Matthew Silva, Director
Environmental Evaluation Group
7007 Wyoming Blvd., N.E.
Suite F-2
Albuquerque, NM 87109

Dear Mr. Silva:

The Environmental Protection Agency (EPA) has completed an evaluation of two recent papers by the Environmental Evaluation Group (EEG) on actinide chemistry and its application at the Waste Isolation Pilot Plant (WIPP). Attached is a report that describes our review and conclusions on this work. This letter, along with the attached report, will be placed in the EPA docket for public access.

Upon reviewing EEG's analysis of several actinide chemistry issues, EPA has the following conclusions:

1) The available scientific evidence on potential plutonium concentrations in the WIPP is consistent with the uncertainty ranges for plutonium solubilities used in the WIPP performance assessment;
2) Experimental data obtained at WIPP-relevant conditions indicate that plutonium will be present as either plutonium (III) or plutonium (IV) in the equilibrium WIPP repository environment;
3) The Source Term Test Program (STTP) experiment results are not applicable to the WIPP environment; and
4) The assumption of equilibrium in the actinide source term model has been thoroughly peer-reviewed and found to be appropriate.

We are currently monitoring experiments by the Department of Energy (DOE) that could provide additional data regarding the expected plutonium concentration in the repository brines.
EPA will continue to evaluate other new information on actinide chemistry as it becomes available.

Please contact Scott Monroe at 202-564-9712 if you have questions regarding this report.

Sincerely,

[Signature]

Frank Marcinowski, Director
Radiation Protection Division

Enclosure

cc: Inés Triay, DOE
    Russ Patterson, DOE
    Steve Zappe, NMED
REVIEW OF EEG'S MATERIALS RESEARCH SOCIETY PAPERS ON WIPP ACTINIDE CHEMISTRY INVESTIGATIONS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Radiation and Indoor Air
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MAY 2002
EXECUTIVE SUMMARY

The Environmental Evaluation Group (EEG) has raised questions regarding actinide solubility and the performance assessment for the Waste Isolation Pilot Plant (WIPP) Compliance Certification Application. Issues related to actinide solubility and performance assessment for WIPP were addressed in papers presented by EEG at the Materials Research Society meeting in Boston, Massachusetts during November 2001 (Haschke and Oversby, 2001; Oversby et al., 2001). These issues concerned: 1) the maximum plutonium concentrations that should be considered in WIPP performance assessment calculations, 2) the possible occurrence of plutonium(V) and/or plutonium(VI) in the long-term repository brines, 3) whether the STTP experiments are applicable to the WIPP repository, and 4) whether the assumption of equilibrium is appropriate for the actinide source term model.

EEG's analysis of these issues is based on information that has already been considered by the USEPA, and these issues have been addressed a number of times (USEPA, 1998a; USEPA, 1998b; USEPA, 2000a; USEPA, 2000b; USEPA, 2001). The available scientific evidence is consistent with the uncertainty ranges used for plutonium solubilities in the WIPP performance assessment. In addition, experimental data obtained at WIPP-relevant conditions indicate that plutonium will be present as either plutonium(III) or plutonium(IV) in the equilibrium WIPP repository environment, although higher plutonium oxidation states may be found initially in localized areas of the repository because of waste heterogeneity. The STTP experiments have been reviewed previously and the results of these tests are not applicable to the WIPP environment. Finally, the assumption of equilibrium in the actinide source term model has been thoroughly peer-reviewed and found to be appropriate.

The predicted plutonium concentrations in the long-term WIPP repository brines used in the ASTM appear to remain in dispute because of the relatively limited data used to demonstrate the stability of plutonium(III) and plutonium(IV) oxidation states in the long-term WIPP repository brines. Additional controversy has been associated with the use of the oxidation-state analogy for predicting the solubility of plutonium(III) and plutonium(IV) solids from americium(III) and thorium(IV) solids data. The USDOE has proposed experiments that could provide additional data regarding the equilibrium plutonium oxidation states and solids solubility under WIPP-relevant conditions. Successful completion of these experiments could assist in resolving these issues.
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1.0 INTRODUCTION

The Environmental Evaluation Group (EEG) has raised issues regarding the Actinide Source Term Model (ASTM) and the performance assessment calculations included in the Compliance Certification Application (CCA) for the Waste Isolation Pilot Plant (WIPP). These issues were addressed in two papers presented by EEG at the Materials Research Society meeting in Boston, Massachusetts during November 2001 (Haschke and Oversby, 2001; Oversby et al., 2001).

