIPP conditions. These efforts will provide a sound technical basis for PA calculations to be used in the recertification of WIPP.

Sincerely,

Bob

Robert H. Neill
Director

RHN:LC:pf

Attachment

Dr. Inés Triay
Attachment
March 22, 2000

Table 1. Actinide concentrations from periodic sampling on the Drum L-28 at LANL (Concentrations in ppb).

	Nd	Th	U	Np	Pu	Am	pcH
AUG 95	15	178	5,230	3,549	5,989	35	5.4
	10	248	7,099	8,150	8,731	59	4.9
	10	312	6,290	8,179	15,678	80	4.7
	32	1,359	10,833	13,931	90,942	352	4.5
MgO Added FEB 97	9	151	106	351	18,097	40	----
	5	36	155	166	41,822	69	----
	54	368	4,520	2,049	174,367	330	5.2
SEP 98	57	531	1,550	1,528	197,984	392	5.0

Enclosure 5

Science Magazine Articles

Home with the harvest. Young girl carrying rice in eastern Bhutan.

carotenoid. The production of various carotenoids other than β-carotene could provide additional health benefits as carotenoids have been implicated in reducing the risk of certain types of cancers, cardiovascular disease, and age-related macular degeneration. Fortunately, excess dietary β-carotene, in contrast to excess vitamin A, has no harmful effects, so plants with enhanced β-carotene content should be a safe and effective means of vitamin delivery.

Field-testing will tell us whether production of carotenoids in rice endosperm will entail any metabolic trade-offs. Shunting more of the common precursor GGPP into carotenoid production might result in a decrease in other compounds whose synthesis is dependent on GGPP. For example, tomatoes engineered to produce more phytoene exhibit signs of dwarfism, attributed to a 30-fold reduction in the plant hormone gibberellic acid, which shares the precursor GGPP with phytoene (*7*). However, unlike tomato plants that express phytoene synthase in all their tissues, the rice plants engineered by Ye *et al.* express the introduced phytoene synthase only in the endosperm, which reduces the potential for metabolic disruption throughout the plant.

Presumably, it should be possible to engineer the pathways for many of the 13 essential vitamins into plants, once the pathways are known and the corresponding genes have been cloned (*8*). Indeed, the model plant *Arabidopsis* has already been successfully engineered to synthesize vitamin E (*9*). Improving the mineral content of plants so that they can serve as sources of the 14 minerals required in the human diet presents researchers with a different set of challenges (*8*). Unlike vitamins, which are synthesized by the plants themselves, plants must take up essential minerals from the soil. Iron deficiency is the leading nutritional disorder

mins, many of the world's staple foods are not good sources of iron. Current efforts are centered on understanding how plants take up and store iron (*10*, *11*). Rice has been engineered to have higher levels of the iron storage protein ferritin in the grain (*12*), but the question remains as to whether these engineered rice plants will be a good source of dietary iron.

The road to better nutrition is not paved with gold and, hence, agribusiness has not centered its efforts on the nutritional value of food. The work that culminated in the production of golden rice was funded by grants from the Rockefeller Foundation, the Swiss Federal Institute of Technology and the European Community Biotech Program. Like the plant varieties that made the green revolution so successful, the rice engineered to pro-

One can only hope that this application of plant genetic engineering to ameliorate human misery without regard to short-term profit will restore this technology to political acceptability.

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13. I thank R. McClung and J. Hirschberg for assistance in preparing this perspective.

PERSPECTIVES: PLUTONIUM CHEMISTRY

Toward the End of PuO_2's Supremacy?

Charles Madic

Owing to the ubiquitous presence of oxygen in the terrestrial environment, oxides occupy a central position in the chemistry of many elements. This is true not only for natural elements but also for artificial elements, particularly for the most famous one: plutonium. On page 285 of this issue, Haschke *et al.* (*1*) demonstrate convincingly that the supremacy of plutonium dioxide (PuO_2), long thought to be the most stable plutonium oxide under oxidizing conditions, is over. The results have implications for both military and civilian applications and for the long-term storage of plutonium.

The element plutonium was first created in December 1940 at the University of Berkeley, California, by a team of American scientists headed by Glenn T. Seaborg (*2*). During the summer of 1942, Cunningham and Werner (*3*) prepared a weighable amount of a solid plutonium compound, PuO_2 (2.77 μg). Thus, for the first time in human history, an artificial element was made visible to human eyes. This historical sample of PuO_2 is still kept at the Lawrence Hall of Science in Berkeley, California (*4*). Humanity became inescapably aware of the implications of these discoveries at the end of World War II: The atomic bomb that destroyed Nagasaki, Japan, on 9 August 1945 was made of plutonium prepared as part of the Manhattan Project.

It was soon recognized that plutonium chemistry is dominated by the existence of numerous oxidation states, from +III to +VI. In 1967, Russian scientists discovered that Pu(VII) can also exist (*5*). Despite the fact that plutonium thus possesses five oxidation states (III to VII), its oxide chemistry is far simpler. According to most textbooks (*4*, *6*–*8*), the plutonium-oxygen phase diagram contains the following crystalline solid oxides: $PuO_{1.50}$, $PuO_{1.52}$, $PuO_{1.61}$, PuO_{2-x}, and $PuO_{2.00}$, all of which involve only plutonium oxidation states III and IV. No plutonium oxide with an O/Pu stoichiometry higher than 2 was observed, despite numerous attempts to prepare PuO_3, the oxide corresponding to Pu(VI) (*4*).

It has therefore been assumed for

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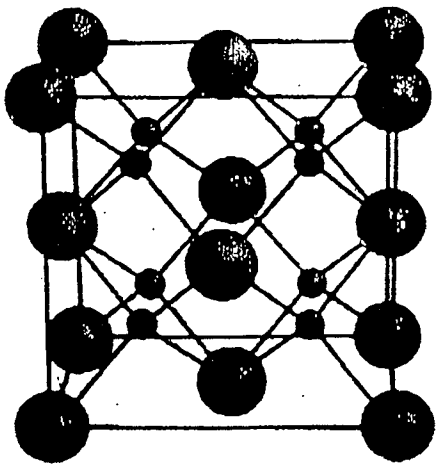

Face-centered-cubic (fcc) crystal structure of PuO_2 (Pu atoms in green, O atoms in red). The lattice constant is 4.3975 Å. PuO_{2+x} has the same structure, with a very similar lattice constant. This is one of the reasons why this compound was not identified prior to the study by Haschke *et al.* (1).

more than 50 years that PuO_2 is the highest plutonium oxide that can be prepared. This oxide, which crystallizes in the face-centered-cubic structure (fcc) (see the figure), was believed to be stable over a wide temperature range (from ambient to more than 2000°C). PuO_2 was therefore considered suitable as a component of nuclear reactor fuels, running either with fast or slow neutrons, for electricity production. To prepare these plutonium fuels, PuO_2 is mixed with depleted uranium dioxide, UO_2. The resulting solid solution $(U,Pu)O_2$ is then used to prepare mixed oxide (MOx) fuels. This plutonium recycling strategy has been an industrial reality in Western Europe and in Russia for many years and will also soon be implemented in Japan, where the first water-cooled nuclear reactor will be loaded with MOx fuel. Recycling of plutonium into MOx fuels requires reprocessing of uranium oxide–spent fuels. This is done industrially, for example, at Cogéma's La Hague plants (France) and British Nuclear Fuel Limited's Sellafield THORP plant (UK). Plutonium recovered from these spent fuels is converted into the semifinal product PuO_2. Plutonium recycling is not used in the United States, but PuO_2 is considered a very important compound for the long-term storage of plutonium from dismantled nuclear weapons.

For both civilian and military applications, the stability of PuO_2 was a key factor underlying the industrial strategy. The discovery by Haschke *et al.* that water and humid oxygen can slowly oxidize PuO_2 to PuO_{2+x}, accompanied by generation of hydrogen gas, calls for new evaluations of different aspects of the industrial operations involving PuO_2. Haschke *et al.* show that PuO_2 is metastable under oxidizing conditions and that it can be converted into PuO_{2+x} with x as high as 0.27, in which more than one-fourth of the plutonium atoms are oxidized from their initial oxidation state +IV into the oxidation state +VI. Surprisingly, water vapor was found to be a more efficient oxidizing agent than oxygen itself for the conversion of PuO_2 into PuO_{2+x}.

Future safety evaluations must take into account the temperature range of PuO_{2+x} stability (ambient to 350°C) and also the increased mobility of its Pu(VI) content in various transfer mechanisms. The new results will also have great consequences for the underground disposal of nuclear wastes. Until now, it was assumed that plutonium would not be very mobile in the underground geological environment because of the insolubility of Pu(IV) compounds. But Haschke *et al.* demonstrate that water can oxidize PuO_2 into PuO_{2+x}, in which more than 25% of the plutonium ions exist as Pu(VI), an ion that is far more water soluble, and thus mobile, than Pu(IV). This new property will have important implications for the long-term storage of plutonium.

The report by Haschke *et al.* will stimulate numerous future studies addressing fundamental questions related, for example, to the structure of the new PuO_{2+x} oxide, its thermodynamics properties, and the fascinating oxidizing property of water toward PuO_2.

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PERSPECTIVES: NEUROBIOLOGY

Diversity in Inhibition

Richard Miles

Yin and yang—inhibition and excitation. In the harmonious brain, excitatory and inhibitory synaptic signals coexist in a purposeful balance. But, whereas the neurons that the brain uses to transmit excitatory signals often have rather stereotyped properties, the cells that signal inhibition in the cortex and hippocampus are highly diverse and strikingly different from their excitable cousins. Inhibitory cells (also called interneurons because their effects are often short-range) signal to other neurons by liberating an inhibitory neurotransmitter from synaptic sites. Two articles in this week's issue add to a flood of new data on interneurons and their importance in brain function. In the first, Martina *et al.* (*1*) show on page 295 how the expression of Na^+ channels in neuronal dendritic branches endows one group of inhibitory neurons with an enhanced excitability and an increased speed of electrical signal transmission. In the second, Gupta *et al.* (*2*) present on page 273 an elegant attempt to classify cortical inhibitory cells by their synaptic effects on target neurons.

Cortical inhibitory neurons differ in many ways from their excitatory pyramidal cell partners. They have an entirely different calcium economy (*3*) and, perhaps consequently, it is difficult to induce long-term potentiation at the synapses that excite them (*4*). More importantly, inhibitory cells and circuits are built for speed. Interneuron action potentials are traditionally faster than those of pyramidal cells. This speed may result from the selective expression of specific K^+ channels that repolarize neurons after each action potential (*5*). Furthermore, the kinetics of synaptic events that excite inhibitory cells are faster than those that excite pyramidal cells (*6*). Rapid excitation probably depends on a distinct form of the postsynaptic AMPA receptor that mediates signaling at excitatory junctions with interneurons (*7*). The functional result is that pyramidal cell action potentials can induce interneuron firing with remarkably

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Reaction of Plutonium Dioxide with Water: Formation and Properties of PuO_{2+x}

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Results show that PuO_{2+x}, a high-composition ($x \leq 0.27$) phase containing Pu(VI), is the stable binary oxide in air. This nonstoichiometric oxide forms by reaction of dioxide with water and by water-catalyzed reaction of dioxide with oxygen. The $PuO_2 + H_2O$ reaction rate is 0.27 nanomoles per meter squared per hour at 25°C; the activation energy at 25° to 350°C is 39 kilojoules per mole. Slow kinetics and a low lattice parameter–composition dependence for fluorite-related PuO_{2+x} are consistent with a failure to observe the phase in earlier studies. Perplexing aspects of plutonium oxide chemistry can now be explained.

A fundamental tenet of plutonium chemistry has been that PuO_2 is the highest composition binary oxide (*1–3*). That description is based on estimated thermodynamic properties suggesting that higher oxides are unstable (*4*) and on unsuccessful attempts by early workers to prepare higher oxides in experiments with strong oxidants such as atomic oxygen, ozone, and nitrogen dioxide (*5, 6*). Higher oxides were also not seen during thermal decomposition of Pu(VI) carbonates (*7*). Excess mass gains observed during atmospheric oxidation of plutonium metal were attributed to adsorption of water on the high–surface area product (*2, 8*). However, results of a recent x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) study of the adherent oxide formed on Pu metal by reaction in water vapor at 250°C showed that a higher oxide formed at the gas-oxide interface had a fluorite-related structure and contained Pu(VI) (*9*).

Here we show that PuO_{2+x}, the stable oxide in air, is formed by reaction of PuO_2 with adsorbed water in at 25° to 350°C.

$$PuO_2(s) + xH_2O(ads.) \rightarrow PuO_{2+x}(s) + xH_2(g) \quad (1)$$

Mass spectrometric analyses show that H_2 is the only gaseous product. Oxidation rates (R) measured at constant temperature and H_2O pressure by microbalance (MB) and pressure-volume-temperature (PVT) methods (*10–12*) were constant over a range of oxide composition as shown by representative linear pressure-time (P-t) data (Fig. 1) and by mass-time curves. Pressure-time data for 25°C gave an R of 0.13 nmol O m^{-2} $hour^{-1}$. The initial oxide composition ($PuO_{1.97}$) used in these tests was as determined from XRD results and lattice parameter (a_o)–composition data for $PuO_{2-\delta}$ (*13*). The x value was 0.17 after the test at 350°C and changed by 0.003 in 4 years at 25°C, but the maximum oxide composition was not attained at any temperature.

The rate of Eq. 1 at 25°C is also derived from P-t and mass spectrometric data obtained after exposing PuO_2 to a 2:1 molar mixture of H_2 and O_2. Water formed in situ by surface-catalyzed association of the elements (*14*) was not detected by mass spectrometry, but remained chemisorbed as OH^- on the oxide surface (*15*) and caused a progressive decrease in the $H_2 + O_2$ combination rate as active sites were blocked. After more than 100 days, the OH^- concentration reached 15 to 20% of monolayer coverage on the oxide and the P-t curve became linear as O_2 reacted at a constant rate (0.25 nmol O m^{-2} $hour^{-1}$) characteristic of the $PuO_2 + H_2O$ reaction.

Data for H_2 generation by reaction of high–surface area (750 m^2 g^{-1}) PuO_2 during hydrolysis of Pu in aqueous salt solution (*16, 17*) give a rate of 0.42 nmol O m^{-2} $hour^{-1}$ for Eq. 1. Three independent results give an average R of 0.27 ± 0.17 nmol O m^{-2} $hour^{-1}$ at 25°C and show that the reaction rate is independent of adsorbed H_2O over a concentration range extending from fractional surface coverage by OH^- to saturation in liquid water. Oxidation is sufficiently slow that the oxidation rate at 25°C is maintained by chemisorbed H_2O at less than 20% monolayer coverage by OH^-.

Results show that the rate of the $PuO_2 + H_2O$ reaction is a function of temperature as described by an Arrhenius relation (Fig. 2) with an activation energy of 39 ± 3 kJ/mol. This result is consistent with chemical reaction and suggests that the contribution from temperature-independent radiolysis of water by decay of plutonium isotopes was negligible in our experiments.

Diffraction and spectroscopic data are consistent with a solid solution PuO_{2+x} phase formed by accommodating a high oxidation state of plutonium and interstitial oxygen in the fluorite structure of PuO_2. Earlier XPS analysis of the oxide formed during oxidation of metal by water (*9*) showed peaks with high binding energies (442 and 429 eV for the $4f_{5/2}$ and $4f_{7/2}$ spectra, respectively) correlated with either the Pu(VI) or Pu(VII) oxidation state and indicating the absence of Pu(V). The O 1s spectrum is consistent with the presence of oxygen as oxide. We attribute the absence of OH^- to continuing reaction after placement in the spectrometer. XRD data for oxides that we synthesized showed fluorite-related face-centered cubic structures and a surprisingly low composition dependence of a_o (Fig. 3). The lattice parameter reached a minimum (5.3975 Å) at $PuO_{2.00}$, increased sharply over a narrow composition range, and increased linearly with O:Pu to values in excess of $PuO_{2.25}$.

Insensitivity of a_o to PuO_{2+x} composition is consistent with substitution of Pu(VI) for Pu(IV) on cationic sites of a fluorite structure and accommodation of additional O^{2-} in octahedral interstices. This structural model is supported by analogy to UO_{2+x} (*18*) and by neutron diffraction results (*19*). Substitution of Pu(VI) tends to shrink the lattice, but addition of O^{2-} causes expansion. These opposing changes are apparently of comparable magnitude and result in a low O:Pu dependence of a_o. The sharp increase in a_o at compositions immediately above that of dioxide suggests that onset of PuO_{2+x} formation is accompanied by expansion of the entire lattice. Frequent appearance of short induction periods at the beginning of rate measurements may result from sluggish lattice dynamics.

Results for the oxide prepared by hydrolysis of Pu in salt solution at room temperature (*16, 17*) confirm the a_o-composition dependence (Fig. 3) and demonstrate that PuO_{2+x} is unstable at elevated temperatures in the absence of water or oxygen. H_2 formed dur-

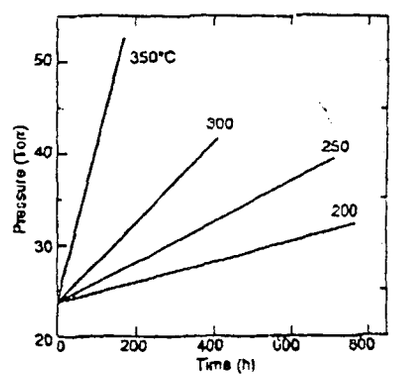

Fig. 1. Time dependence of the H_2 pressure during exposure of PuO_2 to H_2O vapor at experimental temperatures and a constant water pressure of 32 mbar (24 torr).

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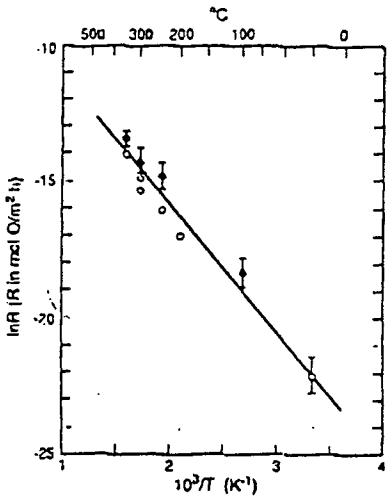

Fig. 2. Arrhenius analysis of rate-temperature data for the $PuO_2 + H_2O$ reaction at 25° to 350°C and 32-mbar H_2O pressure. Data from MB and PVT measurements are indicated by filled and open circles, respectively. The data point at 100°C (triangle) was determined by using the extent of reaction derived from a_o of the product and the lattice parameter–composition correlation (Fig. 3). The Arrhenius equation is $\ln R = -6.441 - (4706/T)$.

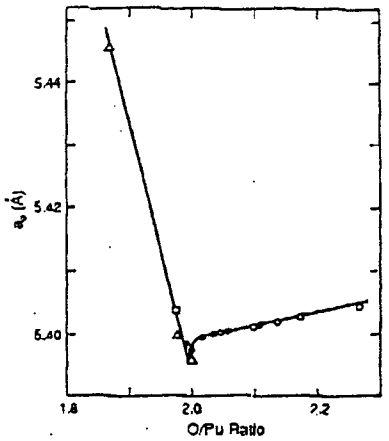

Fig. 3. Dependence of the cubic lattice parameter (a_o) on oxide composition (O:Pu ratio = $2 \pm x$) of the PuO_{2-x} and PuO_{2+x} phases at room temperature. Reference lattice parameter–O:Pu data for $PuO_{2-\delta}$ from Gardner *et al.* (*13*) are shown by triangles and a_o of the starting oxide ($PuO_{1.97}$) is shown by a square. Values of a_o obtained for products from MB and PVT measurements are shown by filled and open circles, respectively. The lattice parameter–composition dependence of PuO_{2+x} is given by a_o (Å) = 5.3643 + 0.01746 O:Pu.

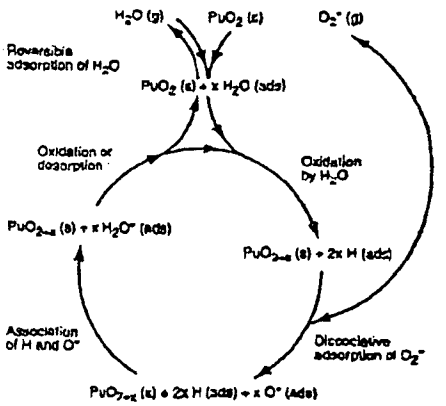

Fig. 4. The chemical cycle for H_2O-catalyzed $PuO_2 + O_2$ reaction and oxide-catalyzed regeneration of H_2O.

ing the $Pu + H_2O$ reaction and continued to form as progressive oxidation produced plutonium monoxide monohydride (PuOH) and a series of oxide hydride and oxide phases. H_2 production continued beyond the dioxide composition in a process that we can now explain by Eq. 1. The measured a_o (5.404 Å) of the $PuO_{2.265}$ product obtained when the test was arbitrarily terminated agrees closely with the correlation derived for O:Pu ratios in the 2.016 to 2.169 range. Thermogravimetric analysis at 25° to 500°C and a_o for the fired oxide showed that PuO_{2+x} decomposes to PuO_2 upon heating in a vacuum (*17*).

Our results show that PuO_{2+x} is formed in moist air or moist oxygen via a catalytic cycle (Fig. 4) driven by Eq. 1. We observed that water formed and accumulated on the oxide surface as H_2 and O_2 dissociatively adsorbed and associated as H_2O, while oxygen simultaneously disappeared at a constant rate characteristic of the $PuO_2 + H_2O$ reaction. As shown by the cycle, adsorbed H_2O reacts to form PuO_{2+x}. However, in the presence of O_2, atomic H that formed on the oxide by the $PuO_2 + H_2O$ reaction does not associate as H_2, but reacts with dissociatively adsorbed oxygen to re-form H_2O. The net result of the cyclic process is the reaction of PuO_2 and O_2 at the rate of $PuO_2 + H_2O$. Water enhances the rate of PuO_{2+x} formation, while the oxide surface catalyzes re-formation of water. This catalytic cycle accounts for all observations in this study, as well as for transformation of isotopically labeled O_2* into H_2O* during oxidation of uranium (*20*).

The descriptive chemistry of plutonium is confused by conflicting reports that the dioxide is green (*1*) or dull yellow to khaki (*3*). We observed that the dioxide is yellow to buff, but that PuO_{2+x} consistently has an intense green color.

Our results show that PuO_{2+x} is the thermodynamically stable oxide of plutonium in air at temperatures below 350°C and contradict earlier evidence that higher oxides are unstable and cannot be prepared. Failure to observe PuO_{2+x} may have resulted from several factors. The stability range was probably exceeded by reaction temperatures (1000° ± 100°C) of some studies (*21*). Exposure of the dioxide to strong oxidants increases the free energy for reaction, but does not necessarily enhance the kinetics. Although oxidation by O_2 is thermodynamically more favorable than oxidation by H_2O, reaction of dry oxygen is slow and the extent is limited after a few-hour experiment (*6*). If oxidation occurred, its detection by XRD is unlikely because of the low a_o-O:Pu dependence of PuO_{2+x} (Fig. 3) and the expectation that a_o would decrease with increasing x as for UO_{2+x} (*21*). Oxidation by water is also slow, but readily detected by production of H_2, a sensitive and definitive indicator of PuO_{2+x} formation.

PuO_{2+x} apparently participates in moisture-enhanced corrosion of the metal (*9, 14*). Reaction of adsorbed water with PuO_2 contributes to H_2 pressurization of sealed storage containers (*22*) until the equilibrium pressure of Eq. 1 is reached. As with uranium oxide, the presence of hexavalent cations should increase oxide solubility. Elimination of Pu(VI) by decomposition of PuO_{2+x} during calcination may account for slow dissolution of "high fired" oxide in aqueous acids (*1, 3*). Leaching of accumulated Pu(VI) from PuO_{2+x} formed by water-catalyzed oxidation of PuO_2 in air accounts for the appearance of Pu(VI) as the predominant species in water coexisting with oxide (*23*) and may be important in the surprisingly rapid (1.3 km in 30 years) groundwater migration of plutonium (*24*).

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12. Oxides prepared by oxidizing electrorefined weapons-grade Pu (100 part per million Am) in air ($PuO_{1.97}$) or the gallium alloy in O_2 ($PuO_{2.00}$) had specific surface areas of 11.3 and 4.0 ± 3 m^{-2} g^{-1}, respectively, and were contained in Pt or stainless steel during exposure to H_2O vapor for periods up to 4 years. Constant H_2O pressures (25 ± 7 mbar) were maintained by using isothermal water reservoirs. Temperatures were measured in the gas phase near the oxides. Oxidation rates in units of mol O m^{-1} $hour^{-1}$ were defined by slopes of mass/P-t data; x was defined by terminal MB and PVT data and Eq. 1. Details are reported elsewhere (*10, 11*), and interpretation is augmented by results of an experiment in which $PuO_{2.00}$ was exposed to a 2:1 molar mixture of D_2 and O_2 at 170 mbar (*10*).

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28 September 1999; accepted 18 November 1999

Communication Through a Diffusive Medium: Coherence and Capacity

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Coherent wave propagation in disordered media gives rise to many fascinating phenomena as diverse as universal conductance fluctuations in mesoscopic metals and speckle patterns in light scattering. Here, the theory of electromagnetic wave propagation in diffusive media is combined with information theory to show how interference affects the information transmission rate between antenna arrays. Nontrivial dependencies of the information capacity on the nature of the antenna arrays are found, such as the dimensionality of the arrays and their direction with respect to the local scattering medium. This approach provides a physical picture for understanding the importance of scattering in the transfer of information through wireless communications.

The ongoing communications revolution has motivated researchers to look for novel ways to transmit information (*1, 2*). One recent development (*3, 4*) is the suggestion that, contrary to long-held beliefs, random scattering of microwave or radio signals may enhance the amount of information that can be transmitted on a particular channel. Prompted by this suggestion, we introduce a realistic physical model for a scattering environment and analytically evaluate the amount of information that can be transmitted between two antenna arrays for a number of example cases. On the one hand, this lays a new foundation for complex microwave signal modeling, an important task in a world with ever-increasing demand for wireless communication, and on the other, it introduces a new arena for physicists to test ideas concerning disordered media.

From information theory (*5*), the capacity of a channel between a transmitter and a receiver, that is, the maximum rate of information transfer at a given frequency, can be described in terms of the average power of the signal S and the noise N at the receiver: $C = \log_2(1 + S/N)$. More generally (*2*), the communication channel connecting several transmitters and receivers is described by a matrix $G_{i\alpha}$ giving the amplitude of the received signal α due to transmitter i. The information carried by the channel can be characterized by using several quantities, such as the capacity or mutual information, which are typically functionals of the matrix G, which must be known in order to predict these quantities. Often G cannot be predicted for actual systems, such as wireless communication networks or optical fibers, because of the complicated scattering and interference of waves that are involved. It is crucial, therefore, to develop physical models for the signal propagation, because it is only through such models that one can understand the real effects of scattering and interference on the amount of information that can be communicated.

In many cases, only partial information is available for prediction; in these situations, one has only a statistical description of G. Instead of making assumptions about G directly, which is the usual procedure in information theory, we introduce statistical models for the physical environment from which we derive the properties of G. The advantage of this procedure is that simple physical models can yield very nontrivial properties of G.

Statistical descriptions of the environment have been quite successful in the physics of disordered media (*6–9*). The simplest of these is diffusive propagation. In our case of electromagnetic propagation in the context of wireless communication, diffusion is known to work well in various circumstances (*10*), and simple extensions seem relevant for many others. From a diffusive approach, one finds the moments of the distribution of G. These will enable us to calculate information-theoretic quantities (for example, the capacity) using a replica field theory approach to random matrix theory (*11*). Implicit in this approach is the assumption that the full distribution of G is sampled, which is realistic in many real-world situations where the environment is changing. However, when the number of antennas is large, many quantities of interest become strongly peaked around their average and this assumption can be relaxed.