The purpose of this report is to evaluate the issues related to actinide chemistry that are addressed in EEG's recent papers (Haschke and Oversby, 2001; Oversby et al., 2001). Section 2.0 includes a brief summary of the important assumptions used in the ASTM. In Section 3.0 of this report, the EEG papers are reviewed. The WIPP actinide solubility experiments planned by the U.S. Department of Energy (USDOE) are summarized in Section 4.0. Section 5.0 provides a discussion of the issues raised by the EEG papers. Based on this information, it is concluded that the issues raised by EEG's recent papers have been addressed previously and no new data are available that challenge the assumptions regarding actinide chemistry used in the ASTM and the performance assessment calculations in the CCA (Section 6.0).
2.0 ASTM AND PERFORMANCE ASSESSMENT ASSUMPTIONS

Actinide solubilities predicted by the ASTM were based on a number of assumptions. Because of the heterogeneity of wastes intended for WIPP, it was believed that performing direct measurements of actinide solubilities in experiments using waste and ensuring that these measurements adequately reflect steady-state WIPP conditions would involve an extremely large number of measurements and considerable uncertainty (USDOE, 1996b). Therefore, the ASTM included the assumption that the repository system will achieve equilibrium over the relatively long time periods relevant to repository compliance and an equilibrium solubility approach was used to predict actinide solubilities in the repository brines.

Oxidation states predicted for actinides in the ASTM were based on an assumption of reducing conditions in the repository because of the large quantities of iron metal that will be present (USDOE, 1996b). Because of these reducing conditions, it was predicted that plutonium will be present in solution in the plutonium(III) or 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 less mobile than plutonium(V) and plutonium(VI). Another important assumption in the ASTM and in the performance assessment calculations was that brine in the repository would be well-mixed with waste, and the effects of heterogeneity need not be considered in the long-term repository (USDOE, 1996b).

The performance assessment in the CCA used a Monte Carlo technique to perform probabilistic analysis; uncertainties associated with the actinide solubilities used in the performance assessment were represented by a cumulative distribution obtained by comparison between calculated solubilities and solubilities from experimental results. This distribution was sampled in the performance assessment calculations, which allowed for the incorporation of uncertainties in actinide solubilities (USDOE, 1996a).
3.0 EEG PAPERS

The papers presented by EEG at the Materials Research Society Meeting in November 2001 were reviewed relative to their importance to the WIPP repository. The following sections provide specific comments regarding these papers. The issues related to WIPP that are raised by these papers are summarized and addressed in Section 5.0.

3.1 Haschke and Oversby (2001)

In the article by Haschke and Oversby (2001), experimental data from a number of studies conducted at temperatures near 25°C were tabulated (Table 1). However, the experimental data compiled by Haschke and Oversby (2001) are not relevant to WIPP conditions, because the experiments were not conducted in the presence of reducing agents such as metallic iron.

Haschke and Oversby (2001) observed that the spread in experimental data for Pu(OH)$_4$(s) is small (less than approximately 2 orders of magnitude), implying that Pu(OH)$_4$(s) solubility is insensitive to Eh and ionic strength. However, the data summarized by Haschke and Oversby (2001) were obtained over a relatively small range of positive Eh values (Table 1), so it is difficult to conclude from these data that Eh does not affect Pu(OH)$_4$(s) solubility. None of the data evaluated by Haschke and Oversby (2001) were obtained in the presence of strong reductants such as metallic iron, which has been shown to cause much lower Eh values, lower oxidation states of plutonium in solution, and lower plutonium solution concentrations (Reed et al., in preparation; Xia et al., 1996).

Haschke and Oversby (2001) observed that the summarized PuO$_2$(s) and Pu(OH)$_4$(s) solubility data differed only by a factor of approximately 100 instead of by $10^8$, the predicted difference based on thermodynamic data and equilibrium modeling. However, they did not address the possibility that radiolysis of PuO$_2$(s) during aging in water could decrease the crystallinity of the solid phase, which would increase the solubility of PuO$_2$(s) to concentrations greater than those predicted by thermodynamic data for PuO$_2$(s) (Rai and Ryan, 1982).
Haschke and Oversby (2001) cite the redox potential data of Rai et al. (1980), and indicate that a sharp increase in redox potential was observed to occur from pH 4 (0.5 V) to pH 3 (0.9 V). However, examination of Figure 3 in Rai et al. (1980) does not reveal such an Eh increase between pH 3 and 4.

The conceptual model of plutonium solubility developed by Haschke and Oversby (2001) is based on kinetically controlled dissolution of PuO$_2$-$_x$(s). However, this solid has not been demonstrated to form under WIPP repository conditions, i.e., high ionic strength, reducing conditions, and pH values from 8.5 to 10.