In a statistical description, the scattering of the signal is characterized by the mean-free path, ℓ, corresponding roughly to the distance between scattering events. When ℓ is large compared to the wavelength λ but small compared to the distance d between the two arrays, the wave propagation becomes diffusive (*8, 9*). This has been analyzed previously in the context of electron diffusion in metals (*6, 7*) and light propagation in solids (*8, 12*). In the case of wireless propagation, with signals in the 2-GHz region, $\lambda \sim 10$ to 15 cm, while ℓ is on the order of meters for indoors and tens of meters for outdoors propagation, so diffusion is applicable.

In the diffusive regime $\lambda \ll \ell$, to leading order in λ/ℓ, only the quadratic correlations $\langle G_{i\alpha} G^*_{j\beta} \rangle$ are nonnegligible and therefore describe the system, where the brackets represent an average over realizations of the disorder. Higher cumulants of G are of higher order in λ/ℓ. Therefore, the distribution of G is Gaussian with zero average (*6–9*). The leading term in $\langle G_{i\alpha} G^*_{j\beta} \rangle$ is evaluated by a summation of so-called ladder diagrams (*8*) corresponding to processes in $\langle G_{i\alpha} G^*_{j\beta} \rangle$ where the waves from antennas i to α and from j to β propagate through the scattering medium along identical paths except for segments of order ℓ at each end.

In several realistic situations discussed be-

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Enclosure 6

EPA Report:
Evaluation of the Reported Presence of Oxidized Plutonium in the STTP Experiments and in Plutonium Oxide Solids
September 2000

EVALUATION OF THE REPORTED PRESENCE OF OXIDIZED PLUTONIUM IN THE STTP EXPERIMENTS AND IN PLUTONIUM OXIDE SOLID

FINAL REPORT

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1.0 INTRODUCTION

The Actinide Source Term Model (ASTM) of the Compliance Certification Application (CCA) for the Waste Isolation Pilot Project (WIPP) was based on the assumption of reducing conditions in the long-term WIPP repository environment (USDOE, 1996b). Because of these reducing conditions, it has been predicted that plutonium will be present in the plutonium(III) and plutonium(IV) oxidation states under long-term WIPP repository conditions (USDOE, 1996b; USEPA, 1998a; USEPA 1998b). The assumed plutonium oxidation states in the repository environment are important because plutonium(III) and plutonium(IV) are typically much less mobile than plutonium(V) and plutonium(VI).

Recent experimental results from the Actinide Source-Term Waste Test Program (STTP) conducted at Los Alamos National Laboratory (LANL) indicated that plutonium(V) and plutonium(VI) species were present in some test solutions. In addition, a recently published experimental investigation has reported the existence of plutonium oxide solids that contain plutonium(VI) in the form of PuO_{2+x} (Haschke and others, 2000). The existence of plutonium(V) or plutonium(VI) oxidation states in solution under equilibrium conditions in the WIPP repository environment could result in higher plutonium concentrations than predicted by the ASTM. Therefore, the relevance of the STTP experiments to WIPP repository conditions and the formation of PuO_{2+x} has been evaluated. Based on this evaluation, we conclude that the recent results of the STTP experiments and plutonium oxide experiments do not provide evidence that plutonium(V) or plutonium(VI) will be present under conditions anticipated in the long-term WIPP repository environment.

This report summarizes USEPA's review of the STTP experiments and the journal article that reported the formation of PuO_{2+x}. This report includes a description of the conditions predicted for the WIPP repository (Section 2.0), a summary of the STTP experimental results (Section 3.0), a summary of the PuO_{2+x} journal article (Section 4.0), and a comparison of the conditions in these experiments with the conditions expected in the long-term WIPP repository (Section 5.0). Finally, the results of this evaluation are summarized in Section 6.0.

2.0 WIPP REPOSITORY CHEMICAL CONDITIONS

The conceptualization of plutonium chemistry in the CCA is that plutonium(III) and plutonium(IV) will exist under long-term equilibrium conditions in the WIPP repository. Numerous experimental results show that long-term reducing conditions will be maintained in the repository by corrosion of iron and degradation of organic materials. These experimental observations showed that plutonium(V) and plutonium(VI) will not persist in the presence of these reductants in the repository environment (USEPA, 1998a, page 6-85).

The long-term chemical conditions in the WIPP repository are described in Appendix SOTERM of the CCA (USDOE, 1996b). The source term conceptual model is based on an assumption of equilibrium because of the extremely long time frames relevant to the repository (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b). Aspects of the repository chemical environment that are likely to significantly affect actinide transport include brine composition, microbial degradation of organic waste, and corrosion of metallic waste (USDOE, 1996b). Brine radiolysis and addition of MgO as backfill will also influence chemical conditions in the repository environment (USDOE, 1996b). These influences on the repository environment are discussed below.

2.1 Brine

The composition of Salado Brine and Castile Brine are expected to bracket the range of possible brine compositions in the WIPP repository (USDOE, 1996b). The range of WIPP brines have been simulated by USDOE using two compositions, Brine A and ERDA-6. Brine A is a synthetic, high-magnesium brine that simulates Salado Brine. ERDA-6 is a synthetic brine formulation simulating Castile Brine, which has a much lower magnesium concentration. These synthetic brines have been used in most of the experiments and modeling of repository chemistry (USDOE, 1996b).

2.2 Biodegradation of Organic Materials

Organic materials will be present in WIPP, primarily in the form of cellulosics, plastics, and rubber (USDOE, 1996b). Microbial degradation of these organic materials is likely to influence the repository environment because of (USDOE, 1996b):

- Oxygen consumption and consequent reducing conditions in the repository;
- Consumption of organic ligands that have the potential for mobilizing actinides;
- Production of humic and microbial colloids that could increase amount of actinides sorbed on colloidal surfaces; and
- Generation of carbon dioxide, which in the absence of added MgO, would increase acidity and carbonate concentrations in the brine and thereby increase actinide solubility.

Reducing conditions and removal of organic ligands are likely to limit actinide mobility (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b). The possible effects of carbon dioxide generation are mitigated by addition of MgO backfill to the repository (Section 2.5).

2.3 Metal Corrosion

Corrosion of steel and other metals in the repository are expected to:

- Produce reducing conditions in the repository and reduce the oxidation states of some actinides;
- Release metal ions such as iron and nickel into solution; and
- Produce colloidal corrosion products which may sorb actinides (USDOE, 1996b).

Oxic corrosion of steel and aerobic biodegradation of organic materials are expected to remove oxygen from the repository environment shortly after closure. After oxygen in the repository is consumed, anoxic corrosion of metals is expected to occur and produce hydrogen, which will also contribute to reducing conditions in the repository (USDOE, 1996b; USEPA, 1998b).

Metal ions in solution and solid metal oxyhydroxides are expected to be produced by corrosion processes. The reduction of plutonium in brine by soluble iron and by metallic iron has been observed in a number of experimental investigations (Felmy and others, 1989; Weiner, 1996; Weiner and others, 1996; USDOE, 1996a, Section 6.0; Xia and others, 1996; USEPA, 1998a; Clark and others (LANL) as cited by Brush, 2000). Metal ions such as ferrous iron and nickel may complex with organic ligands and limit the mobilization of actinides by these ligands (USDOE, 1996b). Metal oxyhydroxides can sorb actinides and further limit actinide mobility.

Two evaluations of iron corrosion at WIPP-relevant conditions have been carried out. The results of these studies are summarized below. Available corrosion information for natural analogues is also addressed below.

2.3.1 Felmy and Others (2000) Iron Corrosion Study

The corrosion of iron coupons in ERDA-6 (Castile) brine has been evaluated at pH values ranging from pH 2.4 to 7.1 (Felmy and others, 2000). The test atmosphere and iron composition were not reported in this study. Evaluation of the metal surfaces after corrosion indicated that the corrosion products contained mostly iron(II) and iron(III) at approximately a 2:1 ratio. The solids appeared to be green rust-like iron(II) and (III) hydroxy salts, and no iron(II)-only solids such as $Fe(OH)_2$ were observed. The corrosion film thickness was found to be heterogeneous, ranging from a few to tens of nanometers in thickness. The corrosion film appeared to be loosely attached to the metal surface (Felmy and others, 2000). Thus, this study indicates that the corrosion layer on the metal surface will not prevent long-term iron oxidation in the repository and iron corrosion can be expected to produce a reducing environment in the repository over the long term.

2.3.2 Telander and Westerman (1997) Iron Corrosion Study

Low-carbon steel corrosion and associated gas generation in anoxic WIPP brines have been evaluated in a series of experiments carried out at 30°C (Telander and Westerman, 1997). Tests were conducted by immersing the steel in brine or by suspending it above the brine to evaluate vapor-phase

corrosion. Vapor-phase corrosion tests showed much lower corrosion rates than tests in which the steel was immersed in brine.

Tests were conducted using low-carbon steel immersed in Brine A (Salado) with overpressures of hydrogen (H_2), nitrogen (N_2), carbon dioxide (CO_2), and hydrogen sulfide (H_2S). Increasing hydrogen gas pressure had little effect on the observed corrosion rate, and the oxidation products were not adherent. Increasing nitrogen pressure only slightly increased the corrosion rate. The post-test pH of the nitrogen-Brine A corrosion tests was approximately 8.3. The corrosion product from the nitrogen atmosphere tests could not be identified by X-ray diffraction (XRD) analysis. Chemically, the corrosion product appeared to be a form of $Fe,Mg(OH)_2$.

Increasing carbon dioxide gas pressures increased the initial corrosion rate, but also increased the possibility of passivation through formation of an impermeable corrosion product film in the form of siderite ($FeCO_3$). Addition of hydrogen sulfide gas after corrosion in the presence of carbon dioxide gas disrupted this passivation of the steel surface. XRD analyses of the reaction products indicated the presence of both siderite and mackinawite (FeS). The pH values of these tests were not reported.

Hydrogen sulfide gas pressures of 5 atm appeared to prevent corrosion through the formation of a layer of mackinawite on the surface. Addition of carbon dioxide gas to experiments with steel passivated by the presence of hydrogen sulfide did not disrupt the passivation of the steel. The pH values of these tests were not reported.

Corrosion tests were also conducted in anoxic ERDA-6 (Castile) brine with a nitrogen overpressure. Magnesium- and calcium-free ERDA-6 brine was selected for this portion of the investigation because of the precipitation of calcium and magnesium constituents of ERDA-6 brine at high pH. The relative reactivity of the ERDA-6 brine with respect to low-carbon steel was found to be similar to the reactivity of Brine A. Corrosion rates were investigated in the ERDA-6 brine at constant pH values from 3 to 11. Corrosion products in the pH 9 and 11 tests were determined by XRD to be akaganeite (α-FeOOH). The results of these experiments indicate that iron corrosion rates decrease with increasing pH values, but that corrosion will still occur at anticipated repository pH values and produce reducing conditions in the repository.

2.3.3 Evaluation of Iron Analogue Corrosion Rates

Inferences concerning the long-term corrosion behavior of steel containers in WIPP disposal rooms may be drawn from studies of the corrosion of analogous iron-bearing materials. Occurrences of native iron in the near-surface environment are rare because iron is thermodynamically unstable with respect to water at hydrostatic pressures less than about 1,000 bar (Neretnieks, 1985). The available native-iron analogues are not particularly useful for purposes of estimating corrosion rates because the iron has either been isolated from contact with water, or stabilized by solid-solution with other elements. Because the WIPP environment may include contact of the steel containers with brine, the available native-iron analogues have limited relevance to iron corrosion in WIPP. On the other hand, available archeological artifacts have been found in a variety of environments and may prove more applicable to WIPP conditions.

Most archeological analogues for evaluating long-term corrosion of iron-based containers (steels) are limited to cast and wrought irons and primitive steels. The range of impurities in ancient iron artifacts compared to modern steel makes it relatively difficult to relate the corrosion of ancient artifacts to the corrosion of modern steels. The applicability of archeological analogue data may also be limited by the fact that the environments in which these artifacts corroded differ from the expected WIPP environment. In addition, archeologically based corrosion rates may be biased by selective sampling (some artifacts may have completely corroded away), as well as poor documentation on the degree of cleaning or restoration performed, and uncertainty as to the location of the original surface of the artifact. Finally, there is always some uncertainty in the age of the artifact. However, evaluation of the corrosion of iron artifacts can help bound and validate projections of short-term laboratory derived corrosion rates over longer time periods.

Johnson and Francis (1980) evaluated iron corrosion rates over long time periods by assessing 44 iron and iron alloy artifacts. These artifacts are from a wide variety of environments, ranging from very wet to arid, and from oxidizing to reducing. Corrosion rates for these artifacts average around 1-2 μm/yr and range from a low of about 0.0025 μm/yr to a high of about 10 μm/yr (Table 1). The corrosion rates for the majority (all but 8) of the artifacts fall between 0.1 and 10 μm/yr, which is a relatively narrow range given the range in environments for these artifacts. In addition, two artifacts located in marine environments had corrosion rates from 2 μm/yr to 430 μm/yr (Table 1). Other studies reported since the publication of Johnson and Francis (1980) are summarized in Table 1. The corrosion rates for all artifacts

in Table 1 range from 0.0025 to 18.7 μm/yr, with the higher corrosion rates associated with artifacts for which environmental conditions are either poorly constrained or associated with more acid, wet coal mines.

The range of corrosion rates assumed for steel containers in the WIPP CCA PA (USDOE, 1996b) is included in Table 1 for comparison with the archaeological data. The WIPP corrosion rates estimated by Wang and Brush (1996) bracket experimental corrosion rates determined by Telander and Westerman (1997) and are consistent with the range of rates estimated on the basis of the natural analogue data (Table 1). This observation supports the implicit assumption in the WIPP CCA PA that laboratory-based corrosion rates can be used to estimate the corrosion behavior of steel containers in WIPP disposal environments over periods of time as long as 10,000 years. Thus, the available iron analogue and laboratory data indicate that iron corrosion is likely to occur in the long-term WIPP repository and produce a reducing environment.

2.4 Brine Radiolysis

Brine radiolysis may affect actinide oxidation states in solution. The radiolysis reactions produce highly reactive peroxide (H_2O_2) and hypochlorites (e.g., NaOCl), as well as hydrogen (H_2) and other gases, such as O_2, N_2, CO, and CO_2 (Büppelman and others, 1986; Büppelman and others, 1988; USDOE, 1996b; Kelm and others, 1999; LANL, 2000b). Higher actinide oxidation states can be produced by reactions of actinides with peroxide and hypochlorite species, with the persistence of hydrogen gas because of its generally slower reaction rates. Alpha-radiolysis has been demonstrated to increase Eh values in brine solutions within relatively short time periods (Büppelman and others, 1986). In the WIPP repository, it is expected that oxidized species produced by radiolysis will react quickly with iron metal and dissolved ferrous iron species, and will not significantly affect actinide oxidation states (USDOE, 1996b).

2.5 MgO Backfill

MgO backfill is included in the repository to absorb water by reaction to form brucite ($Mg(OH)_2$) and to remove carbon dioxide by reactions that form hydrated magnesium carbonate phases such as hydromagnesite ($3MgCO_3 \bullet Mg(OH)_2 \bullet 3H_2O$) and over the long term, magnesite ($MgCO_3$) (Sandia, 1997;

USDOE, 1996b). The amount of MgO included in the repository is significantly greater than the amount necessary to remove all carbon dioxide produced by biodegradation of organics (Sandia, 1997; USDOE, 1996b). Because of the presence of MgO backfill, the brine pH and carbon dioxide fugacity within the repository will be controlled by the $Mg(OH)_2$ - $MgCO_3$ buffer reaction (USDOE, 1996b). This reaction is expected to maintain pH values in the range of 8.5 to 10, and carbon dioxide fugacity at approximately 10^{-6} atm, thereby limiting the mobility of actinide species (USDOE, 1996b; LANL, 2000b).

2.6 Long-Term Reducing Conditions in the Repository

The Fracture-Matrix Transport (FMT) code was used to perform solubility calculations for the actinide elements in the WIPP repository brines (USDOE, 1996b). Because oxidation-reduction reactions are not included in the FMT calculations, assumptions were made regarding equilibrium actinide oxidation states (USDOE, 1996b; USEPA, 1998b). Based on the reducing conditions generated by metal corrosion and biodegradation of organics, it has been assumed that plutonium will exist only in the (III) and (IV) oxidation states in the repository at equilibrium. The presence of plutonium in reduced oxidation states, combined with high pH and low carbon dioxide partial pressure because of the MgO backfill, are expected to limit plutonium solubility (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b).

2.7 Reduction of Actinide Species by Iron Solid Phases

Reed and others (in preparation) investigated the empirical solubility and redox stability of plutonium(VI) in WIPP brines. The experiments were performed in darkness, with an approximately 1 atmosphere hydrogen overpressure. Tests included low- and high-magnesium brines, pH values from 5 to 10, the presence or absence of carbonate, initial plutonium concentrations of 0.1 mm, and durations of up to 18 months. Experiments conducted without added reducing agent indicated that plutonium(VI) was stable under all conditions investigated. Addition of iron coupons to the plutonium(VI) solutions, however, resulted in plutonium(VI) reduction to plutonium(IV) and precipitation of a plutonium(IV) solid phase. Thus, the experiments conducted by Reed and others (in preparation) indicate that iron metal can be an effective reducing agent for plutonium(VI) in WIPP brines.

Xia and others (1996) carried out experiments to evaluate the effects of iron powder on the aqueous oxidation state of plutonium(VI) in dilute NaCl and synthetic brines. These experiments were conducted in an inert (argon) atmosphere chamber in 0.01 M NaCl and in ERDA-6 (Castile) brine, at pcH values from approximately 7 to 12, and for time periods of up to 76 days. In dilute NaCl solutions, addition of iron metal to the plutonium(VI) solutions decreased plutonium concentrations by several orders of magnitude, to concentrations consistent with the precipitation of $Pu(OH)_3(s)$ or $PuO_2 \bullet xH_2O(am)$. The dramatic decrease in plutonium concentrations in the dilute solutions indicates that the iron metal reduced plutonium(VI) to plutonium(III) or plutonium(IV). In the ERDA-6 brine experiments, however, plutonium(VI) reduction by iron appeared to occur more slowly than in the dilute NaCl solutions. After 72 days, iron addition decreased plutonium concentrations in brine solutions with pcH below 9 by nearly four orders of magnitude. However, in brine solutions with pcH of 9 or greater, plutonium concentrations decreased by less than an order of magnitude after addition of iron powder. Further addition of iron powder after 72 days of equilibration decreased plutonium concentrations in a sample with pcH of approximately 9, but had no effect on a sample with pcH of 10.2. The diminished effectiveness of iron powder for reducing plutonium(VI) in basic solutions was attributed to the formation of oxide coatings on the iron. The oxidation state of the plutonium in the brine experiments was determined by solvent extraction, and was found to be predominantly plutonium(V), and the solution concentrations of plutonium in these experiments may have been controlled by the solubility of $PuO_2 \bullet xH_2O(am)$ in equilibrium with aqueous plutonium(V) (Xia and others, 1996). These experiments indicate that reduction of plutonium(VI) may occur slowly in the higher-pH brines anticipated in the WIPP repository.

Grambow and others (1996) evaluated uranium(VI) reduction by iron corrosion products; this investigation was cited as evidence that plutonium(V) and plutonium(VI) would be reduced in the presence of iron corrosion products (Brush and Moore, 2000). The experiments were carried out by addition of uranium(VI) to a fine-grained, low-carbon steel that had been corroded in a magnesium-rich brine at elevated temperatures. An additional experiment was conducted with uranium(VI) added to uncorroded steel in a magnesium-rich brine. The uranium(VI) sorption experiments were carried out at room temperature and at 150°C under an inert atmosphere or in the presence of a mixed argon-hydrogen (8 %) atmosphere. The iron corrosion products in these tests were identified as $(Fe,Mg)(OH)_2/Fe(OH)_3Cl$ and magnetite (Fe_3O_4). Uranium solution concentrations were decreased by contact with the iron corrosion products, principally by sorption of uranium(VI) on magnetite. Uranium that remained in solution was predominantly uranium(VI), and the majority of the solid-phase associated uranium was also present in the

(VI) oxidation state. However, the solution Eh and pH conditions should have favored reduction of uranium to the (IV) oxidation state, and the observation of uranium(VI) may have been an artifact of the oxidation state analysis method (Grambow and others, 1996). Therefore, although the investigation by Grambow and others (1996) does not provide conclusive evidence of (VI) actinide species reduction to the (IV) oxidation state, it does indicate that the presence of iron corrosion products should reduce solution concentrations of (VI) actinides in moderate-pH solutions.

Slater and others (1997) evaluated the removal of plutonium from waste solutions using a magnetite carrier. In these experiments, magnetite was formed in situ at a pH of approximately 12, and the remaining plutonium concentrations in the filtered solutions were evaluated. The magnetite carrier was found to substantially decrease plutonium concentrations through a number of possible mechanisms, including adsorption on the magnetite surface, substitution of plutonium for iron in the magnetite structure, and reduction of higher oxidation states to plutonium(III) with precipitation of $Pu(OH)_3(s)$ (Slater and others, 1997). This investigation indicates that magnetite corrosion product formation may reduce plutonium concentrations in solution.

3.0 STTP EXPERIMENTS

The Actinide Source-Term Waste Test Program (STTP) includes a series of experiments conducted with WIPP brines in contact with actual transuranic (TRU) waste (Phillips and Molecke, 1993; Villarreal, 1996). The stated purpose of the STTP experiments was to confirm that actinide concentrations predicted by the ASTM and used in the CCA provide an upper bound on mobile actinide concentrations in WIPP repository brines (LANL, 2000b). The STTP tests were initiated at Los Alamos National Laboratory (LANL) in 1995. The experiments were designed to simulate anticipated repository conditions based on the conceptualization of the WIPP repository at the time the experiments began (LANL, 2000b).

3.1 Drum-Scale Tests

DOE conducted fifteen drum-scale STTP tests with brine and heterogeneous or debris waste (LANL, 2000b). These tests were carried out using the total contents of standard 55-gallon drums of actual TRU waste. Twelve drums contained combustible debris and three drums contained massive metal waste. The wastes used in the tests contained plutonium and americium, with uranium, thorium, and neptunium added as soluble salts to each test container. Iron mesh was added to each drum, and chelators plus hydrated lime, nitrate plus phosphate, and bentonite were each added to three of the tests (LANL, 2000b). Brine A (simulated Salado Brine) was used in 10 of the tests, and simulated Castile Brine was used in the remaining five tests (LANL, 2000b).

The drum-scale tests were sampled for actinide concentrations over the course of four years. However, all concentrations of plutonium and other actinides were less than the maximum concentrations predicted by the ASTM (LANL, 2000b; Brush, 2000). There were no reported observations of plutonium(V) or plutonium(VI) in the drum-scale experiment solution samples (LANL, 2000b; Brush, 2000). Therefore, the results of the drum-scale experiments are consistent with the ASTM oxidation state assumptions of plutonium(III) or plutonium(IV).

3.2 Liter-Scale Tests

Thirty-nine liter-scale tests were carried out with brine and homogeneous or solidified waste (LANL, 2000b). The wastes used in the liter-scale tests included:

- Aqueous waste solidified with Portland cement (tests L-1 through L-12);
- Organic, aqueous, and inorganic waste solidified by Envirostone (tests L-13 through L-24); and
- Pyrochemical salt waste (tests L-25 through L-39).

The results and interpretation of ~~these~~ the liter-scale tests are described below.

3.2.1 Test Matrix and Results

Two types of pyrochemical salt waste were used in the tests: direct oxide-reduction waste (DOR) and oxygen-sparging waste (OS) (LANL, 2000b; Runde, 2000). Iron mesh, chelators plus hydrated lime, and nitrate plus phosphate were added to some of the liter-scale tests to simulate the range of variables expected in the repository. Brine A (simulated Salado Brine) was used in 26 of the tests, and simulated Castile Brine was used in the other 13 tests. Inoculum obtained from brine near the WIPP site was added to each test container. The containers were filled with additional brine and sealed, and the head space of each container was purged with helium. The containers were then placed in an enclosure at 30°C (Runde, 2000).

Iron mesh was used in some of the STTP tests; this material was a No. 10 steel mesh constructed with 20-gauge wire (0.8 mm). The nominal vendor analysis of the wire is included in Table 2 (Triay, 2000). The wire mesh was analyzed at LANL using Wavelength Dispersive X-ray Fluorescence Spectrometry and Auger Electron Spectroscopy. The wire was identified as a mild steel with a zinc phosphate coating, and a thin film of rust covering about 20% of the surface. The zinc phosphate coating was found to be discontinuous and thin (200 to 2,000 Å). The steel mesh has been identified as a high-carbon steel (Table 2). High-carbon steels are likely to corrode up to twice as fast as the low-carbon steels used for waste drums and boxes in the repository (Brush and Moore, 2000). A 1.25 × 30 inch area of steel mesh was used in the selected liter-scale tests to simulate a surface area with respect to the test volume that is equivalent to the ratio of 4 m^2 of steel surface area per repository waste drum (Triay, 2000). The mesh

was placed in a polypropylene bottle with 1-inch-diameter holes cut in the top and bottom of the plastic lid to allow flow and access of brine to the iron mesh.

Bentonite was added to three pyrochemical salt waste tests (L-31, L-32, and L-33) because it was a proposed backfill material at the time when testing began. Six test containers (L-1, L-2, L-3, L-28, L-29, and L-30) were pressurized to 60 bars (~6 MPa) with carbon dioxide to simulate conditions that could occur in the WIPP repository in the absence of MgO.

Solution samples were obtained from the liter-scale experiments and filtered through 5 μ, 1.2 μ, and 0.01 μ filters before analysis. These samples were removed in a plastic syringe inside an air-filled glove box. The samples remained in the syringes within the glove box for one to two days before filtration and analysis (Mendoza, 2000). The analyses included total alpha activity, pcH, Eh (Figures 1 through 4), metals, anions, total inorganic carbon, total organic carbon, uranium, plutonium, americium, thorium, neptunium, and neodymium. Other analyses that were carried out less frequently included particle size distribution, colloid characterization and microbial analysis. Plutonium was found only on the 5 μ filters, and it appeared to be associated with $SrSO_4$ (Runde, 2000). Head space gases were analyzed periodically for hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide, and nitrous oxide (LANL, 2000b).

Actinide concentrations in the liter-scale test samples were below the concentrations predicted by the ASTM except for test L-3 (Brush, 2000; LANL, 2000a). However, in this test, the predicted and measured plutonium concentrations were very low and near the analytical detection limit (Brush, 2000; LANL, 2000a).

Oxidation states of plutonium were measured in STTP samples using UV/VIS spectroscopy (Runde, 2000). Plutonium oxidation states were measured in STTP samples that had total plutonium concentrations higher than the analytical detection limits, which are approximately 10^{-5} M to 3×10^{-4} M (Runde, 2000). Plutonium(VI) was detected in samples from two of the liter-scale experiments (L-26 and L-28), and plutonium(V) was detected in samples from two other liter-scale experiments (L-27 and L-36) (LANL, 2000b).

Two liter-scale tests (L-31 and L-32) containing pyrochemical salt waste (OS process) and bentonite have been terminated and the contents examined (LANL, 2000b). The pyrochemical salts and bentonite formed a solid that was several inches thick at the bottom of these containers, and the iron mesh was totally enclosed by this solid mass. The iron in these experiments therefore may not have been available to the solution (LANL, 2000b). Three other experiments, L-1 (Portland cement waste and Brine A), L-20 (Envirostone waste and Brine A), and L-21 (Envirostone waste and Castile Brine), were also terminated and the iron mesh was examined (LANL, 2000a; LANL 2000b). The iron mesh in these experiments was coated with magnesio-ferrite, which may have slowed the corrosion process (LANL, 2000a; LANL, 2000b).

3.2.2 Interpretation of Test Results

The STTP tests containing bentonite (L-31, L-32, and L-33) were carried out to simulate the effects of the bentonite backfill that was planned at the time the tests began. MgO was later selected as backfill material in place of bentonite (USDOE, 1996b), so tests containing bentonite are not likely to be representative of anticipated repository conditions.

Tests pressurized with carbon dioxide were performed to simulate the effects of carbon dioxide generated by decomposition of organic wastes in the repository. However, carbon dioxide will be consumed by reaction with MgO backfill, and currently anticipated carbon dioxide partial pressures in the repository are expected to be very low (USDOE, 1996b). The tests pressurized with carbon dioxide therefore are not representative of likely repository conditions. The presence of MgO is also expected to buffer pH values in the repository brines to approximately 8.5. Because MgO was not included in the test matrix, the pH values of some of the tests also are not representative of anticipated repository conditions.

The potential problems associated with measuring redox potentials in complex systems are well understood, e.g., mixed potentials, electrode poisoning, and a number of other possible factors (Lindberg and Runnells, 1984; Mendoza, 2000). However, these data can still provide some indication of the effectiveness of adding iron mesh to control redox conditions in tests with similar materials. For example, plutonium hydroxide solubility experiments conducted using iron metal to control the redox state of the solutions yielded Eh values that ranged from -367 to -252 millivolts in solutions with pH values of

approximately 7 to 9 (Felmy and others, 1989). Similar ranges of Eh values might be expected in the STTP experiments if the iron effectively controls redox conditions.

Eh data for selected liter-scale STTP tests are compared in Figures 1 through 4. Eh measurements as a function of time in STTP experiments using Portland cement and Brine A are compared in Figure 1. Three experimental loadings (with iron, without iron, and with americium salts and no iron) can be compared. The measured Eh values in these experiments generally ranged between 100 and 500 millivolts, which represents somewhat oxidizing conditions. There appears to be no systematic difference between tests that contained iron and tests without iron, and it therefore seems that iron may not have effectively controlled redox conditions in these tests. Figure 2 is a similar comparison for tests carried out with Portland cement and Castile Brine. Although the range of measured Eh values in the Castile Brine experiments is slightly lower than the Eh range observed in the Brine A experiments, there appears to be no significant difference between Eh values measured in Portland Cement/Castile Brine tests with and without iron (Figure 2).

All tests conducted with Envirostone contained iron, so the effects of iron on measured Eh values in these tests cannot be assessed. Some tests were conducted with and without iron using the DOR pyrochemical salts and Brine A (Figure 3) and OS pyrochemical salts and Brine A (Figure 4). The DOR salts tests included experiments with iron, with iron and chelators, and without iron but with chelators (Figure 3). The OS salts tests contained iron and chelators or no iron with added americium salts (Figure 4). The ranges in Eh values are essentially identical to the measured values in the Portland cement tests (approximately 100 to 500 millivolts), and there is no significant difference between tests with and without iron. At the pcH values of these tests (approximately 7.4 to 9.0) these Eh values represent relatively oxidizing conditions, compared to the range of Eh values observed in other tests conducted with plutonium and iron (Felmy and others, 1989).

The absence of significant differences in Eh values between tests conducted with similar waste loadings with and without iron may indicate that iron was ineffective for controlling redox conditions and actinide oxidation states in the STTP experiments. Because the iron mesh in the STTP experiments may have been encapsulated by waste or coated with magnesio-ferrite, iron may not have effectively established reducing conditions in these experiments. This situation differs from conditions expected in the repository, where iron will be present in the container surrounding the waste and where the biodegradation of organics

is also expected to contribute to reducing conditions. However, exposure of the solutions to air during the one to two days between obtaining the samples and Eh measurements (Mendoza, 2000) may have affected measured Eh values. Higher Eh values could have been caused by radiolysis reactions that occurred in the sample or by dissolution of atmospheric oxygen after the samples were removed from the STTP reaction vessel. Thus, the effectiveness of iron for controlling redox conditions in the STTP experiments cannot be assessed using these data.

Uncertainty regarding the identified plutonium(V) and plutonium(VI) oxidation states in samples from L-26, L-27, L-28, and L-36 is related to the one-to-two-day delay between sample removal from the STTP tests and sample filtration and analysis (Mendoza, 2000). During this time when the plutonium-bearing samples were isolated from the iron in the experiments, radiolysis of the samples could have produced oxidizing conditions regardless of the redox conditions in the test (Büppelman and others, 1986). Because plutonium(V) is likely to be a stable oxidation state in solutions exposed to the atmosphere (Rai and others, 1980; Rai, 1984; Orlandini and others, 1986; Choppin, 1990), air oxidation also could have contributed to the formation of plutonium(V) in tests L-27 and L-36.

The four tests with observed plutonium(V) or plutonium(VI) in solution are summarized in Table 3. All four tests contained DOR pyrochemical salts, which contained refractory MgO crucible material (LANL, 2000b). Selected chemical parameters measured in these experiments are summarized in Table 3. The results of these tests are described in the following sections, along with an analysis of the potential causes of the observed plutonium(V) and plutonium(VI) in these tests.

3.2.2.1 Test L-26

Test L-26 contained DOR pyrochemical salt waste, Brine A, and iron mesh (Table 3). In test L-26, plutonium concentrations increased for approximately the first 2 years, then declined during the next two years of testing (LANL, 2000b; Runde, 2000). Other actinides were not present in solution at high concentrations (Runde, 2000). Measured Eh in the solution rose and fell with the total plutonium concentration (Runde, 2000). The pcH in this test declined from an initial value of 8.42 to approximately 7.8 during the first few months of testing, then remained fairly constant for the remainder of the test period (LANL, 2000b; Runde, 2000). Plutonium speciation analysis began in March 1997 and indicated that 80

to 100% of the total plutonium was present as plutonium(VI) (Runde, 2000). Plutonium(VI) was detected in the L-26 test solutions through August 1998, but samples obtained from this test after August 1998 did not show evidence of plutonium(VI). However, the measured total plutonium concentrations in these later samples were close to or below the detection limit for the spectroscopic analysis (Runde, 2000), so it is possible that plutonium(VI) was present in these later samples at concentrations below the detection limit. Total iron concentrations were relatively low during the time period when plutonium(VI) was detected. Because only total iron was measured in the experiments, it is not known if any of this iron was present as reduced (ferrous) iron.

3.2.2.2 Test L-27

Test L-27 contained DOR pyrochemical salt waste, Castile Brine, and iron mesh (Table 3). Total plutonium concentrations in test L-27 reached a maximum concentration within approximately 6 months of the start of this test (October 1995), then declined. The pcH in this experiment remained at relatively high values (10.65 to 11.15) throughout the test. Oxidation state analysis for L-27 samples began in December 1996, after total plutonium concentrations had begun to decline. All oxidation state analyses showed the presence of plutonium(V), except for the last reported analysis in May 1999. Plutonium(VI) was not detected in any of the analyzed L-27 samples (LANL, 2000b; Runde, 2000). Total iron concentrations in the test solution increased and decreased along with the plutonium concentration (LANL, 2000b).

3.2.2.3 Test L-28

Test L-28 contained DOR pyrochemical salt waste, Brine A, and iron mesh and was pressurized with 60 bars of carbon dioxide (Table 3). Total plutonium concentrations in test L-28 increased from approximately 6,000 ppb in August 1995 to approximately 91,000 ppb in December 1996 (LANL, 2000b; Runde, 2000b). The pcH of the samples dropped from an initial value of 5.4 to 4.5 and total iron concentrations increased during this time period (Runde, 2000).

MgO powder was added to Brine A to create a slurry, and the slurry was injected into the depressurized L-28 test container during February 1997. The test container was then repressurized with

carbon dioxide to 60 bars (LANL, 2000b). The MgO addition was difficult to carry out, because the brine slurry became viscous during injection (LANL, 2000b). After MgO was added, the total plutonium concentration measured in March 1997 was lower (18,098 ppb) than the preinjection concentration (90,942 ppb). However, plutonium concentrations increased in May 1997 (41,822 ppb), and increased further to approximately 174,000 to 198,000 ppb between August 1997 and May 1999.

The pcH of the test solution after MgO injection was not recorded until June 1997. The pcH at this time was 7.6, which is higher than the preinjection pcH of 4.5. The pcH declined from June 1997 to the final reported value of 5.1 in May 1999. Thus, injection of MgO appears to have decreased plutonium concentrations and increased pcH in the short term, but these effects did not persist. Total iron concentrations decreased immediately after MgO injection into L-28, but increased to concentrations comparable to those observed before injection after the pcH declined to approximately 5.

The relatively low pcH in Test L-28 after MgO addition indicates that buffering of the solution by $Mg(OH)_2$ and magnesium carbonate phases did not occur. It has been suggested that buffering did not occur because rapid solidification of MgO prevented contact between the MgO hydration products and the solution (LANL, 2000b). Rapid solidification of MgO in the brine slurry injected into test L-28 is cited as evidence that the MgO could have formed such a solid mass in the test vessel (LANL, 2000b).

Plutonium speciation was measured only in the May 1999 and December 1999 samples from L-28. Plutonium(V) was not detected in either sample and plutonium(VI) was detected only in the May 1999 sample (LANL, 2000b; Runde, 2000).

3.2.2.4 Test L-36

Test L-36 was conducted with DOR pyrochemical salt waste, Castile Brine, iron mesh, and added chelators and hydrated lime (Table 3). Initial total plutonium concentrations in this test were approximately 20,000 ppb. Total plutonium concentrations decreased to approximately 3,000 ppb in July 1996. Total plutonium concentrations then began to increase, and fluctuated between approximately 19,000 ppb and 700 ppb. The most recent total plutonium concentration (March 1999) was approximately 1,400 ppb (LANL, 2000b; Runde, 2000). Fluctuations in the pcH were relatively small, and pcH values

were above 11 for most samples (LANL, 2000b, Runde, 2000). Total iron concentrations varied between 24 and 103 ppm during the test (LANL, 2000b).

Plutonium oxidation state measurements began in October 1996. Plutonium (VI) was not detected in any samples from Test L-36 (LANL, 2000b; Runde, 2000). Plutonium(V) was not detected in initial solution samples, but it was detected in samples collected in February 1998 and June 1998. However, plutonium(V) was not detected in the most recent samples collected between August 1998 and March 1999 (LANL, 2000b; Runde, 2000).

3.2.2.5 Possible Causes of Plutonium(V) and Plutonium(VI) in STTP Tests

Higher oxidation states of plutonium are not anticipated in the WIPP repository because of biodegradation of organic materials and oxidation of metals, as these processes consume oxygen and promote a reducing environment. Although iron mesh was included in the experiments in which plutonium(V) and plutonium(VI) were detected, it is possible that the iron mesh was encapsulated in the pyrochemical salt waste or coated with magnesio-ferrite. If either of these conditions occurred in L-26, L-27, L-28, or L-36, the iron may not have been available to react with the solution or the rate of reaction may have been slowed significantly by the magnesio-ferrite coating (LANL, 2000a; LANL, 2000b).

Analysis of head space gases in Tests L-26, L-27, and L-36 indicate the presence of high concentrations of hydrogen and oxygen gas (Table 3). The presence of these gases indicates that brine radiolysis occurred in these tests. If iron was unavailable to react or reacted relatively slowly with the oxidants in solution, oxidants such as peroxide and hypochlorites may have reacted with the plutonium and increased the oxidation states to plutonium(V) and plutonium(VI). Radiolysis in excess of the average amount expected in the repository is likely to have occurred in the tests with pyrochemical salts because of the relatively high plutonium activities in these wastes (LANL, 2000b).

In addition to possible oxidizing conditions in some STTP tests, pcH values lower than anticipated in the repository were observed in L-26 and L-28 (Table 3). These lower pH values were achieved because MgO was absent from the tests, except for the presumably small amount of MgO present from the crucibles in the DOR waste and MgO that was added to L-28 after the test had been conducted for nearly

two years (LANL, 2000b). However, test L-28 was pressurized with carbon dioxide to 60 bar. Because excess MgO will be present in the repository to consume carbon dioxide generated by biodegradation of organics, this carbon dioxide pressure is not representative of repository conditions. The relatively small and transient nature of the effects of adding MgO to L-28 were probably caused by reaction of the MgO with excess carbon dioxide and formation of a solid mass that prevented the complete reaction of MgO (LANL, 2000b).

Finally, there is uncertainty related to the identification of plutonium(V) and plutonium(VI) in the samples from the liter-scale STTP tests. This uncertainty arises because the samples were exposed to air for one to two days before filtration and analysis (Mendoza, 2000). Because radiolytic or air oxidation of plutonium may have occurred prior to sample analysis (Büppelman and others, 1986; Büppelman and others, 1988; Kelm and others, 1999), it is not certain that oxidized plutonium species (V or VI) were actually present in the STTP test solutions.

4.0 PLUTONIUM OXIDE SOLID EXPERIMENTS

Haschke and others (2000) have reported that PuO_{2+x}, (in which x is less than or equal to 0.27) is the stable binary plutonium oxide phase in air. This phase contains a significant amount of plutonium(VI) in addition to plutonium(IV) in its structure. Previous investigations indicated that PuO_2, which contains only plutonium(IV), is the highest stable plutonium oxide. Because plutonium(IV) solids are relatively insoluble, plutonium is generally considered to be relatively immobile under most environmental conditions. Based on the Haschke and others (2000) article, Madic (2000) has stated that the presence of plutonium(VI) in PuO_{2+x} should be considered in safety evaluations of long-term plutonium storage.

The formation of the higher oxide PuO_{2+x} occurs by reaction of PuO_2 with water in moist air or moist oxygen:

$$PuO_2(s) + x\ H_2O(adsorbed) \rightarrow PuO_{2+x}(s) + x\ H_2(g)$$

over the temperature range of 25 to 350°C (Haschke and others, 2000). The progress of this reaction was monitored by evaluating the formation of hydrogen gas. This reaction occurs via a catalytic cycle, in which adsorbed water reacts with the plutonium oxide solid to form PuO_{2+x}, and in the presence of O_2, atomic hydrogen on the solid surface reacts to re-form H_2O. X-ray diffraction (XRD) studies of solids synthesized in this manner show a face-centered cubic fluorite structure, in which the a_0 lattice parameter increases linearly with increasing O:Pu ratios at values in excess of 2.00 (Haschke and others, 2000).

This reaction will be relevant only during the early period of the WIPP repository time period, because this reaction has been reported to occur only in the presence of oxygen. Oxygen is expected to be removed fairly quickly from the WIPP repository by metal corrosion and biodegradation of organic materials (USDOE, 1996b). Thus, formation of PuO_{2+x} in the WIPP repository is likely to be minimal because of the long-term reducing environment predicted for the repository. The WIPP conditions will thus be different than the conditions observed by Haschke and others (2000).

5.0 APPLICABILITY OF THE LITER-SCALE STTP AND PLUTONIUM SOLID EXPERIMENTAL RESULTS TO WIPP CONDITIONS

The liter-scale STTP experiments and the plutonium oxide solid experiments reported by Haschke and others (2000) are not representative of the long-term WIPP repository environment. The differences between these experiments and anticipated WIPP repository conditions are summarized in the following sections.

5.1 STTP Experiments

The liter-scale STTP experiments do not adequately simulate the WIPP repository environment because of the lack of MgO in the tests. The presence of carbonate solution species and low pH values can increase plutonium solution concentrations. Because MgO is expected to remove carbon dioxide and buffer pH, the results of these experiments are unlikely to be directly applicable to general repository conditions.

The pcH values measured in test L-26 samples were less than 8 during the time period when higher plutonium concentrations were observed. Because the $Mg(OH)_2$ - $MgCO_3$ buffer is expected to maintain pcH within the range of 8.5 to 10 in the WIPP repository, the conditions of test L-26 are not applicable to the repository environment.

The addition of MgO to test L-28 resulted in a transient decrease in total plutonium concentrations and higher pH, but did not cause higher pH values and lower plutonium concentrations over long-term testing conditions. The high carbon dioxide partial pressure in test L-28 and addition of MgO in the form of a brine slurry may have resulted in the formation of a solid mass of MgO with limited available surface area for reaction. Also, the high carbon dioxide partial pressure in this experiment is very different from anticipated WIPP repository conditions. Therefore the results of this test are not applicable to WIPP.

Other differences between the liter-scale tests and the repository environment include possible encapsulation of iron mesh in the experiments by the pyrochemical waste. If the iron was encapsulated in the experiments, it would be unavailable for reaction with oxidants such as hypochlorites and peroxides that could be produced by radiolysis. In this case, the oxidants could produce oxidized plutonium(V) and

plutonium(VI) species in solution. Because iron in the containers will surround the waste in the repository, encapsulation of the containers by waste is not a likely scenario.

The possible formation of magnesio-ferrite on metal surfaces, which was observed in tests L-1, L-20, and L-21, cannot be ruled out. If magnesio-ferrite forms on metal surfaces in the repository, metal corrosion and removal of oxygen from the repository through this mechanism may be slowed. However, the biodegradation of organic materials in the repository is another mechanism for establishing reducing conditions in the repository, so the assumption of long-term reducing conditions in the repository is still valid.

Corrosion testing in WIPP brines has been carried out at moderate pH values with Salado brine, which is a relatively high magnesium brine, and at higher pH values with Castile brine, which has a relatively low magnesium concentration (Telander and Westerman, 1997; Felmy and others, 2000). Relatively limited information has been developed regarding the corrosion of low-carbon steel in conditions currently expected in the WIPP repository because of the use of MgO backfill, including high pH and high magnesium concentrations.

The consistency between laboratory and natural-analogue-based corrosion rates of iron-bearing materials suggests that the apparently oxidizing conditions observed in some STTP experiments cannot be attributed to a fundamental misunderstanding of basic mechanisms and rates controlling iron corrosion. That is, there is no evidence from the natural analogue studies to suggest that the corrosion rate of iron will be significantly less than the experimentally predicted rate. Thus, the available information indicates that iron corrosion will occur at a low rate at the expected repository pH values, and this iron corrosion will contribute to a long-term reducing environment in the WIPP repository. Most of the natural analogues in Table 1 were obtained from non-brine environments. Plans to evaluate iron corrosion in brines through natural analogue studies (L. Brush, personal communication) therefore may provide meaningful additional data.

Pyrochemical salt waste is expected to make up less than 0.5% of the waste inventory in the WIPP repository (LANL, 2000a). The pyrochemical waste used in the tests that contained plutonium(V) and plutonium(VI) had relatively high plutonium activity. Therefore, these wastes are likely to initially release higher plutonium concentrations and to cause greater amounts of brine radiolysis than the majority of the

wastes in the WIPP repository (LANL, 2000b). The production of plutonium(V) and plutonium(VI) in localized areas of the WIPP may similarly occur as a consequence of waste heterogeneity. However, as equilibrium is achieved in the repository, it is likely that any oxidized plutonium species produced in such localized areas will be reduced to less-mobile plutonium(III) and plutonium(IV) species.

Because the solution samples removed from the STTP experiments may have been exposed to air for one to two days before sample analysis was carried out, it is possible that radiolysis or air oxidation reactions could have affected solution Eh values and plutonium oxidation states. Due to the potential exposure to air, the existing STTP data cannot be used to evaluate plutonium oxidation states in solution or probable redox conditions in the repository. In addition, because redox conditions in the samples could have changed during the time period before they were analyzed, it is possible that particulate plutonium could have dissolved during these sample holding times. Thus, the available data is likely to be reliable only for total plutonium concentrations, and not for dissolved concentrations as determined by filtration.

5.2 Applicability of Plutonium Oxide Solid Experiments

The plutonium oxide solid experiments that produced PuO_{2+x} were conducted in moist air or moist oxygen (Haschke and others, 2000). Because oxygen is necessary for the autocatalytic reaction that forms PuO_{2+x}, this solid is not expected to be important in the long-term, reducing repository environment.

6.0 CONCLUSIONS

The following is a summary of the potential issues arising from the observation of plutonium(V) and plutonium(VI) oxidation states in the STTP experiments (LANL, 2000a and 2000b) and the formation of PuO_{2+x}.

6.1 STTP Test Results and the Presence of Plutonium(V) and Plutonium(VI) in the Repository

Potential issue: The formation of plutonium(V) and plutonium(VI) in the STTP experiments indicates that these plutonium oxidation states will persist in the repository and lead to increased mobility of plutonium.

Response: There are important differences between the STTP experiments and the WIPP repository environment. These differences include evidence that the tests were probably not at equilibrium, the possibility that iron was encapsulated and could not influence the redox state of the experimental solution, the absence of MgO, and the high plutonium concentrations in the pyrochemical salt waste. In addition, it is possible that the plutonium(V) and plutonium(VI) that was observed in a few experiments may have formed after samples were removed from the experiments, but before analysis was carried out because of the one-to-two-day sample holding times.

The conceptual model developed to describe the actinide source term is based on conditions of chemical equilibrium (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b). Under equilibrium conditions in the repository, redox conditions will be controlled by reaction of brine with iron in the waste drums, and will also be influenced by the reducing effects of microbial degradation of organic materials in the waste (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). The net result of the iron corrosion and biodegradation processes will be to produce a reducing environment in the repository (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). Because of this reducing environment, the source term conceptual model predicts that only plutonium(III) and plutonium(IV) will be present at equilibrium in the repository (USDOE, 1996b, USEPA, 1998a; USEPA, 1998b). The STTP experiments with measurable plutonium(V) and plutonium(VI) concentrations in solution were probably not at equilibrium because of the complex nature of the materials used in the tests, the relatively short duration of the tests, and the transient appearance of plutonium(V) and plutonium(VI) in the tests.

Examination of reaction products from two pyrochemical salt tests indicated that the solids formed a mass encapsulating the iron mesh, and this effect may have prevented interaction between the iron and solution (LANL, 2000b). A similar effect probably will not occur in the repository, where iron in the containers will surround the waste. Thus, although iron may not have influenced redox conditions in the STTP tests because of its encapsulation by waste, this type of encapsulation probably will not occur in the repository.

MgO backfill was not included in the repository design when the STTP experiments were started. Consequently, the experiments did not contain MgO, which is expected to react with water to form $Mg(OH)_2$ and to react with carbon dioxide formed by microbial degradation of organics to form magnesium carbonate phases such as hydromagnesite. The presence of MgO is expected to maintain low carbon dioxide partial pressures and to buffer pH values between 8.5 and 10 (USDOE, 1996b). Thus, the presence of 60 bars of carbon dioxide and low pH values in test L-28 are inconsistent with repository conditions. MgO was later added to this test, but the high sustained carbon dioxide pressure and the addition of MgO as a brine slurry may have caused the MgO to form a solid mass that had limited ability to react with the solution in the test.

The pyrochemical salt waste used in the experiments that contained plutonium(V) and plutonium(VI) in solution had relatively high plutonium concentrations (LANL, 2000b). These high plutonium concentrations likely caused radiolysis that produced peroxide and hypochlorites as well as hydrogen (H_2) in solution (LANL, 2000b). Peroxide and hypochlorites typically react quickly, whereas hydrogen reacts more slowly. In the repository, these peroxide and hypochlorite species are expected to rapidly react with iron in the waste containers. However, because iron may not have been available in the STTP tests to react with the peroxide and hypochlorite, the oxidizing species were able to react with plutonium and formed oxidized plutonium species. Thus, brine radiolysis in the absence of iron may have occurred in the tests, but this process is not expected to occur in the repository.

The transient formation of plutonium(V) and plutonium(VI) in the WIPP repository was considered in the development of the conceptual model of the actinide source term (USDOE, 1996b, USEPA, 1998a; 1998b). However, because of reducing conditions in the repository, plutonium(V) or plutonium(VI) that forms in the repository will be reduced to plutonium(III) or plutonium(IV) as the system approaches equilibrium. Conditions in the STTP experiments were oxidizing, based on the Eh and gas head space data provided (LANL, 2000b; Mendoza, 2000; Runde, 2000). In addition, because MgO was not present in the STTP experiments, pH and carbon dioxide partial pressures also differed in the STTP experiments from conditions predicted for the repository. Finally, the period of time between removal of samples from the STTP experiments and their filtration and analysis could have affected the results of the oxidation state analyses. Therefore, the STTP experimental data do not accurately represent long-term, equilibrium repository conditions and observation of plutonium(V) and plutonium(VI) in these experiments does not contradict the source term conceptual model (USDOE, 1996b).

6.2 Reducing Conditions in Repository

Potential issue: The formation of magnesio-ferrite on the surfaces of the steel mesh in the STTP experiments indicates that iron corrosion may not create reducing conditions in the repository.

Response: The available iron corrosion data obtained with WIPP brines (Telander and Westerman, 1997; Felmy and others, 2000) indicate that coatings may form on iron during corrosion. However, the coatings in these studies were not found to be adherent. Available corrosion data at the pH values relevant to the WIPP repository indicate that corrosion will occur, although higher pH values can slow the corrosion rate (Telander and Westerman, 1997). Available natural analogue data for iron corrosion are similar to the assumed corrosion rates in the WIPP CCA PA. Thus, iron corrosion is expected to occur in the repository and generate reducing conditions. In addition to iron corrosion, biodegradation of organic materials in the repository (cellulosics, plastics, and rubber) will consume oxygen and contribute to a long-term reducing environment.

6.3 Formation of PuO_{2+x} in the Repository

Potential issue: The formation of PuO_{2+x} in the repository rather than PuO_2 will cause higher plutonium solubilities than predicted by the source term model.

Response: The experimental data on PuO_{2+x} formation presented by Haschke and others (2000) indicates that PuO_{2+x} will form only in the presence of oxygen. Because the long-term repository environment will be anoxic, PuO_{2+x} will not form under long-term conditions. Thus, the formation of PuO_{2+x} is not expected to affect equilibrium plutonium solubilities predicted by the source term model.

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TABLES

Table 1

Iron Corrosion Rates

Artifact	Reference	Age (yr)	Corrosion Depth (mm)	Corrosion Rate (μm/yr)	Environment
Various (44 artifacts)	Johnson and Francis (1980)	--	--	0.0025 - 10*	Wet to arid, oxidizing to reducing
Various (2 artifacts)	Johnson and Francis (1980)	--	--	2 - 430	Seawater
Iron Nails	Miller et al. (1994)	1,870	0.1 - 14.2	0.05 - 7.6	Moist
Jewelry	Miller and van der Merwe (1994)	1,330	0.5 - 0.7	0.4	Arid
Iron Chisel	Miller and van der Merwe (1994)	1,330	0.2 - 0.6	0.15 - 0.45	Arid
Iron Blade	Scott (1991)	1,000	1 - 4	1 - 4	Tropical
Iron Knife	Scott (1991)	850	6.4 - 15.9	7.5 - 18.7	--
Gas Pipe	Sasaki et al. (1992)	50	0.5 - 0.4	0.01 - 0.08	Carbon steel in gravel
Water Pipe	Sasaki et al. (1992)	110	3.3 - 5.5	0.03 - 0.05	Carbon steel in clay
Iron Support	Dresselaers et al. (1982)	60	0.3 - 0.9	5 - 15	Coal mine
Iron Support	Dresselaers et al. (1982)	90	0.4 - 1.1	3.9 - 11.7	Coal mine
WIPP CCA PA	USDOE (1996b)	--	--	0.005 - 6.5	WIPP disposal rooms
Low-Carbon Steel	Telander and Westerman (1997)	--	--	1.5 - 5.6	ERDA-6 brine, pH 8.6 to 10.6

Table 2

Vendor Analysis of Steel Used in STTP Experiments

Element	Percent
Iron	98.453
Carbon	0.679
Manganese	0.620
Silicon	0.230
Phosphorus	0.012
Sulfur	0.006

Table 3

Liter-Scale Tests with Measured Plutonium(V) or Plutonium(VI) Concentrations
All Tests Contained Pyrochemical Salt (Direct Oxide Reduction) Waste and Iron Mesh

Test Container	Brine Type	Chelators and $Ca(OH)_2$ added	Pressurized with CO_2	Plutonium(V) or Plutonium(VI)	pcH Range	Total Plutonium Range (ppb)	Last Reported Plutonium (ppb)	Total Iron Range (ppm)	Head Space H_2 (volume %)	Head Space O_2 (volume %)	Head Space N_2 (volume %)
L-26	Brine A (Salado)	No	No	VI	6.78 to 8.42	17 to 70,826	4,141	< 0.1 to 29	73	5.4	0.6
L-27	Castile	No	No	V	10.65 to 11.18	19,717 to 243,438	29,683	43 to 243	65	4.8	5.0
L-28	Brine A (Salado)	No	Yes	VI	4.5 to 7.6	5,989 to 197,984	188,463	1 to 165	high pressure test	high pressure test	high pressure test
L-36	Castile	Yes	No	V	10.58 to 11.44	700 to 19,963	1,439	24 to 103	70	15	0.2

FIGURES

Figure 1. Portland Cement and Brine A

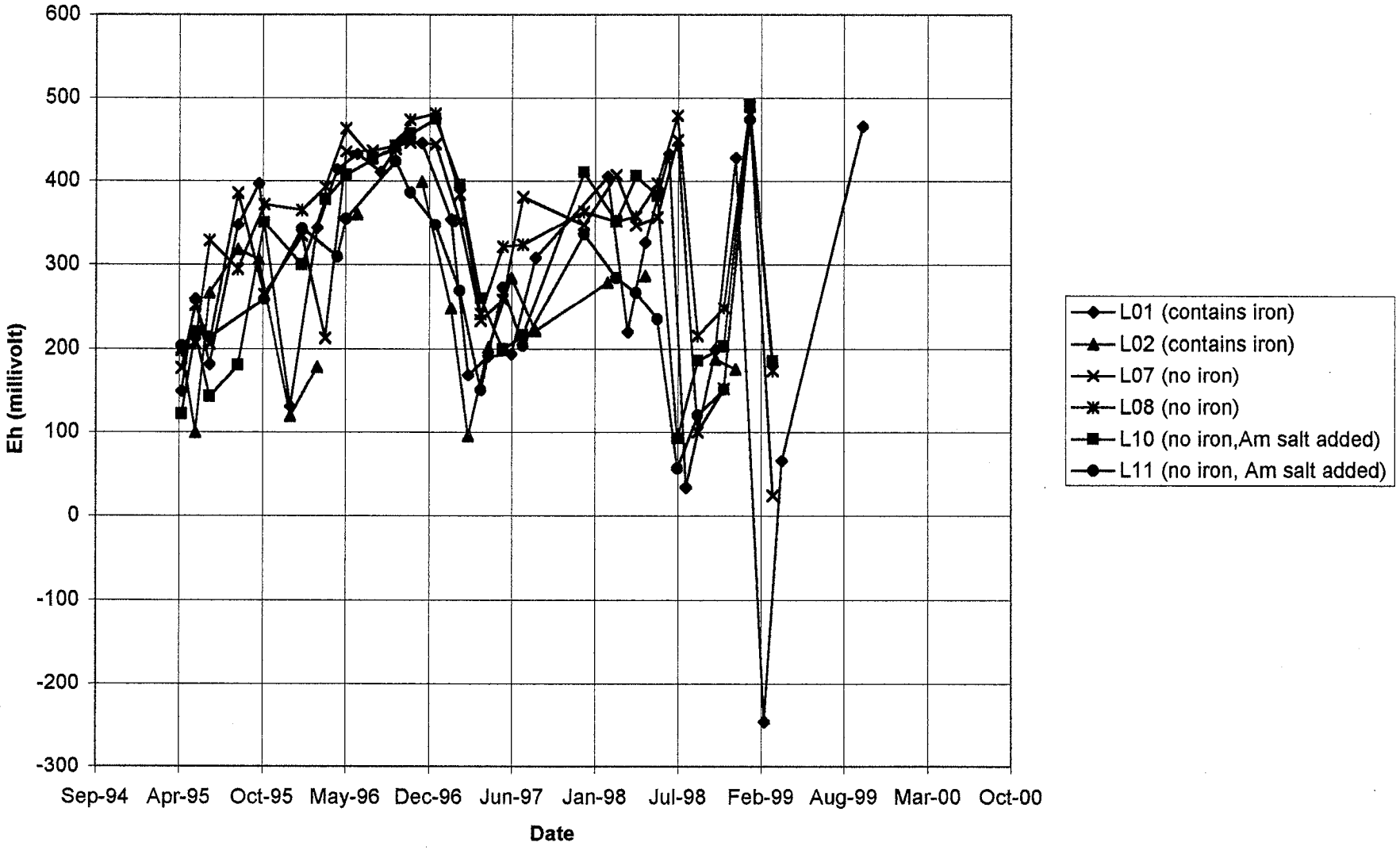


Figure 2. Portland Cement and Castile Brine

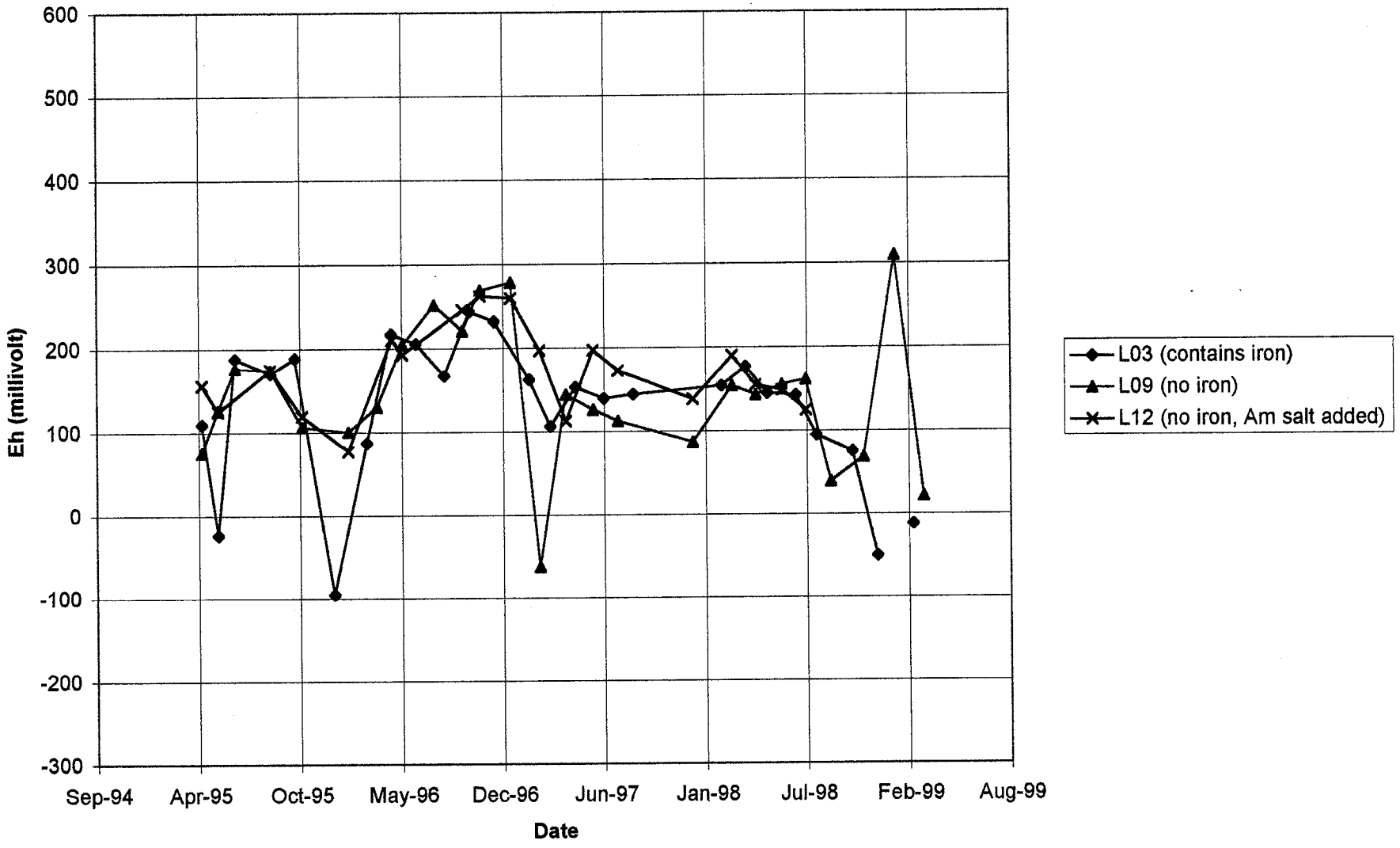


Figure 3. Pyrochemical Salts (DOR) and Brine A

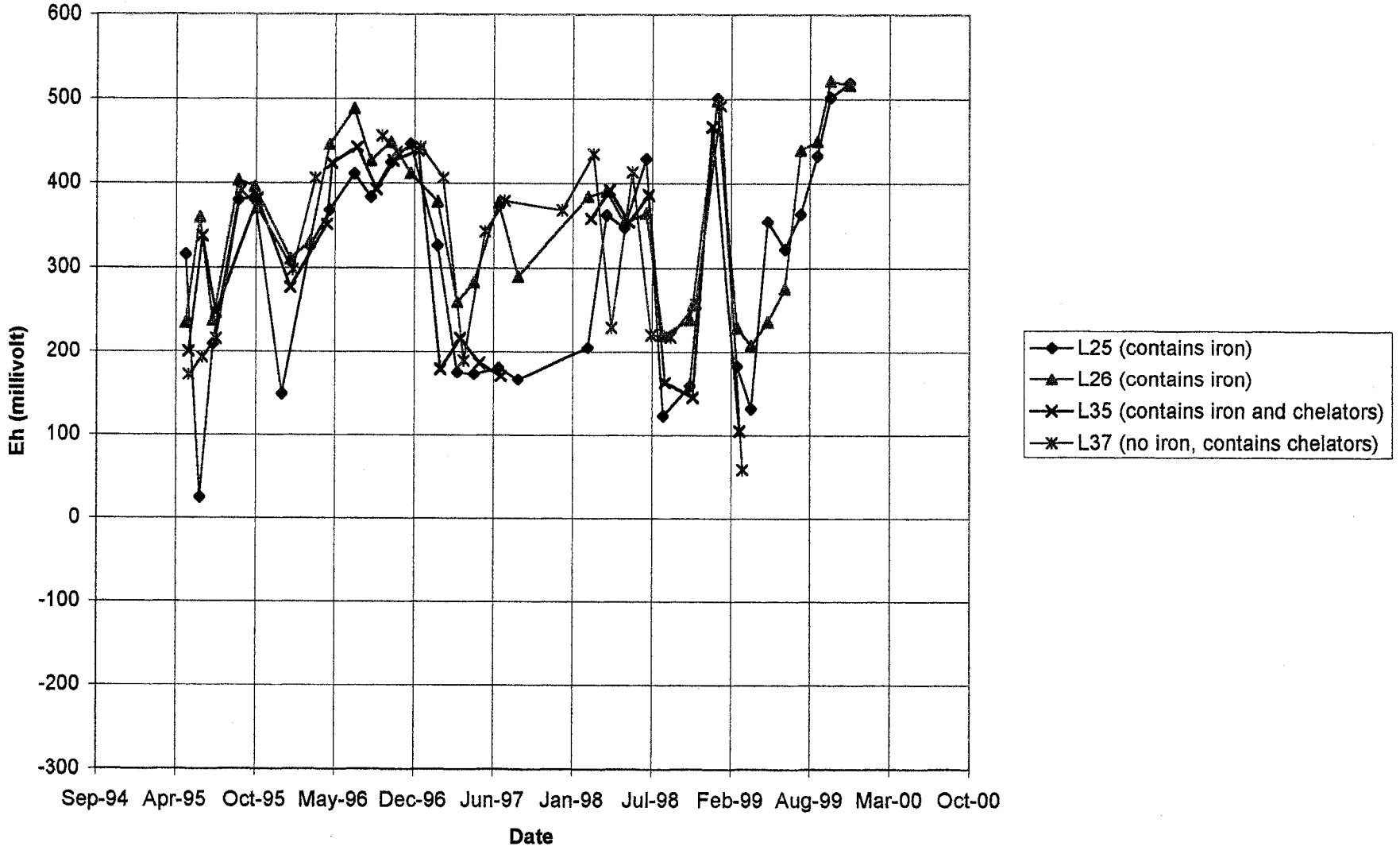
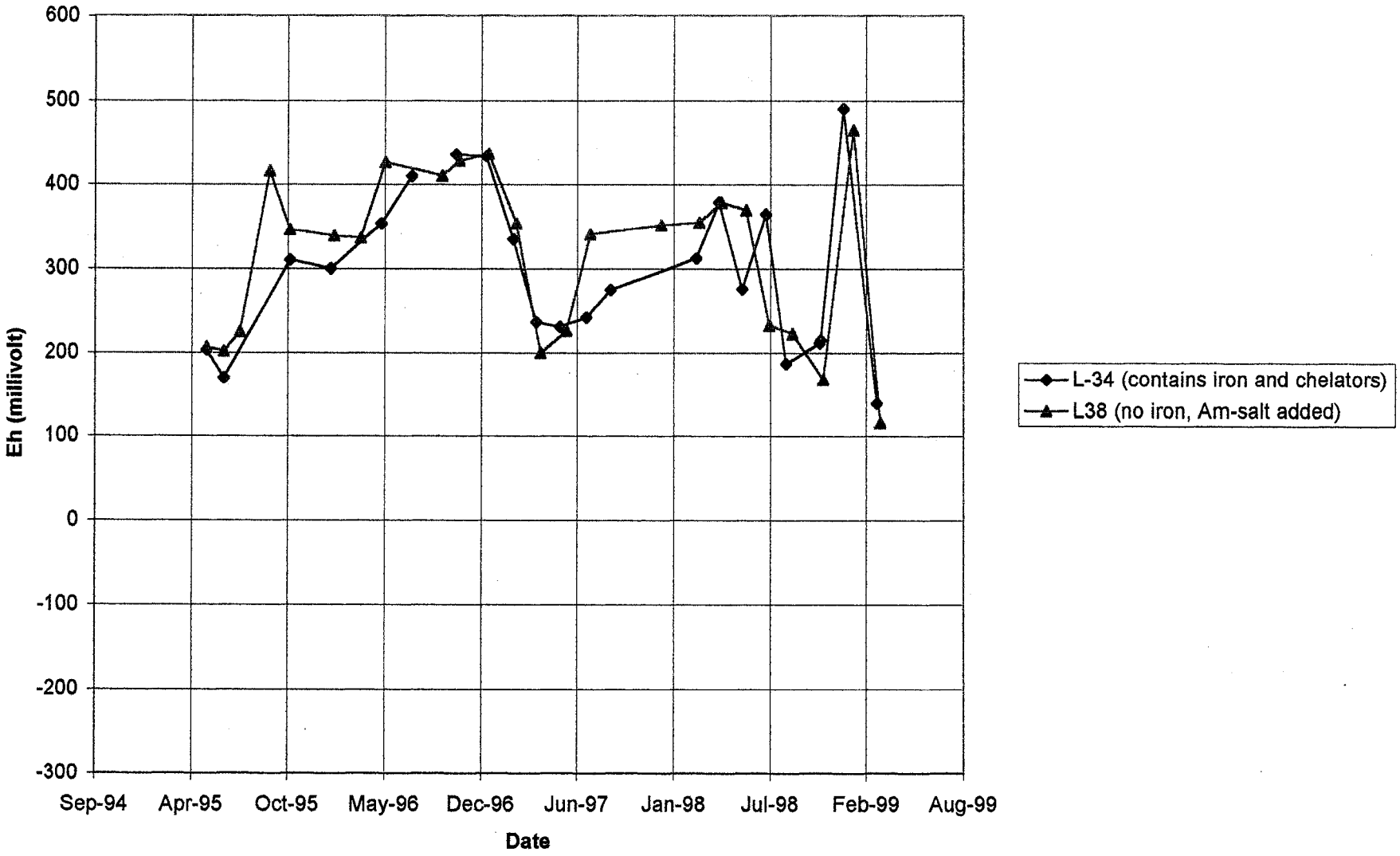


Figure 4. Pyrochemical Salts (OS) and Brine A



Enclosure 7

EPA Report:
Implications Regarding the Efficacy of MgO Backfill Based on Preliminary Results of STTP Liter-Scale Experiment L-28
September 2000

IMPLICATIONS REGARDING THE EFFICACY OF MgO BACKFILL BASED ON PRELIMINARY RESULTS OF STTP LITER-SCALE EXPERIMENT L-28

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September 4, 2000

Implications Regarding the Efficacy of MgO Backfill Based on Preliminary Results of STTP Liter-Scale Experiment L-28

1. Introduction

Experiments initiated in 1995 by Los Alamos National Laboratory (LANL) as part of the Actinide Source-Term Waste Test Program (STTP) are intended to support the Actinide Source-Term Model (ASTM) used in the Waste Isolation Pilot Plant (WIPP) Compliance Certification Application (CCA). The STTP comprises a series of long-term experiments wherein actual contact-handled transuranic (CH-TRU) wastes are immersed in brines representing solutions present in the Salado or Castile Formations at the WIPP site. The primary objective of the experiments is to confirm that actinide concentrations measured in brines equilibrated with real waste are, conservatively, lower than predicted by the ASTM. Preliminary results (based on available documentation referenced below) appear to confirm that the ASTM predictions are generally conservative (as noted below, however, the experimental methodology used in the STTP raises questions about the utility of these results). Actinides were dissolved at concentrations well below the predictions in all but two experiments, where the concentrations were slightly greater, or equal to, predicted values.

A collateral result of the STTP may warrant additional consideration, however. MgO apparently did not function as expected. That is, addition of MgO to one pressurized liter-scale experiment (Experiment L-28) failed to buffer pcH within the expected range of moderately alkaline values.

Our review of this issue found the results of Experiment L-28 to be suspect and unrepresentative of the WIPP waste environment. Our evaluation of these results, and associated interpretations and performance implications, are documented in the present report. Expected reactions involving MgO and WIPP brines are summarized in Section 2. The design and operation of Experiment L-28, and interpretations of experimental results proposed by LANL researchers, are summarized in Section 3. The basis for our conclusion that the results do not raise concerns about the efficacy of MgO backfill at WIPP is summarized in Section 4.

It should be emphasized before proceeding that documentation relating to the STTP experiments is presently incomplete because most of the experiments are currently in a state of safe standby (*i.e.*, they are ongoing but sampling and analysis work has been curtailed). DOE documentation considered in the present report consists of:

- A letter and attachments from I. Triay (DOE/CAO) to F. Marcinowski (EPA/ORIA), dated 02/10/2000,

- A draft report titled "The observation of plutonium in the +VI oxidation state in the actinide source term test program experiments," dated 03/23/2000, and
- Minutes of a joint EPA/DOE technical exchange held in Washington, DC on April 12 and 13, 2000.

These sources of information are referred to below as the EPA 2/10/00 Letter, DOE 3/23/00 Report, and EPA 4/00 Minutes, respectively.

2 Summary of Expected Reactions Involving MgO and WIPP Brines

Previous analyses of the pH buffering properties of MgO are summarized in EPA (1998). Briefly, the initial reaction that is expected to occur on contact of MgO backfill with brine is the hydration of MgO to form brucite [$Mg(OH)_2$]:

$$MgO(s) + H_2O = Mg(OH)_2. \quad (1)$$

Carbon dioxide produced by microbial degradation of organic materials will then react with brucite to form one or more Mg-carbonate phases. Magnesite [$MgCO_3(s)$] is the most stable among these phases at relatively low temperatures and pressures expected in the WIPP repository. Based on thermodynamic considerations alone, magnesite should form from brucite via reactions such as:

$$Mg(OH)_2(s) + CO_2(g) = MgCO_3(s) + H_2O. \quad (2)$$

Magnesite formation is kinetically inhibited at low-temperatures, however, due to the high energy of hydrolysis of the Mg^{2+} ion, which makes it difficult to separate the waters of hydration from the ion during solid formation (*e.g.*, Doner and Lynn, 1977; Lippmann, 1973; Morse and Mackenzie, 1990). Rather, Mg^{2+} carbonation will initially result in formation of metastable hydrated carbonate phases, such as hydromagnesite, by reactions such as

$$5Mg(OH)_2(s) + 4CO_2(g) = Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O(s), \quad (3)$$

and

$$4Mg(OH)_2(s) + 3CO_2(g) = Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O(s) \quad (4)$$

[these two structural formulas for hydromagnesite are reported by Novak (1997)]. Another possible reaction involves formation of nesquehonite [$MgCO_3 \cdot 3H_2O(s)$] from brucite:

$$Mg(OH)_2(s) + CO_2(g) + 2H_2O = MgCO_3 \cdot 3H_2O(s). \quad (5)$$

Nesquehonite is metastable, however, with respect to both magnesite and hydromagnesite. It will convert to hydromagnesite by reactions such as:

$$MgCO_3 \cdot 3H_2O(s) + 3CO_2(g) + 4Mg(OH)_2(s) = Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O(s) + 2H_2O. \quad (6)$$

Hydromagnesite will then dehydrate to form magnesite, e.g.,

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O(s) + CO_2(g) = 5MgCO_3(s) + 5H_2O. \quad (7)$$

The rates of the above reactions have been approximated (EPA, 1998) using the results of limited laboratory studies (Davies and Bubela, 1973; Sayles and Fyfe, 1973; Usdowski, 1994; Davies et al., 1977; SNL, 1997) and field observations of diagenetic sequences of Mg-carbonates in relatively young geologic systems (Irion and Mueller, 1968; Marschner, 1969; Fischbeck and Muller, 1971; Renaut and Long, 1989; Stamatakis, 1995). Based on these studies and observations, the time-sequence of events resulting from brine infiltration and reaction with MgO backfill in the WIPP repository is envisaged to involve the following steps (EPA, 1998):

- Rapid reaction (hours to days) between brine and MgO to produce brucite,
- Rapid carbonation (hours to days) of the brucite to produce nesquehonite and, possibly, hydromagnesite,
- Rapid conversion (days to weeks) of the nesquehonite to hydromagnesite, and
- Slow conversion (hundreds to thousands of years) of the hydromagnesite to magnesite.

There is considerable uncertainty, however, regarding both the nature of the reactions involved in this sequence and the rates at which they occur. For example, although hydromagnesite, and to a lesser extent nesquehonite, are the most commonly observed metastable phases observed in natural and experimental systems, a number of other metastable magnesium carbonates may also exist (*i.e.*, artinite, lansfordite, protohydromagnesite, barringtonite and dypingite). Several of these phases (including protohydromagnesite and dypingite) are implicated as intermediate phases formed as nesquehonite dehydrates to hydromagnesite (SNL, 1997). Thermodynamic data that can be used to define stability/ metastability relations among magnesite, hydromagnesite and nesquehonite are uncertain. For example, published solubility-product constants at 25°C and 1 bar for magnesite (Langmuir, 1965; Christ and Hostetler, 1970, SNL, 1997) and hydromagnesite (Langmuir, 1965; SNL, 1997) vary by more than 5 orders of magnitude. It should also be noted that the above estimated rate of magnesite formation at WIPP-relevant temperatures is extrapolated from an

Arhhenius plot constrained by only three data points at relatively high temperatures [126°C (Sayles and Fyfe, 1973); 60°C and 180°C (Usdowski, 1989, 1994)]. Associated uncertainties are exemplified by the presence of hydromagnesite in late Quaternary (< 27.3 million years) evaporite basins (Stamatakis, 1995), suggesting that hydromagnesite may persist for periods of time greatly exceeding the times estimated in the above sequence of events.

Consistent with the uncertainties noted above, the Environmental Evaluation Group (EEG) of the State of New Mexico has questioned whether the reaction between brine and MgO to produce brucite actually occurs within hours to days[1]. The basis for this question comes from experiments carried out by Sandia National Laboratories (results, cited by EEG, were presented by J. Krumhansl at the ICEM'99 Conference in Nagoya, Japan), in which the presence of brucite was apparently not detected after reaction of MgO with Salado and Castile Formation brines for as long as 443 days. This question may be premature, however. For example, minerals occurring in trace amounts may escape detection by standard analytical methods [e.g., X-ray Diffraction (XRD) or Scanning Electron Microscopy (SEM)]. The failure to detect brucite may therefore mean either that it did not form, or, alternatively, that it was present in such small amounts that it could not be detected. The basis for the question posed by EEG is also directly contradicted by the results of similar experiments involving reaction of MgO pellets with Salado and Castile brines at 30°C for < 60 days, which indicate that brucite is in fact present as a thin layer separating an inner surface of unreacted MgO from outer layers of nesqeuhonite (SNL, 1997; Fig. 4-6, plate C). It is interesting to speculate that such "sandwiching" of small amounts of brucite between MgO and Mg-carbonate phases could complicate efforts to detect brucite by XRD or SEM.

Despite the uncertainty in the nature and rates of reactions involving MgO and carbonated brine, the preponderance of available experimental and field evidence suggests it is reasonable to assume that MgO will hydrate to $Mg(OH)_2$ and that $Mg(OH)_2$ will partially dissolve to form one or more Mg-carbonates. Such reactions will sequester carbonate within the crystalline lattice of the mineral(s) and will tend to buffer the pH of the coexisting solution. This can be seen more clearly by considering a reaction similar to Reaction (3), for example, but written in terms of H^+ and HCO_3^- rather than $CO_2(g)$:

$$5Mg(OH)_2 + 4HCO_3^- + 4H^+ = Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O + 4H_2O \qquad (8)$$

Formation of hydromagnesite from brucite should thus consume HCO_3^- and cause the pH to rise. Addition of MgO to liter-scale Experiment L-28 was apparently attempted to confirm this line of reasoning.

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[1] Letter dated 3/22/00 from R. H. Neill (EEG) to I. Triay (DOE/CAO), Attachment 4.

3 Liter-Scale Experiment L-28

The primary objective of Experiment L-28 was to determine the concentrations of Nd, Am, Th, Np, U and Pu dissolved in "Brine A" (representing brine from the Salado Formation) in contact with Direct Oxide Reduction (DOR) pyrochemical-salt wastes. The experimental system was pressurized to 60 bar with $CO_2(g)$ to simulate conditions originally expected in disposal rooms at WIPP. It was believed by the researchers at the time the experiment was designed that such high partial pressures of $CO_2(g)$ could be generated by microbial degradation of organic matter. MgO was added to Experiment L-28 after it was decided to use MgO as a backfill material at WIPP. The objective of adding MgO to this experiment was to determine whether this mineral would react as expected with carbonate species dissolved in Brine A to produce various Mg-carbonate phases, thereby buffering the pcH to relatively alkaline values.

3.1 Experimental Design and Operation

Aspects of the design and operation of Experiment L-28 that are pertinent to subsequent discussions are summarized below. Additional information on the design and operational procedures used in all the STTP experiments is described in the DOE 3/23/00 Report and the EPA 4/00 Minutes.

A chronology of the initial loading, operation and current status of Experiment L-28 is as follows.

- A total of 907 grams of waste in the form of comminuted MgO crucibles containing DOR pyrochemical salts was added to a 2-liter all titanium container. It was expected that the wastes would be high in NaCl, KCl, $CaCl_2$, MgO, MgCl, fluorides and some unreacted calcium metal and CaO. The waste included 10.46 grams ^{239}Pu (648 mCi) and 1.2 grams ^{241}Am (4.2 mCi). Soluble salts of Th, U and Np (55 gm each), and of Nd (30 mg) were also added to the container. Fifty-five grams of Fe mesh enclosed within a flow-through plastic tube was added to the container to establish and maintain reducing conditions expected in the repository

- Brine A and an anaerobic brine inoculum were added to the test container. The inoculum was obtained from brine obtained at or near the WIPP site. The inoculum contained organic colloids and microorganisms.

- The container was topped off with brine to leave a headspace volume of 150 cm^3.

- The test container was then loaded onto an agitation device that rotated the container through a 360-degree rotation once a week for 15 minutes.

- The test container was pressurized with carbon dioxide to 60 bar at 30°C. This pressure and temperature were maintained throughout the duration of the experiment, except at the time MgO was added (see below).

- The first sample of brine was extracted under pressure in August, 1995. It is not clear when this sampling event occurred in relation to the initial pressurization event. Details regarding the sampling procedure are also unclear.

- Sample preparation and analysis procedures included a filtration step through 5 μm, 1 μm and < 20 nm filters. Solids collected on the filters were analyzed to determine mineralogy and composition, and to characterize colloids. The leachate was analyzed for pcH, Eh, total concentrations of actinides, other elements, RCRA metals, carbonate (TIC), TOC and chelators [the primary references noted above (Section 1) report results only for Nd, Th, Np, U, Pu, Am and Fe (total)]. Although the compositions of headspace gases were routinely analyzed in other liter-scale experiments, including pressurized experiments L-37, L-38 and L-39, these gases were apparently not assayed in experiments L-28, L-29 and L-30.

- In February 1997, a slurry was prepared by mixing 76.4 grams of MgO (Enviromag 98) with 175 ml of Brine A. Experiment L-28 was depressurized and the slurry was then added to the test container. It was observed (DOE 3/23/00 Report) that addition of MgO in this form was difficult because suspended solids formed immediately on mixing and became more pronounced with time. It has also been noted that "the slurry had to be injected very rapidly after mixing or it would become too viscous to inject into the test container through the small-bore tubing used to inject the slurry" (DOE 3/23/00 Report). Once the slurry was successfully injected, the container was re-pressurized to 60 bar with CO_2(g). A sample of brine was apparently taken immediately before re-pressurization (*i.e.*, on 2/27/97; EPA 4/00 Minutes).

- Sampling continued periodically up to 5/17/99. The CO_2(g) pressure was continuously monitored and sustained at 60 bar during this time (EPA 4/00 Minutes). The experiment is currently in a state of safe standby. Plans to terminate the experiment, carry out deactivation and decommissioning operations, characterize material within the container and prepare a final report are unclear.

3.2 Experimental Results

Key results of Experiment L-28 that have a bearing on the efficacy of MgO to sequester CO_2 and to buffer pH are summarized below.

- Addition of MgO to the experimental system initially generated a transient increase in pcH, but pcH values later fell to levels observed prior to MgO addition. Results are shown in Fig. 1 [DOE 3/23/00 Report][2]. As can be seen, pcH increased from 4.5 to 7.7 shortly after addition of MgO to the container, but after a few months pcH decreased to values in the range 5.5 to 5.

---

[2] It should be noted that data presented in the EPA 4/00 Minutes contradict several results shown in Fig.1. The maximum pcH shown in the figure is 7.6, measured in a sample collected on 6/2/97. The EPA 4/00 Minutes indicate a maximum pcH of 7.7, however, based on measurements made on 2/27/97 (the date when MgO was first added to the container). Also, the EPA 4/00 Minutes indicate that a pcH value of 7.1 was measured in a sample collected on 6/2/97, but this sample is not represented in Fig. 1.

- Although total dissolved inorganic carbon was measured in samples from L-28, these data are not reported. These data are important because the researchers could use this information to evaluate whether measured pcH values are controlled by the externally fixed CO_2 partial pressure, in accordance with Henry's law.

- Mineralogical and compositional analyses of suspended solids collected during fluid sampling on the 5 μm, 1 μm and < 20 nm filters indicated that $SrSO_4$ was the only mineral retained by the filters. This suggests that any Mg-carbonates formed by reaction with MgO were not suspended in the brine. If so, the carbonate phases may have precipitated on the surfaces of MgO pellets, as observed in crystal growth experiments involving MgO and Salado and Castile brines (SNL, 1997).

- The interpretation of results from L-28 is based in part on observations resulting from a Deactivation and Decommissioning (D&D) procedure applied to two similar experiments, L-31 and L-32 (EPA 2/10/00 Letter, DOE 3/23/00 Report, and EPA 4/00 Minutes). Experiments L-31 and L-32 contained pyrochemical salts, Fe mesh and Brine A. These experiments differ in four important respects compared to Experiment L-28, however: 1) they were not pressurized with CO_2(g), 2) they contained pyrochemical wastes generated by Oxygen- Sparging (OS) of electrorefined Pu metal and salts rather than by DOR from Pu oxide to Pu metal, 3) they contained bentonite, and 4) MgO was not added to these experiments. The observations from the D&D operation that have been used by researchers to help interpret results from Experiment L-28 are: 1) pyrochemical salts had formed a hard solid mass several inches thick at the bottom of the test container, and 2) the perforated plastic container that contained the Fe mesh was totally enveloped by the solid mass.

3.3 DOE's Interpretations of the Experimental Results

The observed decrease in pcH after the MgO was added (first bullet, Section 3.2) could seem at first to indicate that the MgO failed to buffer pcH. This apparent failure is attributed by DOE to the nature of the MgO after its addition to the container (DOE 3/23/00 Report, EPA 4/00 Minutes). As noted above (eighth bullet, Section 3.1), mixing of MgO and Brine A resulted in formation of a slurry that solidified rapidly. If additional solidification of the material occurred after the slurry was added to the container, a solid mass of MgO could have formed, thus isolating MgO hydration products from reaction with carbonate from the brine. Although it is not clear that the slurry hardened into a solid mass, DOE states with certainty that the bulk of the MgO was not in contact with the brine in L-28 (DOE 3/23/00 Report). A similar mechanism is invoked to explain the apparent failure of Fe mesh in Experiments L-31 and L-32 to buffer redox potentials to strongly reducing values (EPA 2/10/00 Letter, DOE 3/23/00 Report, and EPA 4/00 Minutes).

The relevance of the results of Experiment L-28 with respect to the ability of MgO to sequester CO_2(g) and to buffer pcH is dismissed by the researchers because the experimental conditions differ significantly from conditions expected over long periods of time in disposal rooms at WIPP (DOE 3/23/00 Report, and EPA 4/00 Minutes). More specifically, the experimental conditions are

considered to be irrelevant because the method of addition of MgO to the test container is inconsistent with the expected hydration behavior of MgO in the repository environment (DOE 3/23/00). This difference in hydration behavior appears to refer to the fact that the $CO_2(g)$ partial pressure in L-28 is much higher than is expected to result from microbial degradation of organic matter in the repository. Moreover, the high $CO_2(g)$ pressure in L-28 causes the pcH to fall below values where brucite is stable (DOE 3/23/00 Report), implying that MgO is unable to react with dissolved carbonate unless it is first hydrated to $Mg(OH)_2$. It is therefore concluded by the researchers that "The ability of MgO to buffer the brine pcH in the repository is well established, since the rate of CO_2 production is slow, relative to predicted brine inflow rates" (DOE 3/23/00 Report).

4 EPA's Review of Performance Issues Raised by Experiment L-28

4.1 Issues Relevant to the WIPP CCA Performance Assessment

The apparent failure of MgO to buffer pcH values within the expected range [8.5 to 10 (DOE 3/23/00 Report)] conflicts with a key assumption underpinning the Actinide Source-Term Model (ASTM) used in the WIPP CCA. That is, brines in disposal rooms at WIPP are expected to be moderately alkaline. Relatively acidic solutions, as were observed in L-28, could increase actinide solubilities, possibly to levels outside the range considered in the CCA. This raises the question whether the CCA is incomplete because the effects of relatively acidic conditions on actinide solubilities are not considered.

4.2 EPA's Review

The objective in adding MgO to Experiment L-28 appears to be ill-conceived for two reasons:

1) the relatively high and externally fixed $CO_2(g)$ partial pressure in the experiment is much higher than the $CO_2(g)$ partial pressures expected at WIPP, and

2) the experimental $CO_2(g)$ pressure is thermodynamically incompatible with the stable coexistence of MgO/ brucite and Mg-carbonate phases.

The first reason is also acknowledged by DOE (Section 3.3). To illustrate the latter point, mineral-stability relations in the MgO-CO_2-H_2O system at 30 °C are shown in Fig. 2, where analytical data from L-28 (EPA 4/00 Minutes) are also shown (crosses). Before conclusions can be drawn from this diagram it is important to emphasize that this figure represents a significant simplification of actual stability relations expected under the experimental conditions considered in L-28. It is arbitrarily assumed in the figure, for example, that the activity of Mg^{2+} is equal to unity. The actual activity of this species in L-28 solutions is unknown because analytical data on the compositions of these solutions have not been reported. If higher, or lower, Mg^{2+} activities are assumed, this would

cause the mineral-solution equilibrium boundaries to shift to the left or right, respectively, not up or down. It is also assumed in the figure that pcH and pH are equivalent, which is, at best, a rough first approximation. The figure is drawn assuming that magnesite, dolomite, huntite, artinite and nesquehonite do not form. Inclusion of these minerals would significantly affect the stability relations shown in the figure. Thermodynamic data used to construct this diagram were taken at face value from the ".com" database (ver. 3245) supporting the EQ3/6 software package (Wolery, 1992).

Despite the cautions noted above, it is apparent that brucite and hydromagnesite cannot coexist at equilibrium if, as in L-28, the partial pressure of $CO_2(g)$ is fixed at 60 bar (log $P_{CO2(g)}$ = 1.8). This suggests that any MgO added to the test container dissolved completely, or, as suggested by DOE (DOE 3/23/00 Report), was somehow isolated, either completely or partially, from contact with the brine.

To summarize, the issue arising from the apparent lack of buffering of pH and dissolved carbonate concentrations when MgO was added to Experiment L-28:

1) is not relevant to the WIPP CCA PA because experimental conditions are not representative of those expected in the repository, and

2) lacks a credible scientific basis because experimental conditions are incompatible with conditions permitting the metastable coexistence of hydromagnesite (or other Mg carbonates) and brucite. In other words, the apparent inability of MgO to buffer pH and sequester CO_2 is an experimental artifact resulting from external control of $CO_2(g)$ partial pressure at a constant value of 60 bar.

4.3 Unresolved Questions

The suggestion by DOE that brucite was unable to react with brine in Experiment L-28, because a solid mass of MgO formed when the slurry came into contact with the brine (DOE 3/23/00 Report, EPA 4/00 Minutes), raises the question whether similar formation of a solid mass could also occur when brine comes into contact with MgO in disposal rooms at WIPP. Although it is concluded in the DOE 3/23/00 Report that because a solid mass may well have formed in L-28, it is "difficult to relate these results to WIPP-relevant conditions", the question remains whether these conditions have been simulated (to the extent possible) in the laboratory. It is certainly unrealistic to assume that such conditions would involve interaction of an MgO slurry with brine, but extensive experiments carried out by Sandia National Laboratories (SNL, 1997) have also documented cementing of MgO pellets in contact with Salado and Castile brines. An explanation why similar cementing would not occur in the repository environment is based on the reasonable argument that because concentration gradients in the repository involving dissolved carbonate species are expected to be relatively low compared with those in the SNL experiments, Mg-carbonate phases would not form on the surface of MgO pellets (as they did in the experiments), but rather at some distance away from the surface.

It does not appear, however, that this suggestion has been backed up by any detailed modeling studies or experimental investigations.

The efficacy of MgO in sequestering CO_2 and in buffering pcH appears to have been evaluated only in terms of the MgO-CO_2-H_2O system. A number of solid-solution carbonate phases are also known to be stable, however, in other chemical systems such as CaO-MgO-FeO-CO_2-H_2O. It seems likely that such solid-solution phases would form in contact with WIPP brines, where Ca^{2+} concentrations are relatively high, and also in brines contacting ferrous materials in the WIPP repository. The kinetics of precipitation of such phases (e.g., dolomite) may be too slow to be observed over experimental time frames, but such precipitation may occur over periods of time (hundreds to thousands of years) that are relevant to the performance of the repository. The effects of solid-solution behavior may in fact enhance the expected performance of MgO backfill. Such effects are illustrated in Fig. 3, which is identical to Fig. 2 with the single exception that dolomite is now assumed to exist. As can be seen, equilibration of the brine with dolomite and brucite would significantly lower the equilibrium partial pressure of $CO_2(g)$ compared with conditions shown in Fig. 2. The robustness of the performance strategy for using MgO backfill at WIPP may therefore be enhanced if the effects of solid solution are accounted for.

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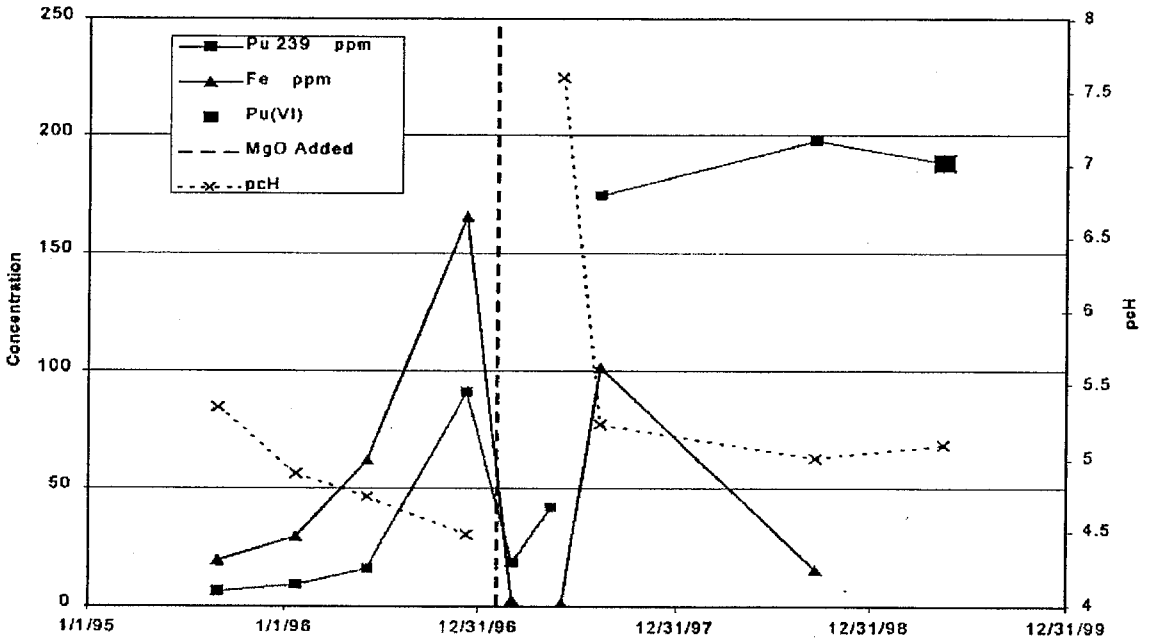

Figure 1. Concentrations of ^{239}Pu and Fe (total), and pcH values measured in liter-scale Experiment L-28 (from the DOE 3/23/00 Report).

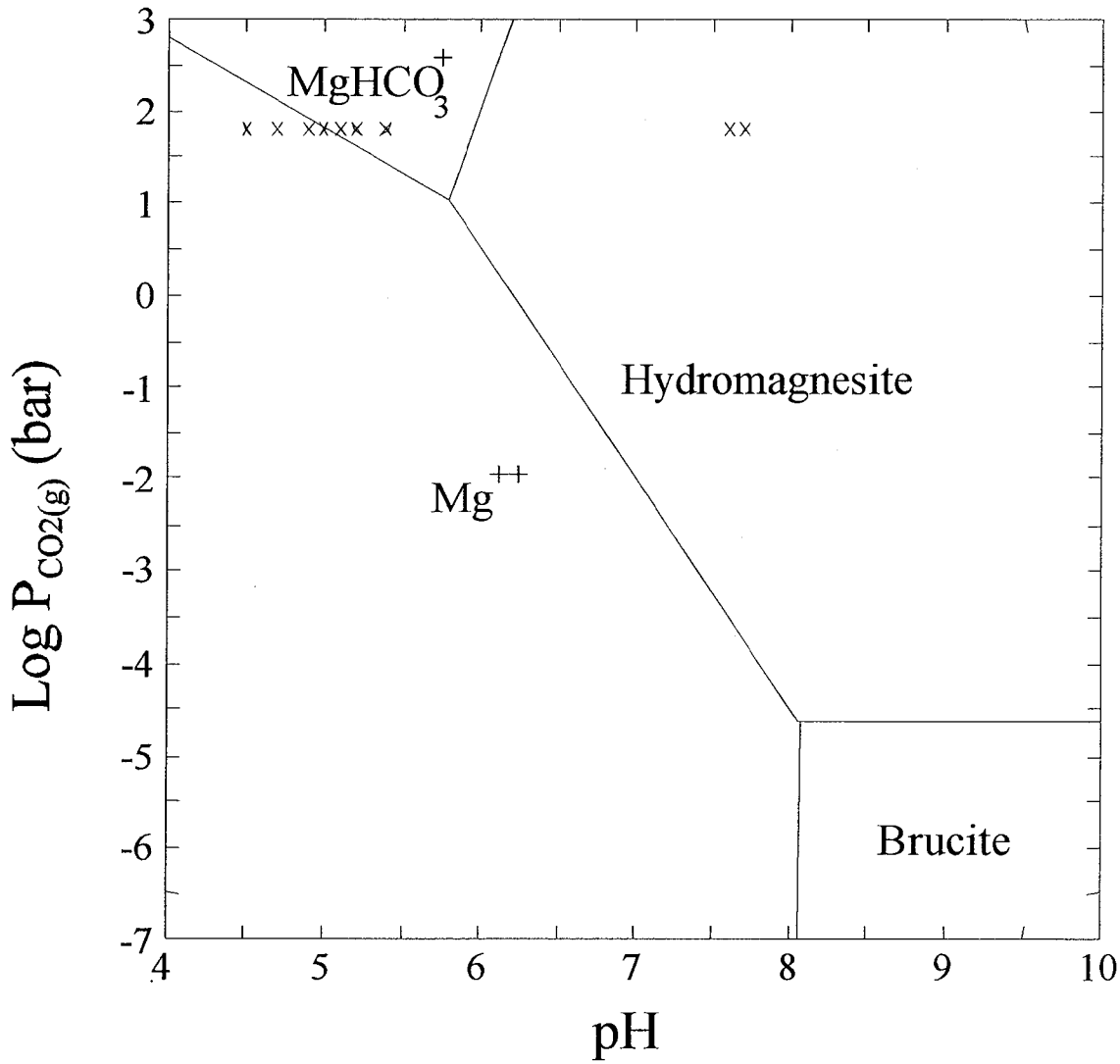

Figure 2. Mineral metastability relations in the MgO-CO_2-H_2O system at 30°C. The symbols (crosses) refer to conditions in Experiment L-28. Hydromagnesite is metastable with respect to magnesite, dolomite [$CaMg(CO_3)_2$; including ordered and disordered phases], huntite [$CaMg_3(CO_3)_4$] and artinite [$Mg_2(CO_3)(OH)_2 \cdot 3H_2O$], *i.e.*, these phases are more stable than hydromagnesite, but it is assumed that these phases do not form, possibly for kinetic reasons. Nesquehonite is stable relative to hydromagnesite when log $P_{CO2(g)}$ is greater than about 100 bar. This relation is not shown in the figure for the sake of clarity.

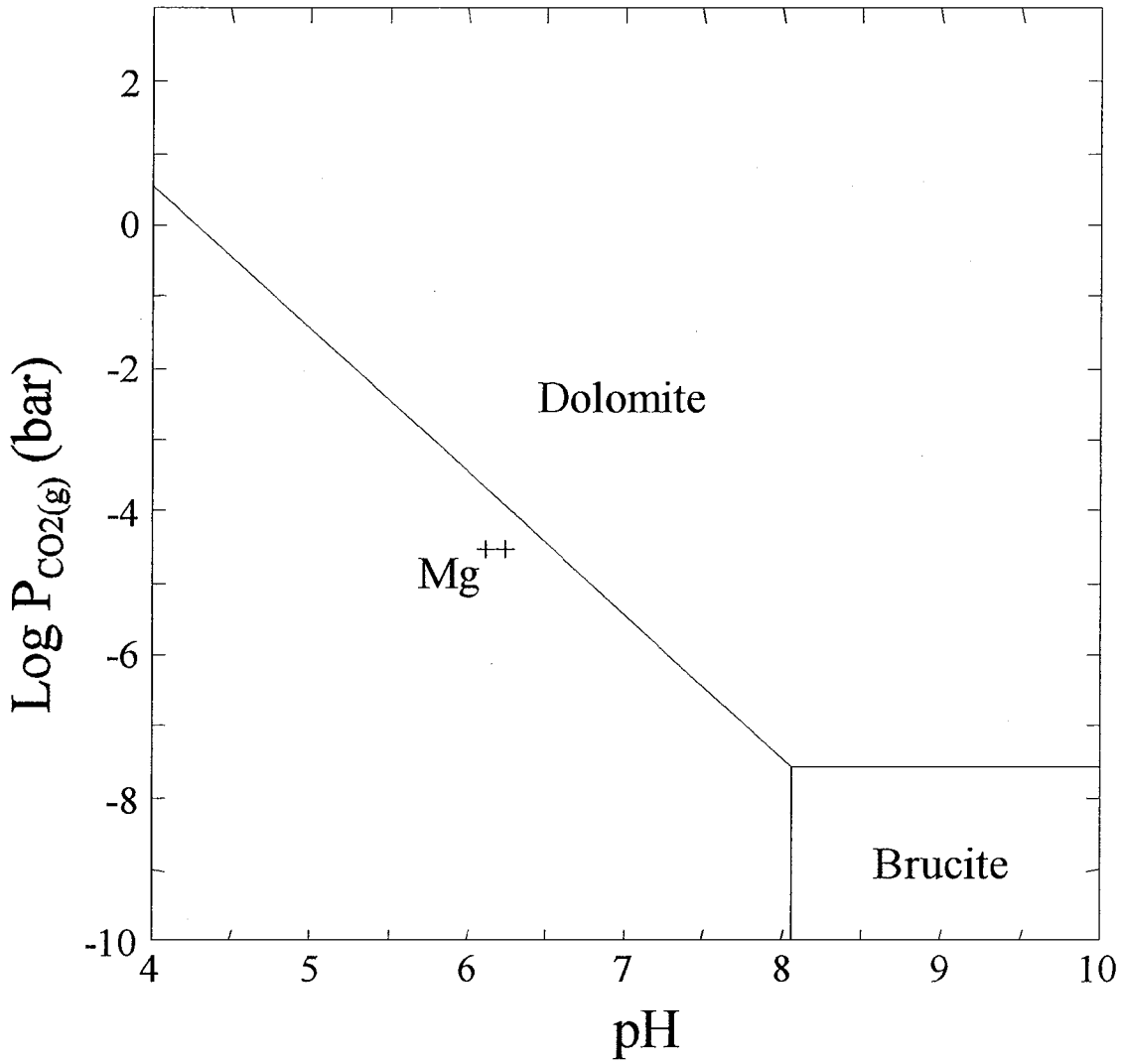

Figure 3. Mineral metastability relations in the MgO-CO_2-H_2O system at 30°C. Conditions in this figure are identical to those considered in Fig. 2, except that dolomite is now assumed to be stable. Equilibration of dolomite and brucite significantly lowers the equilibrium partial pressure of $CO_2(g)$ compared with the equilibrium $CO_2(g)$ partial pressure established by equilibrium between hydromagnesite and brucite (as shown in Fig. 2). Extended periods of time (e.g., hundreds to thousands of years) may be required for dolomite to precipitate from solutions that are supersaturated with respect to this mineral.

Enclosure 8

EEG-77
September 2000

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EEG-77

Plutonium Chemistry under Conditions Relevant for WIPP Performance Assessment: Review of Experimental Results & Recommendations for future work

September 2000

REVIEW OF COMMENTS AND ISSUES RAISED BY THE ENVIRONMENTAL EVALUATION GROUP IN REPORT EEG-77 - "PLUTONIUM CHEMISTRY UNDER CONDITIONS RELEVANT FOR WIPP PERFORMANCE ASSESSMENT"

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Enclosure 9

EPA Report on EEG-77

EXECUTIVE SUMMARY

The Environmental Evaluation Group (EEG) recently issued report EEG-77, *Plutonium Chemistry Under Conditions Relevant for WIPP Performance Assessment - Review of Experimental Results and Recommendations for Future Work*, by Dr. Virginia M. Oversby. Dr. Oversby identifies three issues that could potentially affect the mobility of Pu and other actinides in the WIPP repository; 1) the impact of organic ligands on actinide solubilities, 2) the validity of the assumption of analogous solubility behavior between Th(IV) and other quadravalent actinides (the so-called actinide analogy adopted in the CCA source-term model), and 3) the need to determine uncertainties in calculated actinide solubilities.

The results of EPA's review of EEG-77 are documented in this report, and are summarized in the following paragraphs.

1. EEG contends that citrate could significantly increase actinide solubilities because this ligand forms strong complexes with An(IV) cations and weak complexes with other cations. The validity of this contention is questionable, however, because it is based only on the relative stabilities of the citrate complexes, and does not consider additional, mass-balance constraints on the aqueous concentration of the citrate ligand. Citrate concentrations could be estimated using a computational approach similar to that described for EDTA in Appendix SOTERM of the WIPP CCA, but such calculations have not been carried out by EEG.

2. EEG's contention that the actinide analogy is not appropriate for Th(IV) and Pu(IV) may be valid for some chemical environments, but not those expected at WIPP. The analogy adopted in the CCA source term is based on the assumption that the WIPP environment will be such that all actinide aqueous species and solids exist in either the +3, +4 or +5 oxidation state. The analogy does not extended to cases where the oxidation state of an actinide differs in the solid and aqueous phase. It is conceivable that a Pu(IV) solid could coexist with brines in which the stable oxidation state is Pu(III) (roughly at pH < 8.5) or, less likely, Pu(V) or Pu(VI) (in strongly oxidizing solutions). In such cases, the Th(IV) analogy for Pu(IV) would not be appropriate. It should be emphasized, however, that under strongly reducing conditions expected in the repository (controlled by corrosion of the waste containers and degradation of organics) and pH in the range 8.5 to 10 (controlled by reaction of brine with MgO backfill), Pu in aqueous and solid phases will likely exist only in the +4 oxidation state. The Th(IV) analogy for Pu(IV) is therefore valid for the expected chemical environment at WIPP.

   EPA anticipates that the actinide analogy will continue to draw criticism because it is possible, although extremely unlikely, that the long-term chemical environment at WIPP may evolve to conditions for which the analogy is invalid. For this reason, an approach similar to that proposed by EEG (see below) may be useful for establishing limits to the validity of the analogy with respect to the full range of probable-to-improbable repository conditions.

3. EEG proposes to move beyond further discussion of the conceptual model and numerical techniques incorporated in DOE's FMT code, recommending a new

approach consisting of the following tasks to address their concerns regarding uncertainties in actinide solubilities:

- generate actual experimental data for Pu in WIPP-relevant brines,
- develop an aqueous speciation-solubility model for Pu (and possibly other actinides) appropriate for all relevant oxidation states of the element in aqueous and solid phases, and
- support these models using the NEA/OECD thermochemical database for the actinides, and the Specific Ion Interaction Theory (SIT), instead of the Pitzer approach currently employed by DOE, to calculate ionic activities in concentrated solutions.

EEG's proposed approach differs from that used by DOE in the WIPP CCA PA because realistic models of actinide speciation-solubility behavior would be used in place of the actinide analogy preferred by DOE. EEG does not challenge the validity of this analogy for the strongly reducing and mildly alkaline disposal conditions expected over the long term at WIPP, and the need for their approach under such conditions is therefore questionable. EEG's approach could be useful in establishing bounding environmental conditions beyond which the actinide analogy is no longer valid, and for estimating Pu solubilities under these unexpected, though remotely possible, disposal conditions. It should be emphasized, however, that the actinide analogy appears to be valid for expected disposal conditions at WIPP, and that associated upper-bound estimates of actinide solubilities are adequate and scientifically defensible for performance assessment purposes. If necessary, the merits of EEG's approach should be more rigorously evaluated on the basis of a thorough review of technical, cost, PA, QA and programmatic issues arising from the proposed adoption of the NEA/OECD thermochemical database, the associated partial or complete abandonment of the thermochemical database developed by DOE, and possible uses of alternative methods for calculation of ionic activities in WIPP brines.

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1 ISSUE 1: EFFECTS OF ORGANIC LIGANDS ON ACTINIDE SOLUBILITIES

1.1 Description of the Issue

EEG contends that a scenario providing potentially higher releases from the WIPP repository has been overlooked in the WIPP CCA PA. To support this contention, EEG follows two distinct, but closely related, lines of reasoning.

First, EEG contends that a key assumption adopted in the CCA PA is inappropriate. That assumption requires any brine entering the repository during a human-intrusion scenario to be well mixed with waste (SOTERM 2.2.1). Repository conditions consistent with this assumption are referred to as being *homogeneous*. EEG asserts, however, that a waste container partially breached by drilling may still provide a hindrance to mixing of brine inside the container with a larger pool of brine outside the container. Two (or more) brines of distinctly different compositions could therefore coexist in the repository for an indefinite period of time. Repository conditions consistent with this assumption are referred to as being *heterogeneous*.

Second, EEG agrees with EPA that it is not possible to consider every possible combination of chemical mixtures in specific drums in a performance assessment. Thus, although EEG rejects the notion of a homogeneous repository, EEG acknowledges that heterogeneous conditions cannot be realistically accounted for in performance assessments. EEG takes issue, however, with DOE's bounding calculation to deal with this problem. DOE assumed that the organic ligand with the largest actinide complexation constant will be the most important in increasing actinide solubilities. DOE then calculates the competition between non-actinide cations and actinides for the ligand EDTA, which exhibits the largest An(IV) complexation constant among all organic ligands in WIPP wastes. DOE concludes that almost all the EDTA will be bound to transition-metal cations, and that the effects of organic complexing on actinide solubilities will therefore be minimal. EEG's position is that this conclusion is incorrect because other organic ligands, notably citrate, exhibit relatively large complexation constants for Th(IV) [representing An(IV)], but relatively small complexation constants for the non-actinide cations. EEG believes that complexation of the non-actinide cations with citrate will not be effective in significantly reducing citrate concentrations in the brines, and this ligand will therefore be available to form complexes with the actinides. EEG notes that because Pu in particular is likely to be present in waste drums containing high concentrations of citrate, the effect of organic ligands on the solubility of Pu in WIPP-brines should be accounted for in bounding calculations.

To more clearly distinguish these interrelated lines of reasoning, ISSUE 1 is subdivided for discussion purposes below into:

ISSUE 1a; Should heterogeneous repository conditions be considered in performance assessments of a human-intrusion scenario at WIPP?, and

ISSUE 1b; If such conditions are considered, should bounding calculations of the effects on actinide solubilities consider complexation reactions involving citrate as well as EDTA?

1.2 Summary of EEG Comments in EEG-77 on ISSUES 1a and 1b

1.2.1 EEG Comments on ISSUE 1a.

1.2.1.a "There has been no attempt by EPA to assess the degree to which the [solubility] calculations might represent the conditions expected for WIPP disposal." (4th para., p.5).

1.2.1.b "...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." (5th para. , p.5).

1.2.1.c "Both DOE and EPA assumed that the actinides would be evenly distributed throughout the repository and that 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." (5th para., p.6).

1.2.1.d "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." (3rd para, p. 8).

1.2.1.e "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 represent 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." (3rd para., p. 24).

1.2.1.f "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." (4th para., p. 24).

1.2.2 EEG Comments on ISSUE 1b.

1.2.2.a "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 evaluated." (4th para., p. 4).

1.2.2.b "...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 of 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." (5th para., p. 5).

1.2.2.c "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 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 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 on p. 39 of the SOTERM appendix - is orders of magnitude larger than for other ion complexes with citrate." (2nd para., p.7).

1.2.2.d "...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 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." (3rd para., p. 10).

1.2.2.e "The [STTP] 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, the 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 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..." (4th para., p. 17).

1.2.2.f "Concentrations of Pu in brines increase if chelating agents are present." (conclusion drawn from comment 1.2.2.e, p. 18).

1.2.2.g "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" (4th para., p. 25).

1.2.2.h "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." (2nd para., p. 26).

1.3 EEG's Recommendations to Resolve ISSUE 1

EEG believes that experiments involving Th(IV), citrate, EDTA, Ca^{+2} and one or more transition metals should be performed to demonstrate the extent of organic-ligand complexation of each type of cation in the presence of other cations. Additional experiments are recommended by EEG to evaluate the lability of Pu oxidation states in the presence of organic ligands. The results of the experiments could be used to test the reliability of chemical equilibrium models supporting performance assessments.

1.4 EPA's Previous Responses to Comments Related to ISSUE 1

1.4.1 EPA's Responses to Comments Related to Issue 1a

The following paragraph is from EPA's response to Issue V - Effect of Organic Ligands on Solubility [see USEPA (1998a)].

1.4.1.a "The repository is represented as a completely mixed system with evenly distributed chemical components and conditions. Numerous "what if" scenarios could be imagined in which specific drums are filled with mixtures of chemicals that could maximize actinide mobility, such as a drum with both plutonium and some form of citrate. The 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. However, rather than dismiss this potential problem entirely, DOE conducted a series of bounding calculations to determine the maximum possible effect that the organic ligands might have on actinide concentrations, and also included uncertainties in their representations of actinide solid solubilities for input to PA calculations".

1.4.2 EPA Responses to Comments Related to Issue 1b

The following paragraphs are from EPA's response to Issue V - Effect of Organic Ligands on Solubility [see USEPA (1998a)].

1.4.2.a "Organic chemicals were expected to be part of the wastes, especially because many were used in the separation of actinides during chemical processing of nuclear materials. [Appendix BIR] Hence, DOE made an effort to determine what kind and how much of the organic chemicals might be present in the waste because, in part, strong complexants, such as EDTA, could potentially affect the solubilities and aqueous speciation of actinides. Using the estimates of the weights of the organic chemicals present in the waste, the potential solution concentrations were calculated by dividing by the volume of brine required to inundate the void volume of the repository after closure. The results of these calculations are provided in Table SOTERM-4 in Appendix SOTERM of the CCA. They indicate the following estimated concentrations: 1.1×10^{-3} m acetate, 4.7×10^{-4} m oxalate, 7.4×10^{-3} m citrate, 4.2×10^{-6} m EDTA. The calculations of the effects of organic chemicals on the aqueous speciation of actinides were based on these calculated organic concentrations.

In the bounding calculations ..., the effects of EDTA complexing of Th(IV) were examined to determine the potential for organic ligands to affect the aqueous speciation of the actinides. The combination of EDTA and Th(IV) was chosen as the bounding case because this reaction, i.e.,

$$\text{Th(IV)} + \text{EDTA} = \text{Th(IV)-EDTA}$$

has the highest affinity of the possible actinide-organic ligands reactions for producing a high proportion of an organically complexed actinide, simplistically represented in the above reaction as Th(IV)-EDTA. The affinity for organic ligand complexation is proportional to the product of the stability constant and the reactants, i.e.,

$$[\text{Th(IV)-EDTA}] = \beta[\text{Th(IV)}][\text{EDTA}]$$

where the brackets refer to concentrations. The substitution in this equation of the estimated EDTA concentration of 4.2×10^{-6} m EDTA, the mid-range value for the stability constant of $10^{16.25}$ for the formation of Th-EDTA from Table SOTERM-5 in the CCA, and any arbitrary concentration of Th(IV) expected for the repository (e.g., 1×10^{-8} m), the product obtained is 747. The same operation can be applied to the other organic ligand

complexes, as shown in the following table.

Organic Complex	log Stability Constant	Organic Ligand (m)	Th(IV) (m)	Product β[Th(IV)][EDTA]
Th(IV)-EDTA	16.25	4.2×10^{-6}	1×10^{-8}	747
Th(IV)-acetate	3.93	1.1×10^{-3}	1×10^{-8}	9.7×10^{-8}
Th(IV)-oxalate	7.26	4.7×10^{-4}	1×10^{-8}	8.6×10^{-5}
Th(IV)-citrate	9.75	7.4×10^{-3}	1×10^{-8}	0.4

As shown by these calculations, the affinity for Th(IV) to form an organic complex with EDTA is about 3 orders of magnitude greater than for citrate, which has the next highest affinity. Consequently, it is appropriate to use the Th(IV)-EDTA complex for any bounding calculations to assess the effects of organic ligands on the aqueous speciation of the actinides and solubilities of the actinide solids for the brine solutions expected to infiltrate into the repository over time. There is no reason to consider the other organic ligands (i.e., acetate, oxalate, and citrate) because their potential to complex the actinides is so much less than EDTA.

To assess the effects of EDTA to complex Th(IV) in a brine solution, DOE conducted a series of speciation calculations, considering the probable concentrations of major solutes (e.g., Mg^{2+}) and metals (e.g., Fe^{2+}, Ni^{2+}) expected to be present in the brines and also known to form complexes with EDTA. These calculations are described on pp. SOTERM-40 to 41 in Appendix SOTERM of the CCA. The calculation results indicated that only 3% of the EDTA was complexed with EDTA. The remainder of the EDTA was tied up with Mg^{2+}, Fe^{2+}, and Ni^{2+}. This finding indicates that even for the organic complex with the highest potential to form an organic complex [i.e., Th(IV)-EDTA] very little of that organic complex will actually be present because of the vast majority of the EDTA will form complexes with other ions present in much higher concentrations than the actinides.

In EPA's review of the actinide source term, an independent calculation of the potential effects of EDTA on the solubility of ThO_2(am) was conducted to determine whether the calculations were sensitive to the EDTA concentration. The solid, ThO_2(am), was used because it is expected to control the Th(IV) concentrations in the repository environment based on experimental investigations and FMT model calculations.... Also, as noted above, among the actinides, aqueous Th(IV) has the highest tendency to be complexed by EDTA. Based on these factors, the EDTA-Th(IV)-brine system should provide the greatest possibility for an organic ligand to affect the prediction of the solubility of an actinide solid.

The PHREEQC geochemical computer code (version 1.5) ... was used for the solubility calculations. PHREEQC is a well established computer code that has been used for a variety of problems in aqueous geochemistry for a number of years.

The formulations for activity coefficients incorporated in PHREEQC are not representative of high ionic strength solutions, hence the ThO_2(am) solubility calculations were performed for the SPC (Salado Primary Constituent) brine diluted 10 times. Although this solution composition may not be exactly representative of the repository environment, the resulting calculations still provide a reasonable representation of the effects of EDTA concentration on ThO_2(am) solubility. Additionally, the solubility calculations were conducted for a constant CO_2(g) partial pressure of $10^{-5.5}$ bars, which is the level expected for equilibrium between brucite [$Mg(OH)_2$] and hydromagnesite [$Mg_5(CO_3)_4(OH)_2.4H_2O$] resulting from reactions between the MgO backfill and SPC (Salado Primary Constituent) brine (see Sections 3 and 4). The representative EDTA concentrations expected for the repository is estimated at about 4.2×10^{-6} m. [Table SOTERM-4 in the CCA] Thus, the ThO_2(am) solubility calculations were conducted for an EDTA concentration range of 4.2×10^{-6} m to 4.2×10^{-2} m.

The results of the solubility calculations for ThO_2(am) indicate that the effect of EDTA is negligible at concentrations less than about 4.2×10^{-4} m ..., which is 100 times the concentration estimated for the inundated repository. At an EDTA concentration 4.2×10^{-2} m, which is 10,000 times the level estimated for the repository, an increase in Th(IV) concentrations is predicted for pH less than about 7.5. At higher pH, the EDTA has no substantial effect on ThO_2(am) solubility because aqueous Th(IV) speciation is dominated by hydroxyl, carbonate, and sulfate complexes rather than EDTA complexes. The EDTA is predicted to be present primarily as complexes with Ca^{2+} and Mg^{2+} under alkaline conditions.

These bounding calculations clearly show that the organic ligands will not affect the solubilities of the actinide solids for the expected conditions. Thus, there is no need to conduct a formal sensitivity analysis because even the worst case does not show an effect. However, it should also be pointed out that the PA calculations were not conducted with single values for the solubilities of the actinide solids but used a distribution based on an uncertainty range for the solubilities. Within the well-mixed conceptual model, the potential effects of deviations from the average situation, such as the potential scenario of having a drum with both plutonium and citrate, are accounted for by the inclusion of uncertainties and uncertainty distributions in the performance assessment calculations. For instance, in the source-term portion of the performance assessment, the concentrations of actinides were assigned an uncertainty band of 100 times less than (-2.0 log units) and 25 times greater than (+1.4 log units) the calculated solubilities of actinide solids for the expected repository conditions, i.e., the average case. Depending on the uncertainty distribution, some performance assessment realizations would have used actinide concentrations at the

outer bounds of the uncertainty range. Because the effects of the organic ligands are so small, it is expected that they would have been included within the uncertainty range, hence incorporated into the overall PA calculation.

In summary, DOE's bounding calculations, independent bounding calculations, and incorporation of uncertainty ranges to represent actinide concentrations in the PA calculations indicate the organic ligands will have only a minor effect on the solubilities of actinide solids under the expected repository conditions. Consequently, there is no substantive information that could be gained by conducting a sensitivity analysis for the effects of the organic ligands or conducting the calculations with citrate rather than EDTA. EPA agrees with the conclusions of the Waste Characterization Independent Review Panel in their supplementary report, which states: "*The Panel agrees that under the conditions of MgO backfill, chelating agents will have a negligible effect on repository performance. The Panel notes that, even at the basic pH in the repository, the availability of transition metals may be enhanced due to the formation of soluble halo complexes, making an even stronger case that base metals control ligand chemistry.*" ..."

1.5 Issue Resolution Status

1.5.1 Issue 1A

EEG's recommended approach for dealing with heterogeneous conditions in the repository seems inherently reasonable. EEG acknowledges that it is not feasible to consider all possible combinations of chemical mixtures in specific waste drums in a performance assessment. The point of contention thus centers on whether DOE's bounding calculation involving complexation of the actinides with EDTA is adequate, or whether a similar calculation accounting for complexation of Pu with citrate should also be included as a distinct feature in FEPS considered in a human intrusion scenario. This point is taken up in Section 1.5.2.

EEG also recommends that the concentration of citrate inside a partially breached container should be used in their proposed bounding calculation. The rationale for this recommendation is that Pu and citrate are likely to be collocated in a waste drum (Comment 1.2.1.f). EEG's approach therefore differs from that used in the CCA PA, where solution concentrations of soluble organic ligands were estimated by dividing the weights of organic chemicals in the waste (i.e., their total inventory) by the volume of brine required to inundate the void volume of the repository after closure. The dissolved concentration of citrate in an individual drum could be much higher than that estimated in the CCA PA. However, the range of dissolved actinide concentrations adopted in the CCA PA were, as noted in Section 1.4.2, estimated based on uncertainties in actinide solubilities calculated over a range of waste inventory values. Depending on the uncertainty distribution, some performance assessment realizations would have used actinide concentrations at the outer bounds of the uncertainty range. Because the effects of organic ligands on actinide solubilities is small (Section 1.4.2), it is expected that such effects would be accounted for within the range of uncertainties in actinide concentrations,

and thus incorporated into the overall PA calculation. It is likely that this range of actinide concentrations provides an upper bound on actinide concentrations inside an individual waste drum containing citrate, particularly if complex formation with citrate is rendered ineffective by competitive effects with non-actinide cations (see Section 1.5.2).

1.5.2 Issue 1B

EEG asserts that citrate forms strong complexes with An(IV) and very weak complexes with other cations (Comments 1.2.2.a, 1.2.2.d). Support for this view is provided in Comment 1.2.2.g, which compares the stability constant of the Th-citrate complex with that of Fe(II)-citrate. Based on this comparison, EEG asserts that "Other ions will not compete with Pu sufficiently to prevent complex formation because the stability for (IV) actinide complexation ... is orders of magnitude larger than for other ion complexes with citrate" (Comment 1.2.2.c).

EEG's contention, which is based on a simple comparison of stability constants among citrate complexes of actinide and non-actinide elements, may be somewhat misleading because it does not take into account mass balance constraints on the aqueous concentration of the citrate ligand. The concentration of citrate available to form complexes with the actinides will depend in part on the stabilities of similar citrate complexes with other cations (i.e., transition metals, Mg^{2+}, Ca^{2+}, etc.), and on the aqueous concentrations of these cations. Thus, although the relative stabilities of the actinide-citrate complexes are significantly greater than citrate complexes with non-actinide cations, as noted by EEG, most of the available citrate may still be bound in these latter complexes if the concentrations of non-actinide cations are sufficiently high. EEG is correct in pointing out that the stabilities of citrate-actinide complexes may be significantly greater than those of similar complexes with non-actinide elements, but this observation alone does not mean that actinide-citrate complexes will significantly increase actinide concentrations in WIPP brines. A basis for evaluating whether citrate could significantly increase actinide concentrations should follow the calculational approach, based on both mass-action and mass-balance constraints, described by DOE for EDTA [USDOE (1996b), see also EPA's response to comments summarized above (Section 1.4.2.a)].

It should also be pointed out that EEG's use of selected results from the STTP experiments to support Comments 1.2.2.e, 1.2.2.f and 1.2.2.g may be inappropriate. Their comparison of Pu concentrations in "similar" STTP experiments that differ depending on whether chelating agents (160 ppm each of acetamide, acetate, citrate, oxalate and thiocyanate) are present overlooks the fact that Pu concentrations are influenced by a number of experimental parameters, none of which were actually controlled in the STTP systems. The difference between "similar" experiments of three orders of magnitude in dissolved Pu concentrations (Comment 1.2.2.e) could result, for example, from differences in pH and/or redox potential, but EEG does not indicate whether such differences were observed. Moreover, EEG assumes that the measured Pu concentrations are controlled by solubility equilibrium (Comment 1.2.2.e), but there is no supporting analysis addressing whether equilibrium was actually attained in these experiments.

2 ISSUE 2: OXIDATION-STATE ANALOGY

2.1 Description of the Issue

An oxidation-state analogy is used in the WIPP CCA to deal with actinide chemistry. The analogy is based on the observation that actinides in the same oxidation state exhibit similar chemical behavior (USDOE, 1996b). Calculated solubilities for Am(III), Th(IV) and Np(V) solids are therefore used in the CCA to approximate the solubilities of actinide elements in the +3, +4 and +5 oxidation state, respectively. Application of the Th(IV) model to other actinides in the +4 oxidation state is conservative, because Th(IV) [as ThO_2(am)] is the most soluble solid among these elements under WIPP conditions. EEG questions the validity of the oxidation-state analogy as used in the CCA because it treats each possible oxidation state in isolation, and does not allow for different oxidation states of a single element to interact in response to other conditions in the reacting system. Specifically, adoption of Th(IV) as an analog for Pu(IV) is inappropriate according to EEG because Th can exist only in the +4 oxidation state under WIPP-relevant conditions, whereas Pu may exist in the +3, +4, +5 or +6 oxidation state depending on the chemical environment.

2.2 Summary of EEG Comments in EEG-77 Related to ISSUE 2

2.2.a "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" (3rd para., p. 6).

2.2.b "The DOE response concerning the use of the Th(IV) analog for plutonium (IV) 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 U(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)." (2nd para., p.8).

2.2.c "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. ...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." (2nd para., p. 9).

2.2.d. "The EPA addressed the 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 ...[referring in to the STTP experiments, Hascke et al. (2000), Rollin (1999), Oilla (1999) and the NEA/OECD Thermodynamic Database Project]..., 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..." (3rd para., p. 10 - see also Item 2.3.b below).

2.2.e "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) [STTP experiments], this issue needs to be revisited." (3rd para., p. 11).

2.2.f "Th concentrations in the non-pressurized Portland cement tests ...[STTP experiments]... were, with one exception, lower to much lower than the 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." (2nd para., p. 14).

2.2.g "Tests ...[STTP experiments]... 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. ...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." (3rd para., p. 14).

2.2.h "For some ...[STTP]... tests that had high Pu concentrations, spectroscopy was done to determine speciation of Pu. Pu(VI) was positively identified in tests L26 and L27. The Pu(VI) appears to have been present after the MgO was added to L-28. ...All of these tests contained 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 releases under the dynamic conditions expected for the Human Intrusion scenario." (3rd para., p. 17).

2.2.i "Some conclusions can be drawn from the results of the STTP tests:

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

...4. The addition of MgO to a test that contained a high concentration of 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)." (p. 18)

2.2.j "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...*". This position contrasts with that taken by a National Research Council review team, who stated in their report "*...Although the oxidation state model (the assumption that the chemistry of a given oxidation state is similar for all 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 the analogy* [reference cited in EEG-77]" (5th para., p. 26).

2.2.k "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 Pu solids, leading to production of Pu(V) and/or Pu(VI) solution species. (3rd para., p. 27).

2.2.l "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 valence states available for responding to changes in environmental conditions." (3rd para., p. 28).

2.3 EEG's Recommendations to Resolve ISSUE 2

EEG's recommendations to resolve this issue are expressed in a number of comments in various sections of EEG-77. These comments are documented below.

2.3.a "EEG recommends that the (solubility) 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." (2nd bullet, p. 4).

2.3.b "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." (5th bullet, p. 4).

2.3.c "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 " (3rd para., p. 10).

2.3.d "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. (4th para., p. 28).

2.3.e. "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 corroding metal pieces. The evolution of the solution chemistry, especially Pu concentration and speciation, should be monitored. Measurements using the sensitive analytical method developed by Rollin (1999) would be most informative." (1st para., p. 29).

2.3.f "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 Pu. Type 1 wastes would be likely to release Pu(VI) directly to solution, while type 2 wastes may not." (1st para., p. 23).

2.4 EPA's Previous Responses to Comments Related to ISSUE 2

2.4.1 EPA Responses to Comments Dealing with the Actinide Analogy

The following paragraphs are from EPA's responses to Comments 6.Y.1 through 6.Y.8 dealing with the appropriateness of the actinide analogy [see USEPA (1998a)]

2.4.1.a "EPA ... address three related issues regarding the appropriateness of the actinide analogy for representing the actinide concentrations for the actinide source term model. These issues are:

- Reliance of the FMT code on the actinide analogy
- Verification of the actinide analogy
- The use of Th(IV) solids to represent the solubilities of other +IV actinides [i.e., Pu(IV), U(IV), and Np(IV)].

With respect to the first issue, the statement in Comment 6.Y.1 *"FMT relies heavily upon analogy...."* is incorrect. The actinide analogy is just part of the conceptual model for defining the actinide source term. The FMT (Fracture-Matrix Transport) computer code is only a numerical model for aqueous speciation and solubility. The calculations that can be made with FMT are based solely on the thermodynamic data for individual aqueous species and solids contained in its database not on any empirical or conceptual data, such as the actinide analogies.

With respect to the second issue, the oxidation state analogy is based on standard inorganic chemistry principles. In short, the actinide oxidation analogy means that actinides of the same oxidation state tend to have similar chemical properties under similar conditions. This generalization can be made because chemical reactions involving ionic species are related primarily to the charge densities of the reacting species. [CCA, Appendix SOTERM] Actinides with the same oxidation state have the same core electronic structure...; hence have similar ionic radii and charge densities, which in turn leads to analogous chemical behavior in solubility and aqueous speciation reactions... A similar phenomenon occurs for the lanthanide group elements (i.e., rare-earth elements of atomic numbers 57 through 71), which have the same core electronic structure for ionic species. In addition to the theoretical basis, DOE conducted experimental studies and analyses that confirmed the validity of the oxidation state analogy, and subsequently employed it in their representation of the solubilities of actinides. [CCA, Appendix SOTERM]

With regard to the third issue, the application of the actinide analogy to the +IV actinides is a good example of its appropriate application to the actinide source term. Besides the oxidation state analogy, another generalization that can be made is that there is decreasing trend in the solubilities of actinide solid phases across the actinide series. This generalization is based on the fact that ionic radii of the lanthanides and actinides decrease with increasing atomic number. With decreasing radii, the stabilities of actinide-oxide and actinide-hydroxide bonds are increased, leading to decreased solubility products, which is a direct indication of solubility, for similar compounds. This effect is exemplified by the decrease in the solubility products of both hydrous actinide dioxides and crystalline actinide dioxides with increasing atomic number as shown by Rai et al. [1987, p.40] The data from Rai et al. [1987, p.40] show that the solubility product for Th(IV) dioxides, which is the actinide with the lowest atomic number, is about 8 orders of magnitude greater than for U(IV) dioxides, about 9 orders of magnitude greater than for Np(IV) dioxides, and about 10 orders of magnitude greater than for Pu(IV) dioxides. These experiments confirm the validity of the actinide analogy for the +IV actinides in that Th(IV) solids are more soluble than U(IV), Np(IV), and Pu(IV) oxide solids.

The data compiled by Rai et al. [1987, p. 40] are most relevant to low ionic strength conditions. However, more recent experimental data from Rai et al. [1997, pp. 242-243,245] show that the actinide analogy for the order of solubilities of +IV actinides is also relevant to high ionic strength conditions expected for the WIPP. Rai et al. [1997, p. 239] indicate that the solubility products for ThO_2(am) is about 8 orders of magnitude greater than for UO_2(am) in concentrated NaCl and $MgCl_2$ solutions, consistent with the earlier data discussed above.

Based on these established trends for the +IV actinides, DOE used the solubility of ThO_2(am) to represent the concentrations of the other +IV actinides [i.e., U(IV), Np(IV), and Pu(IV)] under the expected repository conditions. The experimental evidence provided by Rai et al. [1997, p. 239] and Rai et al. [1987, p.40] clearly indicate that ThO_2(am) is more soluble than the other +IV actinides as indicated by the solubility products determined for the various solids in the following table (Note: higher solubility products indicate higher solubilities for the same chemical conditions).

Actinide	Solid	Reaction	Solubility Product (25°C)	Reference
Th(IV)	$ThO_2(am)$	$ThO_2(am) + 2H_2O = Th^{4+} + 4OH^-$	-45.4	Rai et al. (1997, p. 239)
U(IV)	$UO_2(am)$	$UO_2(am) + 2H_2O = U^{4+} + 4OH^-$	-53.45	Rai et al. (1997, p. 239)
Np(IV)	$NpO_2{:}xH_2O(am)$	$NpO_2{:}xH_2O(am) = Np^{4+} + 4OH^- + (x-2)H_2O$	-54.5	Rai et al. (1987, p. 35)
Pu(IV)	$PuO_2{:}xH_2O(am)$	$PuO_2{:}xH_2O(am) = Pu^{4+} + 4OH^- + (x-2)H_2O$	-56.85	Rai (1984, p. 97)
Pu(IV)	$Pu(OH)_4$	$Pu(OH)_4 = Pu^{4+} + 4OH^-$	-57.85	Kim and Kanellakopoulos (1989, p. 145)
Pu(IV)	PuO_2	$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	-60.20	Kim and Kanellakopoulos (1989, p. 145)

While the concerns of the NAS, as described in Comment 6.Y.6 are noted, EPA finds from evaluations of the available data, consideration of chemical conditions, and theoretical aspects of actinide chemical behavior, that the actinide oxidation state analogy and its application to the +IV actinides (as exemplified by the use of $ThO_2(am)$ solubility, to represent the solubilities of other +IV actinide solids) is an appropriate and verified approach that bounds the potential concentrations that the +IV actinides might reach in any brines that infiltrate into the repository."

2.4.2 EPA Responses to Comments Dealing with MgO Backfill

The only specific comment in EEG-77 pertaining to MgO backfill contends that it is not known how long the reaction product nesquehonite will persist. This issue is addressed in EPA's responses to comments (USEPA, 1998a) on the use of MgO backfill. Aspects of EPA's responses concerning the rates of reactions involving MgO and reaction products, including nesquehonite, are summarized below.

2.4.2.a "Experiments conducted by DOE, which are described in SNL (1997), show that reactions between MgO and carbonated brines are rapid. Solution pH values were found to increase in a matter of hours, indicating that the MgO backfill-type material is very reactive. [SNL, 1997, p. 8, 11] Also, significant amounts (a few weight percentages) of uptake of carbon were observed to take place after only days to weeks, indicating that the rates of formation of magnesium carbonates are also rapid. (SNL, 1997, p. 10, 12, 15). These rapid rates of reaction are consistent with experimental results of the transformation of nesquehonite to hydromagnesite after three to seven days of reaction at 52°C (Davies and Bubela, 1973, p. 290, 291). The formation of protohydromagnesite from nesquehonite after 10 months at

10 to 28°C in a simulated sedimentary column indicates that the formation and recrystallization reactions involving magnesium carbonates occur rapidly (Davies et al.,1977, p. 188, 189, 197,198). The results of these experiments provide adequate information to conclude that reactions involving the MgO backfill material, brines, and carbon dioxide will be rapid and will produce the geochemical conditions expected for chemical equilibrium between brucite and hydromagnesite and/or magnesite.

The estimates of the rates of magnesium carbonate formation made from experimental results are generally consistent with observations of their occurrence in nature. Overall, occurrences of nesquehonite are rare and found primarily in young deposits from precipitation from meteoric waters (Fischbeck and Muller, 1971, p. 87; Marschner, 1969, p. 1119 ...). Natural occurrences of hydromagnesite and magnesite are more common and typically found in saline environments, such as sabkhas, evaporites, and alkaline lake sediments (Irion and Muller, 1968, p. 1309, 1310; Renaut and Long, 1989, p. 239; Stamatakis, 1995, p. B179 ...). A good example of the occurrence of magnesium carbonates is provided by Stamatakis (1995, p. B179-B181), who has described a Quaternary age deposit of hydromagnesite, magnesite, dolomite [$CaMg(CO_3)_2$] and huntite [$Mg_3Ca(CO_3)_4$] in northern Greece. The genetic model developed by Stamatakis (1995, p. B183, B184) indicates that the magnesium carbonates formed as magnesium-enriched spring waters, derived from sources in mafic and ultramafic rocks, flowed into an enclosed basin and evaporated. As the solutions became more saline and alkaline with evaporation, the magnesium carbonates were precipitated from solution. It is important to note, however, that while these precipitates include hydromagnesite and magnesite, nesquehonite was not found in the deposit. This finding is consistent with the short-lived nature of nesquehonite in saline environments as a result of its relatively rapid rate of conversion to hydromagnesite and magnesite. This field observation is consistent with the experimental results.

Based on the above discussion, the sequence of events resulting from brine infiltration and reaction with the MgO backfill in the repository may be conceptualized by the following reactions, in order:

- Rapid reaction (hours to days) between the brine and MgO to produce brucite.
- Rapid carbonation (hours to days) of the brucite to produce nesquehonite and possibly hydromagnesite.
- Rapid conversion (days to weeks) of the nesquehonite to hydromagnesite.
- Slow conversion (few hundred to few thousands of years) of the hydromagnesite to magnesite.

The available rate data indicate that some portion, perhaps all, of the hydromagnesite will be converted to magnesite over the 10,000-year period for repository performance. The exact time required for complete conversion has not been established for all chemical conditions. However, the available laboratory and field data clearly indicate that magnesite formation takes from a few hundred to, perhaps, a few thousand years. Thus, the early repository conditions can be best represented by the equilibrium between brucite and hydromagnesite. These conditions will eventually evolve to equilibrium between brucite and magnesite. In fact, the Salado Formation contains magnesite in its mineral assemblage, hence its brine is saturated with respect to magnesite solubility..., indicating that conditions conducive to magnesite formation from reactions between brine and the MgO backfill are already present in the repository surroundings. This overall conceptualization is also consistent with the thermodynamic approach used to model the actinide source term, in that solution conditions would be expected to be controlled by the metastable hydromagnesite until it is completely converted to magnesite.

In summary, information from the SNL experimental studies, experimental studies reported in the scientific literature, observations of natural occurrences of magnesium carbonates, and peer review panel findings, overwhelmingly indicate that nesquehonite will not persist in the repository environment, but will rapidly alter to hydromagnesite or hydromagnesite-like solids. The hydromagnesite is eventually expected to alter to magnesite, but this process could take up to a few thousand years. Consequently, EPA considers the conceptual model most appropriate for representing the effects of reactions between brines and the MgO backfill to be the equilibrium chemical conditions imposed by the presence of hydromagnesite."

2.4.3 EPA Responses to Comments Dealing with the Oxidation State of Pu

A number of comments in EEG-77 raise questions arising from recent experiments dealing with the oxidation state of Pu in WIPP brines and solid phases. These comments are pertinent to the question of whether the oxidation state analogy is valid, because adopting Th(IV) as a suitable analog for Pu in the CCA PA is based on the assumption that Pu exists only in the +4 oxidation state. A recent report (USEPA 2000) addresses a number of the Pu oxidation-state issues raised in EEG-77. These issues include:

- the formation of PuO_{2+x} in the repository rather than PuO_2 will cause higher plutonium solubilities than predicted by the source term model,

- the formation of magnesio-ferrite on the surfaces of the steel mesh in the STTP experiments indicates that iron corrosion may not create reducing conditions in the repository, and

- the formation of Pu(V) and Pu(VI) in the STTP experiments indicates that these plutonium oxidation states will persist in the repository and lead to increased mobility of plutonium.

In response to the first issue, EPA notes (USEPA 2000) that the experimental data on PuO_{2+x} formation presented by Haschke et al. (2000) indicates that PuO_{2+x} will form only in the presence of oxygen. Because the long-term repository environment will be anoxic, PuO_{2+x} will not form under long-term conditions. Thus, the formation of PuO_{2+x} is not expected to affect equilibrium plutonium solubilities predicted by the source term model.

With regard to the second issue, EPA notes (USEPA 2000) that the available iron corrosion data obtained with WIPP brines (Telander and Westerman, 1997; Felmy, and others, 2000) indicate that coatings may form on iron during corrosion. However, the coatings in these studies were not found to be adherent. Available corrosion data at the pH values relevant to the WIPP repository indicate that corrosion will occur, although higher pH values can slow the corrosion rate (Telander and Westerman, 1997). Available natural analogue data for iron corrosion are similar to the assumed corrosion rates in the WIPP CCA PA. Thus, iron corrosion is expected to occur in the repository and generate reducing conditions. In addition to iron corrosion, biodegradation of organic materials in the repository (cellulosics, plastics, and rubber) will consume oxygen and contribute to a long-term reducing environment.

EPA's response to the third issue (USEPA 2000) stresses important differences between the STTP experiments and the WIPP repository environment. These differences include evidence that the tests were probably not at equilibrium, the possibility that iron was encapsulated and could not influence the redox state of the experimental solution, the absence of MgO (in all but one experiment), and the high plutonium concentrations in the pyrochemical salt waste. In addition, it is possible that the Pu(V) and Pu(VI) that was observed in a few experiments may have formed after samples were removed from the experiments, but before analysis was carried out because of the one-to-two-day sample holding times. Each of these differences between the STTP experiments and the WIPP repository environment are summarized in the following paragraphs, extracted from USEPA (2000).

2.4.3.a "The conceptual model developed to describe the actinide source term is based on conditions of chemical equilibrium (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b). Under equilibrium conditions in the repository, redox conditions will be controlled by reaction of brine with iron in the waste drums, and will also be influenced by the reducing effects of microbial degradation of organic materials in the waste (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). The net result of the iron corrosion and biodegradation processes will be to produce a reducing environment in the repository (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). Because of this reducing environment, the source term conceptual model predicts that only plutonium(III) and plutonium(IV) will be present at equilibrium in the repository (USDOE, 1996b, USEPA, 1998a; USEPA, 1998b). The STTP experiments with measurable plutonium(V) and plutonium(VI) concentrations in solution were probably not at equilibrium because of the complex nature of the materials used in the

tests, the relatively short duration of the tests, and the transient appearance of plutonium(V) and plutonium(VI) in the tests.

Examination of reaction products from two pyrochemical salt tests indicated that the solids formed a mass encapsulating the iron mesh, and this effect may have prevented interaction between the iron and solution (LANL, 2000b). A similar effect probably will not occur in the repository, where iron in the containers will surround the waste. Thus, although iron may not have influenced redox conditions in the STTP tests because of its encapsulation by waste, this type of encapsulation probably will not occur in the repository.

The pyrochemical salt waste used in the experiments that contained plutonium(V) and plutonium(VI) in solution had relatively high plutonium concentrations (LANL, 2000b). These high plutonium concentrations likely caused radiolysis that produced peroxide and hypochlorites as well as hydrogen (H_2) in solution (LANL, 2000b). Peroxide and hypochlorites typically react quickly, whereas hydrogen reacts more slowly. In the repository, these peroxide and hypochlorite species are expected to rapidly react with iron in the waste containers. However, because iron may not have been available in the STTP tests to react with the peroxide and hypochlorite, the oxidizing species were able to react with plutonium and formed oxidized plutonium species. Thus, brine radiolysis in the absence of iron may have occurred in the tests, but this process is not expected to occur in the repository.

The transient formation of plutonium(V) and plutonium(VI) in the WIPP repository was considered in the development of the conceptual model of the actinide source term (USDOE, 1996b, USEPA, 1998a; 1998b). However, because of reducing conditions in the repository, plutonium(V) or plutonium(VI) that forms in the repository will be reduced to plutonium(III) or plutonium(IV) as the system approaches equilibrium. Conditions in the STTP experiments were oxidizing, based on the Eh and gas head space data provided (LANL, 2000b; Mendoza, 2000; Runde, 2000). In addition, because MgO was not present in the STTP experiments, pH and carbon dioxide partial pressures also differed in the STTP experiments from conditions predicted for the repository. Finally, the period of time between removal of samples from the STTP experiments and their filtration and analysis could have affected the results of the oxidation state analyses. Therefore, the STTP experimental data do not accurately represent long-term, equilibrium repository conditions and observation of plutonium(V) and plutonium(VI) in these experiments does not contradict the source term conceptual model (USDOE, 1996b)."

2.5 Issue Resolution Status

2.5.1 Actinide Analogy

EEG's comments call into question the validity of the actinide analogy as a reasonable approximation

to the solubility and speciation behavior of the actinide elements in complex brines. Specifically, EEG contends that Th(IV) is a poor analog for Pu because Pu can exist in oxidation states other than +4 depending on "details of the chemical environment", whereas "Th can only exist in geologic systems as Th(IV)" (Comment 2.2.b). EEG suggests that a situation could exist at WIPP where, for example, a Pu(IV) solid phase is in contact with a brine that is sufficiently oxidizing to stabilize Pu(V) or Pu(VI). If so, the Th(IV) analogy for Pu(IV) would be invalid because Pu exists in different oxidation states in the solid and aqueous phases, whereas analogous behavior among Th solids and aqueous species is not possible.

EEG's reasoning on this issue is technically correct, but inconsistent with the fact that the actinide analogy, as used in the CCA source term model, is based on the assumption that the chemical environment at WIPP is such that all actinide aqueous species and solids exist in either the +3, +4 or +5 oxidation state. As noted by EEG, the analogy does not extended to cases where the oxidation state of an actinide differs in the solid and aqueous phase. It is conceivable that a Pu(IV) solid could coexist with brines where the stable oxidation state of Pu is +3 (roughly at pH < 8.5) or, less likely, +5 or +6 (in strongly oxidizing solutions). In such cases, the Th(IV) analogy for Pu(IV) would be inappropriate. It should be emphasized, however, that under conditions expected in the WIPP repository of strongly reducing conditions (controlled by corrosion of the waste containers and degradation of organics) and pH in the range 8.5 to 10 (controlled by reaction of brine with MgO backfill), Pu in aqueous and solid phases will exist only in the +4 oxidation state. The Th(IV) analogy for Pu is therefore valid for the expected chemical environment at WIPP.

With this conclusion in mind, EPA anticipates that the actinide analogy may nevertheless continue to provoke criticism because it may not be valid over the full range of possible, however unlikely, environmental conditions that could occur at WIPP. For this reason, EEG's proposal to directly calculate actinide solubilities using values for solubility and complex ion formation contained in the peer-reviewed data compilation by OECD/NEA may be a useful approach for establishing limits to the validity of the analogy with respect to a range of probable-to-improbable repository conditions. Alternative techniques to the Pitzer formalism for calculating activity coefficients in concentrated electrolyte solutions might also be usefully employed in this approach. These techniques are less accurate than the Pitzer approach, but they are easier to use and provide reasonable estimates of activity coefficients as a function of the ionic strength of the solution.

With regard to comments based on results of the STTP experiments, EEG suggests that Th(IV) is not a valid analog for the solubility behavior of the +4 actinides because Th concentrations are on occasion lower to much lower than those of Pu, Np and U (Comments 2.2.f, 2.2.g and 2.2.i). EEG assumes that the measured actinide concentrations are controlled by solubility equilibrium, but no analysis of the experimental data is offered to support this contention. Moreover, actinide concentrations may be influenced by many experimental variables, none of which were actually controlled in the experimental systems. The simple observation that Th concentrations are lower than those for Pu, Np or U in these experimental solutions is therefore not a reasonable basis for suggesting that the Th analogy for these actinides is invalid.

2.5.2 MgO Backfill

Despite EEG's contention that "... it is not known how long the early reaction product, nesquehonite, will persist." (Item 2.3.b), both experimental and field investigations by DOE and others provide convincing evidence that nesquehonite will persist for only a short period of time - from days to weeks (Section 2.4.b). EEG does not provide any compelling evidence to suggest this conclusion is seriously in error. Also, EEG's contention that "...the behavior of MgO in brines has far-reaching implications and merits its own investigation" (Comment 2.2.c) is unsupported by any direct evidence indicating that MgO backfill will not behave as expected in the repository.

2.5.3 Oxidation State of Pu

Based on the discussion in Section 2.4.3, EPA appears to have adequately addressed all the comments in EEG-77 dealing with the oxidation state of Pu in solid oxides (Comment 2.2.d) and the detection of Pu(V) and Pu(VI) in some STTP experimental solutions (Comments 2.2.e, 2.2.h and 2.2.i) (USEPA 2000). To summarize EPA's position, the STTP experimental data do not appear to accurately represent long-term, equilibrium repository conditions, and observation of Pu(V) and Pu(VI) in these experiments does not contradict the source term conceptual model. Moreover, because the repository environment will be anoxic, PuO_{2+x} will not form in the repository under conditions expected over the long term.

3 ISSUE 3: UNCERTAINTY RANGES FOR SOLUBILITY ESTIMATES

3.1 Description of the Issue

EEG contends that estimates of uncertainties in Pu(IV) and U(VI) solubilities, and evaluations of the potential for Pu to exist in the +5 or +6 oxidation states in WIPP brines, should be carried out on the basis of equilibrium calculations that are constrained by thermochemical data for the relevant aqueous species and solids. EEG asserts that DOE's approach for estimating uncertainties in the solubilities of the An(IV) actinides is inadequate because it is constrained solely by comparisons between calculated and measured solubilities for the +3 actinides and lanthanides. EEG also notes that the CCA source term does not include a solubility model for U(VI) because a suitable model has not yet been developed by DOE. EEG suggests that an extensively peer-reviewed thermodynamic database for the actinide elements developed under the auspices of the NEA/OECD, and an alternative approach to that used by DOE for calculating ionic activities in concentrated solutions, could be used to directly estimate the solubilities and associated uncertainties of all An(III), An(IV) An(V) and An(VI) actinides, and to assess the potential for Pu to exist in the +5 or +6 oxidation states in WIPP brines.

3.2 Summary of EEG Comments in EEG-77 Addressing ISSUE 3

3.2.a "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." (2nd bullet, p. 5).

3.2.b "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." (3rd bullet, p. 5).

3.2.c "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. ...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." (3rd para., p. 5).

3.2.d "There has been no evaluation by EPA of the thermodynamic properties data used in the database for the solubility calculations. ..." (4th para., p. 5).

3.2.e "...concerns about the use of the FMT computer code have been documented previously. Rather than revisit that conceptual model and computer code, this report [EEG-77] 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 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. ..." (3rd para., p. 9).

3.2.f "The uncertainty range used by DOE for solubility estimates attracted several criticisms that were discussed in the EPA response to comments. ...EPA stated that in the uncertainty analysis *"solubility data for the 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...." (2nd para., p. 11).

3.2.g "This position ...[to omit an An(VI) solubility model in the CCA source term]... 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 ..., and that the work accomplished by early 1996 ...[to develop an An(VI) solubility model]... under contract to WIPP appears to have as sound a footing as the database for Th(IV) used as a model for all An(IV) species". (4th para., p. 29).

3.2.h "While EPA seems to have understood the limitations of the uncertainty analysis conducted by DOE, they conclude that *"the experimental procedures for determining the solubilities of +IV actinide solids are not substantially different from those used to determine the solubilities 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..."*. 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 the data. Unfortunately, it is the solution chemistry of the An(IV) elements that presents the difficulties, not the methods used in the analysis." (4th para., p. 30).

3.3.i "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 species, such as are frequently encountered with the An(IV) elements, there are significant uncertainties in the estimation of the Pitzer parameters. ..." (1st para., p. 31).

3.3 EEG's Recommendations to Resolve ISSUE 3

EEG recommends that DOE should construct a thermodynamic database for U and Pu that is based on a database for the actinide and other elements developed, and periodically revised and updated, by the OECD/NEA. It is also recommended by EEG that the so-called SIT method, rather than the Pitzer approach, be used to calculate ionic activities in concentrated salt solutions. Predictive calculations using the thermodynamic database and the SIT approach are then recommended to simulate conditions in the STTP experiments that showed high Pu and U concentrations. EEG indicates that this would provide guidance for improvement of the database.

3.4 EPA's Previous Responses to Comments Related to ISSUE 3

3.4.1 EPA Responses to Comments on Solubility Estimates

The following paragraphs are from EPA's responses to Comments 6.EE.1 through 6.EE.6 dealing with uncertainties in solubility estimates [see USEPA (1998a)].

3.4.1.a "The Fracture Matrix Transport (FMT) code solves chemical equilibrium problems using the Pitzer activity coefficient formalism. The Pitzer approach is the most accurate method for calculating activity coefficients for ionic species under conditions of high ionic strength as found in the WIPP brines. The FMT model computes activities and concentrations of constituents in brine solutions based on thermodynamic data and Pitzer parameters ... for the following major components; hydrogen, oxygen, sodium, potassium, magnesium, calcium, chlorine, sulfur, carbon, boron, bromine, chlorate, phosphorus. This database has been augmented to include data for Am(III), Th(IV), and Np(V) which are relevant to use of FMT at WIPP. Positions in the database exist for U(VI) species, but no data actually exist in the database for these species, and consequently the FMT code is not used to model uranium chemistry.

For implementation in the PA, the FMT code is used to calculate the concentrations of Am(III), Th(IV), and Np(V) from the solubilities of specified actinide solids under conditions of chemical equilibrium. The code is not actually used for transport calculations as might be implied from its name. The effects on chemical conditions caused by equilibrium with specific solid phases part of the database are also included in the FMT calculation scheme. This capability is important for determining the effects of specific reactions, such as between magnesium hydroxide and magnesium carbonates, that are expected to be important for controlling pH and $CO_2(g)$ fugacity in the repository -- i.e., parameters that strongly affect the solubilities of actinide solids. The FMT model is not used for calculating redox equilibria. Instead, actinides are specified to exist completely in a single oxidation state, i.e., Am(III), Th(IV), and Np(V). Using oxidation state analogies, the results for these actinides are extrapolated to Pu(III), Np(IV), U(IV), and Pu(IV).

A fundamental precept of the representation of the repository environment in the performance assessment is that the actinide source term can be described by chemical equilibrium processes. The FMT code is a model of chemical equilibrium as applied to actinide chemistry that incorporates the Pitzer approach for calculating activity coefficients relevant to the high ionic strength conditions present in the Salado and Castile brines. This conceptualization is summarized in Appendix SOTERM".

3.4.1.b "In summary, the chemical equilibrium concept as applied to the repository environment involves the following assumptions:

- The system of brine and wastes is well-mixed [Appendix SOTERM].

- The brine composition entering the repository is constant with time. [Appendix SOTERM]

- The brines are in chemical equilibrium with the common minerals found in the Salado and Castile formations (e.g., halite and anhydrite). [Appendix SOTERM ...]

- The brine pH (or pcH) and fugacity of $CO_2(g)$ will be buffered to specific values by the equilibrium between brucite [$Mg(OH)_2$] and magnesite [$MgCO_3$] as a result of brine interactions with the MgO backfill material. [Appendix SOTERM ...]

- The concentrations of actinides released to the brines can be represented by the experimentally determined solubilities of the actinide-bearing solids expected to form under the prevailing solution conditions. [Appendix SOTERM ....]

- The effects of redox reactions can be adequately represented by assuming dominant valence states for the actinides expected to be stable under the reducing conditions of the repository, where reducing conditions are generated from the consumption of oxygen by decaying organic material and ferrous metals. [Appendix SOTERM]

- Oxidation state analogies can be used to represent the concentrations of actinides for which solid-phase solubility data are not available or inadequate, i.e., Am(III) is used to represent Pu(III), where Th(IV) is used to represent Np(IV), Pu(IV) and U(IV), etc. [Appendix SOTERM ...]

- Solubility and aqueous speciation data are inadequate to model U(VI), hence a model solubility of 8.8×10^{-6} M (in Castile brine) is used to provide a conservative representation of expected U(VI) concentrations based on a variety of empirical measurements. [Appendix SOTERM ...]

- The uncertainty in predicted solubilities of actinide solids can be represented by the deviances between solubilities determined in individual experimental studies and concentrations predicted by models used to fit experimental data to aqueous speciation schemes. [Appendix SOTERM ...]

- The Pitzer approach provides the best representation of activity coefficient for the high ionic strength solutions found in the Salado and Castile brines. [Appendix SOTERM ...]

To determine conditions of chemical equilibrium for a solid/solution system, the FMT model uses the criteria of minimization of free energy given the constraints of the chemical composition of the fluid in question and principles of mass and charge balance and mass action defined for individual chemical reactions. [FMT User's Manual] This method is entirely consistent with the definition of chemical equilibrium as being the state of lowest free energy. The equations of mass action and mass balance are defined in the

thermodynamic database of the FMT model in terms of specific reactions for aqueous speciation and solid phase solubility. [FMT User's Manual]

The FMT model was designed for application to high ionic strength solutions and contains algorithms that incorporate the Pitzer approach to calculating activity coefficients for dissolved species .... These databases were developed for representing chemical equilibrium in the high ionic strength solutions found in evaporative lakes and are directly applicable to representing chemical reactions in the high ionic strength brines of the Salado and Castile formations."

3.5 Issue Resolution Status

According to EEG, EPA's previous responses to comments related to ISSUE 3, as summarized in Section 3.4, do not adequately address all of EEG's concerns on this issue. EEG maintains that the chemical model for the actinides incorporated in the FMT code is not appropriate for evaluating uncertainty ranges for solubilities used in the CCA source term. As noted in the 3rd paragraph, page 9 of EEG-77, EEG proposes to move beyond further discussion of the conceptual model and numerical techniques incorporated in FMT and to adopt two new approaches to address their concerns:

1. Deal with the uncertainty issue by generating experimental data for Pu in WIPP-relevant brines, and

2. Use the NEA/OECD thermochemical database for the actinides, and the Specific Ion Interaction Theory (SIT), instead of the Pitzer approach currently employed by DOE, to calculate ionic activities in concentrated solutions.

EEG contends that these two tasks together would provide the basis for developing reliable models of actinide speciation-solubility behavior, and that such models are needed to provide credible bounds on uncertainties in actinide solubilities.

EEG's proposed approach is a significant departure from that used by DOE to support the CCA PA. Although the proposal may have merit, it raises a number of issues that should be considered carefully:

1. EEG's approach would require direct experimental investigation of the solubility and speciation behavior of Pu (and presumably other actinides) in "WIPP-relevant" brines. It is questionable, however, whether such work is actually necessary. DOE's current strategy invoking analogous chemical behavior between Pu(IV) and Th(IV) appears to provide credible upper bounds on Pu solubilities. EEG contends, however, that this "actinide analogy argument" (ISSUE 2) may be invalid for certain, remotely possible, environmental conditions at WIPP. If so, then

experimental investigation of plutonium's speciation-solubility behavior under these specific environmental conditions may be warranted.

2. EEG's proposal to use the NEA/OECD database raises the question whether this database is reliable and relevant for conditions at WIPP, and whether the database has been developed, and controlled, to applicable NQA standards.

3. Although the SIT method is widely acknowledged to be easier to use than the Pitzer approach, it is also less accurate. This raises the question whether the SIT method is suitable for WIPP-relevant brines, and, if so, whether its ease of use justifies the associated losses in accuracy.

The first issue is also addressed in Section 2.5.1, where it is noted that if chemical conditions at WIPP are moderately alkaline and strongly reducing, as expected, then the Th(IV) analogy for Pu(IV) is appropriate. In such case, there would be no need to adopt the approach proposed by EEG. In other words, direct experimental investigation of Pu speciation-solubility behavior in "WIPP-relevant" brines is unnecessary as long as the brines are representative of environmental conditions expected at WIPP. As noted earlier (Section 2.5.1), however, the actinide analogy may not be valid if conditions are oxidizing or relatively acidic - conditions that are not representative of WIPP. EEG's proposed approach may therefore have some limited use in providing a chemical model for Pu (and other actinides) that could be used to evaluate associated effects on solubilities resulting from such unexpected, but remotely possible, conditions. Before committing the considerable resources in terms of time and costs to carry out such work, however, it would seem prudent to explore whether alternative approaches to estimating defensible upper bounds on Pu solubilities under these specific conditions exist, or can be developed. Such approaches could be based on the existing thermochemical database for the actinides developed by the NEA/OECD.

If necessary, the second issue could be addressed by a thorough review of the NEA/OECD database, focusing in particular on whether the database is reliable, and relevant with respect to WIPP disposal conditions. The issue of reliability entails consideration of the level of internal consistency of the database, as well as evaluation of the fundamental approach and associated mathematical techniques used to retrieve values of thermodynamic properties from basic experimental data. The issue of relevance of the database addresses whether thermochemical data are available for all actinide-bearing solids and aqueous species that are expected to be important in WIPP brines. It is possible, if not highly likely, that such data may be unavailable in the NEA/OECD database for some important, WIPP-relevant aqueous species. If so, can such gaps in the database be filled without significant impact on the reliability (i.e. internal consistency) of the database?

The third issue could also be addressed by thorough review of the SIT method, focusing on the relative strengths and limitations of this approach compared to the Pitzer approach. The basic difference between the approaches is that the former uses an extended Debye-Huckel expression for activity coefficients parameterized in terms of ionic charge and ionic strength, whereas the latter uses a medium-dependent expression parameterized in terms of empirically derived virial coefficients

appearing in the Pitzer equations. The Pitzer model can provide calculations of log K values that are practically within experimental accuracy, but the large number of parameters in this model and their strong interrelations and correlations, makes it difficult to apply the model to systems where complex formation is important. The SIT model, on the other hand, uses a much smaller number of regression parameters, resulting in less accurate calculation of log K values, but ion-pairing and complex formation are explicitly accounted for in this model. Ultimately, the question of whether the SIT method can be used in place of the Pitzer approach for actinide speciation-solubility calculations appropriate for WIPP brines may depend on the purpose of the calculation. If the calculations are for bounding purposes, or perhaps to support performance assessment models, then the accuracy of the Pitzer approach may not be as important as the ability of the SIT method to account for ion-pairing and complex formation, as long as the associated loss in accuracy is acceptable.

In summary, EEG's proposed approach involving direct experimental investigation of plutonium's speciation-solubility behavior in WIPP-relevant brines, adoption of the NEA/OECD thermochemical database for the actinides, and consideration of alternative techniques for calculation of ionic activities in concentrated brines, differs significantly from the approach used by DOE to support the WIPP CCA. EEG's approach may have limited use in providing bounding estimates of Pu solubilities under WIPP disposal conditions that are unexpected, though remotely possible. More generally, the approach could in principle be used to calculate actinide solubilities directly, eliminating the present need to estimate upper bounds based on analogous chemical behavior. It should be emphasized, however, that there is no compelling reason to question the validity of the actinide analogy argument under expected disposal conditions at WIPP, and that associated upper-bound estimates of actinide solubilities are adequate for performance assessment purposes. If necessary, the merits of EEG's proposed approach should be further assessed on the basis of a thorough review of issues pertaining to the adoption of the NEA/OECD thermochemical database, and possible uses of alternative methods for calculation of ionic activities in WIPP brines.

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10 to 28°C in a simulated sedimentary column indicates that the formation and recrystallization reactions involving magnesium carbonates occur rapidly (Davies et al.,1977, p. 188, 189, 197,198). The results of these experiments provide adequate information to conclude that reactions involving the MgO backfill material, brines, and carbon dioxide will be rapid and will produce the geochemical conditions expected for chemical equilibrium between brucite and hydromagnesite and/or magnesite.

The estimates of the rates of magnesium carbonate formation made from experimental results are generally consistent with observations of their occurrence in nature. Overall, occurrences of nesquehonite are rare and found primarily in young deposits from precipitation from meteoric waters (Fischbeck and Muller, 1971, p. 87; Marschner, 1969, p. 1119 ...). Natural occurrences of hydromagnesite and magnesite are more common and typically found in saline environments, such as sabkhas, evaporites, and alkaline lake sediments (Irion and Muller, 1968, p. 1309, 1310; Renaut and Long, 1989, p. 239; Stamatakis, 1995, p. B179 ...). A good example of the occurrence of magnesium carbonates is provided by Stamatakis (1995, p. B179-B181), who has described a Quaternary age deposit of hydromagnesite, magnesite, dolomite [$CaMg(CO_3)_2$] and huntite [$Mg_3Ca(CO_3)_4$] in northern Greece. The genetic model developed by Stamatakis (1995, p. B183, B184) indicates that the magnesium carbonates formed as magnesium-enriched spring waters, derived from sources in mafic and ultramafic rocks, flowed into an enclosed basin and evaporated. As the solutions became more saline and alkaline with evaporation, the magnesium carbonates were precipitated from solution. It is important to note, however, that while these precipitates include hydromagnesite and magnesite, nesquehonite was not found in the deposit. This finding is consistent with the short-lived nature of nesquehonite in saline environments as a result of its relatively rapid rate of conversion to hydromagnesite and magnesite. This field observation is consistent with the experimental results.

Based on the above discussion, the sequence of events resulting from brine infiltration and reaction with the MgO backfill in the repository may be conceptualized by the following reactions, in order:

- Rapid reaction (hours to days) between the brine and MgO to produce brucite.
- Rapid carbonation (hours to days) of the brucite to produce nesquehonite and possibly hydromagnesite.
- Rapid conversion (days to weeks) of the nesquehonite to hydromagnesite.
- Slow conversion (few hundred to few thousands of years) of the hydromagnesite to magnesite.

The available rate data indicate that some portion, perhaps all, of the hydromagnesite will be converted to magnesite over the 10,000-year period for repository performance. The exact time required for complete conversion has not been established for all chemical conditions. However, the available laboratory and field data clearly indicate that magnesite formation takes from a few hundred to, perhaps, a few thousand years. Thus, the early repository conditions can be best represented by the equilibrium between brucite and hydromagnesite. These conditions will eventually evolve to equilibrium between brucite and magnesite. In fact, the Salado Formation contains magnesite in its mineral assemblage, hence its brine is saturated with respect to magnesite solubility..., indicating that conditions conducive to magnesite formation from reactions between brine and the MgO backfill are already present in the repository surroundings. This overall conceptualization is also consistent with the thermodynamic approach used to model the actinide source term, in that solution conditions would be expected to be controlled by the metastable hydromagnesite until it is completely converted to magnesite.

In summary, information from the SNL experimental studies, experimental studies reported in the scientific literature, observations of natural occurrences of magnesium carbonates, and peer review panel findings, overwhelmingly indicate that nesquehonite will not persist in the repository environment, but will rapidly alter to hydromagnesite or hydromagnesite-like solids. The hydromagnesite is eventually expected to alter to magnesite, but this process could take up to a few thousand years. Consequently, EPA considers the conceptual model most appropriate for representing the effects of reactions between brines and the MgO backfill to be the equilibrium chemical conditions imposed by the presence of hydromagnesite."

2.4.3 EPA Responses to Comments Dealing with the Oxidation State of Pu

A number of comments in EEG-77 raise questions arising from recent experiments dealing with the oxidation state of Pu in WIPP brines and solid phases. These comments are pertinent to the question of whether the oxidation state analogy is valid, because adopting Th(IV) as a suitable analog for Pu in the CCA PA is based on the assumption that Pu exists only in the +4 oxidation state. A recent report (USEPA 2000) addresses a number of the Pu oxidation-state issues raised in EEG-77. These issues include:

- the formation of PuO_{2+x} in the repository rather than PuO_2 will cause higher plutonium solubilities than predicted by the source term model,

- the formation of magnesio-ferrite on the surfaces of the steel mesh in the STTP experiments indicates that iron corrosion may not create reducing conditions in the repository, and

- the formation of Pu(V) and Pu(VI) in the STTP experiments indicates that these plutonium oxidation states will persist in the repository and lead to increased mobility of plutonium.

In response to the first issue, EPA notes (USEPA 2000) that the experimental data on PuO_{2+x} formation presented by Haschke et al. (2000) indicates that PuO_{2+x} will form only in the presence of oxygen. Because the long-term repository environment will be anoxic, PuO_{2+x} will not form under long-term conditions. Thus, the formation of PuO_{2+x} is not expected to affect equilibrium plutonium solubilities predicted by the source term model.

With regard to the second issue, EPA notes (USEPA 2000) that the available iron corrosion data obtained with WIPP brines (Telander and Westerman, 1997; Felmy, and others, 2000) indicate that coatings may form on iron during corrosion. However, the coatings in these studies were not found to be adherent. Available corrosion data at the pH values relevant to the WIPP repository indicate that corrosion will occur, although higher pH values can slow the corrosion rate (Telander and Westerman, 1997). Available natural analogue data for iron corrosion are similar to the assumed corrosion rates in the WIPP CCA PA. Thus, iron corrosion is expected to occur in the repository and generate reducing conditions. In addition to iron corrosion, biodegradation of organic materials in the repository (cellulosics, plastics, and rubber) will consume oxygen and contribute to a long-term reducing environment.

EPA's response to the third issue (USEPA 2000) stresses important differences between the STTP experiments and the WIPP repository environment. These differences include evidence that the tests were probably not at equilibrium, the possibility that iron was encapsulated and could not influence the redox state of the experimental solution, the absence of MgO (in all but one experiment), and the high plutonium concentrations in the pyrochemical salt waste. In addition, it is possible that the Pu(V) and Pu(VI) that was observed in a few experiments may have formed after samples were removed from the experiments, but before analysis was carried out because of the one-to-two-day sample holding times. Each of these differences between the STTP experiments and the WIPP repository environment are summarized in the following paragraphs, extracted from USEPA (2000).

2.4.3.a "The conceptual model developed to describe the actinide source term is based on conditions of chemical equilibrium (USDOE, 1996b; USEPA, 1998a; USEPA, 1998b). Under equilibrium conditions in the repository, redox conditions will be controlled by reaction of brine with iron in the waste drums, and will also be influenced by the reducing effects of microbial degradation of organic materials in the waste (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). The net result of the iron corrosion and biodegradation processes will be to produce a reducing environment in the repository (USDOE, 1996b; USEPA, 1998a, USEPA, 1998b). Because of this reducing environment, the source term conceptual model predicts that only plutonium(III) and plutonium(IV) will be present at equilibrium in the repository (USDOE, 1996b, USEPA, 1998a; USEPA, 1998b). The STTP experiments with measurable plutonium(V) and plutonium(VI) concentrations in solution were probably not at equilibrium because of the complex nature of the materials used in the

tests, the relatively short duration of the tests, and the transient appearance of plutonium(V) and plutonium(VI) in the tests.

Examination of reaction products from two pyrochemical salt tests indicated that the solids formed a mass encapsulating the iron mesh, and this effect may have prevented interaction between the iron and solution (LANL, 2000b). A similar effect probably will not occur in the repository, where iron in the containers will surround the waste. Thus, although iron may not have influenced redox conditions in the STTP tests because of its encapsulation by waste, this type of encapsulation probably will not occur in the repository.

The pyrochemical salt waste used in the experiments that contained plutonium(V) and plutonium(VI) in solution had relatively high plutonium concentrations (LANL, 2000b). These high plutonium concentrations likely caused radiolysis that produced peroxide and hypochlorites as well as hydrogen (H_2) in solution (LANL, 2000b). Peroxide and hypochlorites typically react quickly, whereas hydrogen reacts more slowly. In the repository, these peroxide and hypochlorite species are expected to rapidly react with iron in the waste containers. However, because iron may not have been available in the STTP tests to react with the peroxide and hypochlorite, the oxidizing species were able to react with plutonium and formed oxidized plutonium species. Thus, brine radiolysis in the absence of iron may have occurred in the tests, but this process is not expected to occur in the repository.

The transient formation of plutonium(V) and plutonium(VI) in the WIPP repository was considered in the development of the conceptual model of the actinide source term (USDOE, 1996b, USEPA, 1998a; 1998b). However, because of reducing conditions in the repository, plutonium(V) or plutonium(VI) that forms in the repository will be reduced to plutonium(III) or plutonium(IV) as the system approaches equilibrium. Conditions in the STTP experiments were oxidizing, based on the Eh and gas head space data provided (LANL, 2000b; Mendoza, 2000; Runde, 2000). In addition, because MgO was not present in the STTP experiments, pH and carbon dioxide partial pressures also differed in the STTP experiments from conditions predicted for the repository. Finally, the period of time between removal of samples from the STTP experiments and their filtration and analysis could have affected the results of the oxidation state analyses. Therefore, the STTP experimental data do not accurately represent long-term, equilibrium repository conditions and observation of plutonium(V) and plutonium(VI) in these experiments does not contradict the source term conceptual model (USDOE, 1996b)."

2.5 Issue Resolution Status

2.5.1 Actinide Analogy

EEG's comments call into question the validity of the actinide analogy as a reasonable approximation

to the solubility and speciation behavior of the actinide elements in complex brines. Specifically, EEG contends that Th(IV) is a poor analog for Pu because Pu can exist in oxidation states other than +4 depending on "details of the chemical environment", whereas "Th can only exist in geologic systems as Th(IV)" (Comment 2.2.b). EEG suggests that a situation could exist at WIPP where, for example, a Pu(IV) solid phase is in contact with a brine that is sufficiently oxidizing to stabilize Pu(V) or Pu(VI). If so, the Th(IV) analogy for Pu(IV) would be invalid because Pu exists in different oxidation states in the solid and aqueous phases, whereas analogous behavior among Th solids and aqueous species is not possible.

EEG's reasoning on this issue is technically correct, but inconsistent with the fact that the actinide analogy, as used in the CCA source term model, is based on the assumption that the chemical environment at WIPP is such that all actinide aqueous species and solids exist in either the +3, +4 or +5 oxidation state. As noted by EEG, the analogy does not extended to cases where the oxidation state of an actinide differs in the solid and aqueous phase. It is conceivable that a Pu(IV) solid could coexist with brines where the stable oxidation state of Pu is +3 (roughly at pH < 8.5) or, less likely, +5 or +6 (in strongly oxidizing solutions). In such cases, the Th(IV) analogy for Pu(IV) would be inappropriate. It should be emphasized, however, that under conditions expected in the WIPP repository of strongly reducing conditions (controlled by corrosion of the waste containers and degradation of organics) and pH in the range 8.5 to 10 (controlled by reaction of brine with MgO backfill), Pu in aqueous and solid phases will exist only in the +4 oxidation state. The Th(IV) analogy for Pu is therefore valid for the expected chemical environment at WIPP.

With this conclusion in mind, EPA anticipates that the actinide analogy may nevertheless continue to provoke criticism because it may not be valid over the full range of possible, however unlikely, environmental conditions that could occur at WIPP. For this reason, EEG's proposal to directly calculate actinide solubilities using values for solubility and complex ion formation contained in the peer-reviewed data compilation by OECD/NEA may be a useful approach for establishing limits to the validity of the analogy with respect to a range of probable-to-improbable repository conditions. Alternative techniques to the Pitzer formalism for calculating activity coefficients in concentrated electrolyte solutions might also be usefully employed in this approach. These techniques are less accurate than the Pitzer approach, but they are easier to use and provide reasonable estimates of activity coefficients as a function of the ionic strength of the solution.

With regard to comments based on results of the STTP experiments, EEG suggests that Th(IV) is not a valid analog for the solubility behavior of the +4 actinides because Th concentrations are on occasion lower to much lower than those of Pu, Np and U (Comments 2.2.f, 2.2.g and 2.2.i). EEG assumes that the measured actinide concentrations are controlled by solubility equilibrium, but no analysis of the experimental data is offered to support this contention. Moreover, actinide concentrations may be influenced by many experimental variables, none of which were actually controlled in the experimental systems. The simple observation that Th concentrations are lower than those for Pu, Np or U in these experimental solutions is therefore not a reasonable basis for suggesting that the Th analogy for these actinides is invalid.

2.5.2 MgO Backfill

Despite EEG's contention that "... it is not known how long the early reaction product, nesquehonite, will persist." (Item 2.3.b), both experimental and field investigations by DOE and others provide convincing evidence that nesquehonite will persist for only a short period of time - from days to weeks (Section 2.4.b). EEG does not provide any compelling evidence to suggest this conclusion is seriously in error. Also, EEG's contention that "...the behavior of MgO in brines has far-reaching implications and merits its own investigation" (Comment 2.2.c) is unsupported by any direct evidence indicating that MgO backfill will not behave as expected in the repository.

2.5.3 Oxidation State of Pu

Based on the discussion in Section 2.4.3, EPA appears to have adequately addressed all the comments in EEG-77 dealing with the oxidation state of Pu in solid oxides (Comment 2.2.d) and the detection of Pu(V) and Pu(VI) in some STTP experimental solutions (Comments 2.2.e, 2.2.h and 2.2.i) (USEPA 2000). To summarize EPA's position, the STTP experimental data do not appear to accurately represent long-term, equilibrium repository conditions, and observation of Pu(V) and Pu(VI) in these experiments does not contradict the source term conceptual model. Moreover, because the repository environment will be anoxic, PuO_{2+x} will not form in the repository under conditions expected over the long term.

3 ISSUE 3: UNCERTAINTY RANGES FOR SOLUBILITY ESTIMATES

3.1 Description of the Issue

EEG contends that estimates of uncertainties in Pu(IV) and U(VI) solubilities, and evaluations of the potential for Pu to exist in the +5 or +6 oxidation states in WIPP brines, should be carried out on the basis of equilibrium calculations that are constrained by thermochemical data for the relevant aqueous species and solids. EEG asserts that DOE's approach for estimating uncertainties in the solubilities of the An(IV) actinides is inadequate because it is constrained solely by comparisons between calculated and measured solubilities for the +3 actinides and lanthanides. EEG also notes that the CCA source term does not include a solubility model for U(VI) because a suitable model has not yet been developed by DOE. EEG suggests that an extensively peer-reviewed thermodynamic database for the actinide elements developed under the auspices of the NEA/OECD, and an alternative approach to that used by DOE for calculating ionic activities in concentrated solutions, could be used to directly estimate the solubilities and associated uncertainties of all An(III), An(IV) An(V) and An(VI) actinides, and to assess the potential for Pu to exist in the +5 or +6 oxidation states in WIPP brines.

3.2 Summary of EEG Comments in EEG-77 Addressing ISSUE 3

3.2.a "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." (2nd bullet, p. 5).

3.2.b "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." (3rd bullet, p. 5).

3.2.c "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. ...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." (3rd para., p. 5).

3.2.d "There has been no evaluation by EPA of the thermodynamic properties data used in the database for the solubility calculations. ..." (4th para., p. 5).

3.2.e "...concerns about the use of the FMT computer code have been documented previously. Rather than revisit that conceptual model and computer code, this report [EEG-77] 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 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. ..." (3rd para., p. 9).

3.2.f "The uncertainty range used by DOE for solubility estimates attracted several criticisms that were discussed in the EPA response to comments. ...EPA stated that in the uncertainty analysis *"solubility data for the 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...." (2nd para., p. 11).

3.2.g "This position ...[to omit an An(VI) solubility model in the CCA source term]... 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 ..., and that the work accomplished by early 1996 ...[to develop an An(VI) solubility model]... under contract to WIPP appears to have as sound a footing as the database for Th(IV) used as a model for all An(IV) species". (4th para., p. 29).

3.2.h "While EPA seems to have understood the limitations of the uncertainty analysis conducted by DOE, they conclude that *"the experimental procedures for determining the solubilities of +IV actinide solids are not substantially different from those used to determine the solubilities 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... "*. 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 the data. Unfortunately, it is the solution chemistry of the An(IV) elements that presents the difficulties, not the methods used in the analysis." (4th para., p. 30).

3.3.i "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 species, such as are frequently encountered with the An(IV) elements, there are significant uncertainties in the estimation of the Pitzer parameters. ..." (1st para., p. 31).

3.3 EEG's Recommendations to Resolve ISSUE 3

EEG recommends that DOE should construct a thermodynamic database for U and Pu that is based on a database for the actinide and other elements developed, and periodically revised and updated, by the OECD/NEA. It is also recommended by EEG that the so-called SIT method, rather than the Pitzer approach, be used to calculate ionic activities in concentrated salt solutions. Predictive calculations using the thermodynamic database and the SIT approach are then recommended to simulate conditions in the STTP experiments that showed high Pu and U concentrations. EEG indicates that this would provide guidance for improvement of the database.

3.4 EPA's Previous Responses to Comments Related to ISSUE 3

3.4.1 EPA Responses to Comments on Solubility Estimates

The following paragraphs are from EPA's responses to Comments 6.EE.1 through 6.EE.6 dealing with uncertainties in solubility estimates [see USEPA (1998a)].

3.4.1.a "The Fracture Matrix Transport (FMT) code solves chemical equilibrium problems using the Pitzer activity coefficient formalism. The Pitzer approach is the most accurate method for calculating activity coefficients for ionic species under conditions of high ionic strength as found in the WIPP brines. The FMT model computes activities and concentrations of constituents in brine solutions based on thermodynamic data and Pitzer parameters ... for the following major components; hydrogen, oxygen, sodium, potassium, magnesium, calcium, chlorine, sulfur, carbon, boron, bromine, chlorate, phosphorus. This database has been augmented to include data for Am(III), Th(IV), and Np(V) which are relevant to use of FMT at WIPP. Positions in the database exist for U(VI) species, but no data actually exist in the database for these species, and consequently the FMT code is not used to model uranium chemistry.

For implementation in the PA, the FMT code is used to calculate the concentrations of Am(III), Th(IV), and Np(V) from the solubilities of specified actinide solids under conditions of chemical equilibrium. The code is not actually used for transport calculations as might be implied from its name. The effects on chemical conditions caused by equilibrium with specific solid phases part of the database are also included in the FMT calculation scheme. This capability is important for determining the effects of specific reactions, such as between magnesium hydroxide and magnesium carbonates, that are expected to be important for controlling pH and $CO_2(g)$ fugacity in the repository -- i.e., parameters that strongly affect the solubilities of actinide solids. The FMT model is not used for calculating redox equilibria. Instead, actinides are specified to exist completely in a single oxidation state, i.e., Am(III), Th(IV), and Np(V). Using oxidation state analogies, the results for these actinides are extrapolated to Pu(III), Np(IV), U(IV), and Pu(IV).

A fundamental precept of the representation of the repository environment in the performance assessment is that the actinide source term can be described by chemical equilibrium processes. The FMT code is a model of chemical equilibrium as applied to actinide chemistry that incorporates the Pitzer approach for calculating activity coefficients relevant to the high ionic strength conditions present in the Salado and Castile brines. This conceptualization is summarized in Appendix SOTERM".

3.4.1.b "In summary, the chemical equilibrium concept as applied to the repository environment involves the following assumptions:

- The system of brine and wastes is well-mixed [Appendix SOTERM].

- The brine composition entering the repository is constant with time. [Appendix SOTERM]

- The brines are in chemical equilibrium with the common minerals found in the Salado and Castile formations (e.g., halite and anhydrite). [Appendix SOTERM ...]

- The brine pH (or pcH) and fugacity of $CO_2(g)$ will be buffered to specific values by the equilibrium between brucite [$Mg(OH)_2$] and magnesite [$MgCO_3$] as a result of brine interactions with the MgO backfill material. [Appendix SOTERM ...]

- The concentrations of actinides released to the brines can be represented by the experimentally determined solubilities of the actinide-bearing solids expected to form under the prevailing solution conditions. [Appendix SOTERM ...]

- The effects of redox reactions can be adequately represented by assuming dominant valence states for the actinides expected to be stable under the reducing conditions of the repository, where reducing conditions are generated from the consumption of oxygen by decaying organic material and ferrous metals. [Appendix SOTERM]

- Oxidation state analogies can be used to represent the concentrations of actinides for which solid-phase solubility data are not available or inadequate, i.e., Am(III) is used to represent Pu(III), where Th(IV) is used to represent Np(IV), Pu(IV) and U(IV), etc. [Appendix SOTERM ...]

- Solubility and aqueous speciation data are inadequate to model U(VI), hence a model solubility of 8.8×10^{-6} M (in Castile brine) is used to provide a conservative representation of expected U(VI) concentrations based on a variety of empirical measurements. [Appendix SOTERM ...]

- The uncertainty in predicted solubilities of actinide solids can be represented by the deviances between solubilities determined in individual experimental studies and concentrations predicted by models used to fit experimental data to aqueous speciation schemes. [Appendix SOTERM ...]

- The Pitzer approach provides the best representation of activity coefficient for the high ionic strength solutions found in the Salado and Castile brines. [Appendix SOTERM ...]

To determine conditions of chemical equilibrium for a solid/solution system, the FMT model uses the criteria of minimization of free energy given the constraints of the chemical composition of the fluid in question and principles of mass and charge balance and mass action defined for individual chemical reactions. [FMT User's Manual] This method is entirely consistent with the definition of chemical equilibrium as being the state of lowest free energy. The equations of mass action and mass balance are defined in the

thermodynamic database of the FMT model in terms of specific reactions for aqueous speciation and solid phase solubility. [FMT User's Manual]

The FMT model was designed for application to high ionic strength solutions and contains algorithms that incorporate the Pitzer approach to calculating activity coefficients for dissolved species.... These databases were developed for representing chemical equilibrium in the high ionic strength solutions found in evaporative lakes and are directly applicable to representing chemical reactions in the high ionic strength brines of the Salado and Castile formations."

3.5 Issue Resolution Status

According to EEG, EPA's previous responses to comments related to ISSUE 3, as summarized in Section 3.4, do not adequately address all of EEG's concerns on this issue. EEG maintains that the chemical model for the actinides incorporated in the FMT code is not appropriate for evaluating uncertainty ranges for solubilities used in the CCA source term. As noted in the 3rd paragraph, page 9 of EEG-77, EEG proposes to move beyond further discussion of the conceptual model and numerical techniques incorporated in FMT and to adopt two new approaches to address their concerns:

1. Deal with the uncertainty issue by generating experimental data for Pu in WIPP-relevant brines, and

2. Use the NEA/OECD thermochemical database for the actinides, and the Specific Ion Interaction Theory (SIT), instead of the Pitzer approach currently employed by DOE, to calculate ionic activities in concentrated solutions.

EEG contends that these two tasks together would provide the basis for developing reliable models of actinide speciation-solubility behavior, and that such models are needed to provide credible bounds on uncertainties in actinide solubilities.

EEG's proposed approach is a significant departure from that used by DOE to support the CCA PA. Although the proposal may have merit, it raises a number of issues that should be considered carefully:

1. EEG's approach would require direct experimental investigation of the solubility and speciation behavior of Pu (and presumably other actinides) in "WIPP-relevant" brines. It is questionable, however, whether such work is actually necessary. DOE's current strategy invoking analogous chemical behavior between Pu(IV) and Th(IV) appears to provide credible upper bounds on Pu solubilities. EEG contends, however, that this "actinide analogy argument" (ISSUE 2) may be invalid for certain, remotely possible, environmental conditions at WIPP. If so, then

experimental investigation of plutonium's speciation-solubility behavior under these specific environmental conditions may be warranted.

2. EEG's proposal to use the NEA/OECD database raises the question whether this database is reliable and relevant for conditions at WIPP, and whether the database has been developed, and controlled, to applicable NQA standards.

3. Although the SIT method is widely acknowledged to be easier to use than the Pitzer approach, it is also less accurate. This raises the question whether the SIT method is suitable for WIPP-relevant brines, and, if so, whether its ease of use justifies the associated losses in accuracy.

The first issue is also addressed in Section 2.5.1, where it is noted that if chemical conditions at WIPP are moderately alkaline and strongly reducing, as expected, then the Th(IV) analogy for Pu(IV) is appropriate. In such case, there would be no need to adopt the approach proposed by EEG. In other words, direct experimental investigation of Pu speciation-solubility behavior in "WIPP-relevant" brines is unnecessary as long as the brines are representative of environmental conditions expected at WIPP. As noted earlier (Section 2.5.1), however, the actinide analogy may not be valid if conditions are oxidizing or relatively acidic - conditions that are not representative of WIPP. EEG's proposed approach may therefore have some limited use in providing a chemical model for Pu (and other actinides) that could be used to evaluate associated effects on solubilities resulting from such unexpected, but remotely possible, conditions. Before committing the considerable resources in terms of time and costs to carry out such work, however, it would seem prudent to explore whether alternative approaches to estimating defensible upper bounds on Pu solubilities under these specific conditions exist, or can be developed. Such approaches could be based on the existing thermochemical database for the actinides developed by the NEA/OECD.

If necessary, the second issue could be addressed by a thorough review of the NEA/OECD database, focusing in particular on whether the database is reliable, and relevant with respect to WIPP disposal conditions. The issue of reliability entails consideration of the level of internal consistency of the database, as well as evaluation of the fundamental approach and associated mathematical techniques used to retrieve values of thermodynamic properties from basic experimental data. The issue of relevance of the database addresses whether thermochemical data are available for all actinide-bearing solids and aqueous species that are expected to be important in WIPP brines. It is possible, if not highly likely, that such data may be unavailable in the NEA/OECD database for some important, WIPP-relevant aqueous species. If so, can such gaps in the database be filled without significant impact on the reliability (i.e. internal consistency) of the database?

The third issue could also be addressed by thorough review of the SIT method, focusing on the relative strengths and limitations of this approach compared to the Pitzer approach. The basic difference between the approaches is that the former uses an extended Debye-Huckel expression for activity coefficients parameterized in terms of ionic charge and ionic strength, whereas the latter uses a medium-dependent expression parameterized in terms of empirically derived virial coefficients

appearing in the Pitzer equations. The Pitzer model can provide calculations of log K values that are practically within experimental accuracy, but the large number of parameters in this model and their strong interrelations and correlations, makes it difficult to apply the model to systems where complex formation is important. The SIT model, on the other hand, uses a much smaller number of regression parameters, resulting in less accurate calculation of log K values, but ion-pairing and complex formation are explicitly accounted for in this model. Ultimately, the question of whether the SIT method can be used in place of the Pitzer approach for actinide speciation-solubility calculations appropriate for WIPP brines may depend on the purpose of the calculation. If the calculations are for bounding purposes, or perhaps to support performance assessment models, then the accuracy of the Pitzer approach may not be as important as the ability of the SIT method to account for ion-pairing and complex formation, as long as the associated loss in accuracy is acceptable.

In summary, EEG's proposed approach involving direct experimental investigation of plutonium's speciation-solubility behavior in WIPP-relevant brines, adoption of the NEA/OECD thermochemical database for the actinides, and consideration of alternative techniques for calculation of ionic activities in concentrated brines, differs significantly from the approach used by DOE to support the WIPP CCA. EEG's approach may have limited use in providing bounding estimates of Pu solubilities under WIPP disposal conditions that are unexpected, though remotely possible. More generally, the approach could in principle be used to calculate actinide solubilities directly, eliminating the present need to estimate upper bounds based on analogous chemical behavior. It should be emphasized, however, that there is no compelling reason to question the validity of the actinide analogy argument under expected disposal conditions at WIPP, and that associated upper-bound estimates of actinide solubilities are adequate for performance assessment purposes. If necessary, the merits of EEG's proposed approach should be further assessed on the basis of a thorough review of issues pertaining to the adoption of the NEA/OECD thermochemical database, and possible uses of alternative methods for calculation of ionic activities in WIPP brines.

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