Haschke and Oversby (2001) state that:

Failure to prevent the chemical cycle under reducing conditions is implied by efforts to control O$_2$ activity and stabilize solid Pu(OH)$_3$, with iron powder in solution (0.33 g Fe/L, measured Eh = -0.3 V) after oversaturation with 8 x 10$^{-4}$ M Pu(III) [Felmy et al., 1989]. Formation of PuO$_2$-$_x$ and partial reduction of Pu(V) and Pu(VI) formed via the chemical cycle are suggested by a steady-state average of 7% of those ions in water at pH 6.6-8.2 and by as much as 52% Pu(V) plus Pu(VI) in one instance. A steady-state average of 11% Pu(V) plus Pu(VI) was observed at an effective pH near 8 in Fe-containing, high-ionic-strength chloride brine (1.23 g/cm$^3$).

Plutonium oxidation states in the PBB1 and PBB3 brine experiments conducted by Felmy et al. (1989) were determined using a solvent-extraction technique described by Rai (1984). This solvent extraction method was tested on solutions made up with PBB1 and PBB3 brines and plutonium(IV), plutonium(V), and plutonium(VI) stock solutions that were checked spectrophotometrically to ensure that only the intended plutonium oxidation state was present (Schramke et al., 1989). The results of these tests are summarized in Table 2. These results indicate that even with stock solutions of known plutonium oxidation states, the extraction method was subject to some error.

For example, using a plutonium(IV) stock solution, the extraction method indicated that up to 13% of the plutonium(IV) in brine was present as plutonium(V) plus plutonium(VI) (Table 2). These errors are likely caused by the difficulties associated with phase separation or by oxidation of the plutonium(IV) during extraction (Schramke et al., 1989). Thus, in the Felmy et al. (1989) experiments, the detection of relatively small percentages of plutonium(V) plus plutonium(VI) is likely related to errors inherent in the extraction method and the data do not reliably indicate that these oxidation states were present in solution. The experiment in which 51.8% of the plutonium appeared to be present as plutonium(V) plus
plutonium(VI) is clearly an outlier: replicate results indicated only 8.7% plutonium(V) plus plutonium(VI), and results obtained at pH values that bracketed this experiment also indicated much lower (1.1 to 4.9%) plutonium(V) plus plutonium(VI) concentrations (Felmy et al., 1989).

Haschke and Oversby (2001) develop a conceptual model for the kinetic control of steady-state plutonium concentrations. However, this model does not take into account the effects of reducing agents such as iron metal, which will be abundant in the repository, and humic acid and methane (CH4) that may be generated by degradation of the cellulosic, plastic, and rubber materials in the repository. In addition, Haschke and Oversby (2001) do not demonstrate that the assumption of equilibrium is invalid for the long time period relevant to the repository.

3.2 Oversby et al. (2001)

Oversby et al. (2001) calculates the expected plutonium concentrations generated in the WIPP repository by the dissolution of pyrochemical salts. This analysis assumes that the long-term plutonium concentration in the brine will depend on the initial form of the waste. However, because of the assumption of equilibrium in the ASTM, the initial waste form is not relevant for predicting long-term plutonium concentrations in WIPP repository brine. The pyrochemical salt waste in the WIPP repository will represent less than 1% by volume of the waste (Brush et al., 2001). Based on the assumption of equilibrium, these relatively reactive wastes will dissolve and plutonium solution concentrations will be controlled by another, more stable phase.

The wording that describes the STTP tests (last paragraph, page 2 of Oversby et al., 2001) may be slightly misleading. Some of the STTP tests with pyrochemical salts (containers L-37, L-38, and L-39) did not contain iron (LANL, 2000), some of the tests included oxygen-sparging (OS) pyrochemical salt waste (containers L-31, L-32, L-33, L-34, L-38, and L-39) instead of direct oxide reduction (DOR) waste, and neodymium was not added to pyrochemical salt test containers L-28, L-29, L-30, L-37, L-38, and L-39. However, the description of the tests is accurate for containers L-25, L-26, and L-27.

Oversby et al. (2001) state that:
“Reduction of Pu(V) and Pu(VI) to lower oxidation states increases the steady-state [Pu] and alters the distribution of oxidation states, but the presence of Fe does not eliminate Pu(V) and Pu(VI) from a brine at steady state.”

However, evidence is not presented to support this assertion. Available experimental studies (Reed et al., in preparation; Xia et al., 1996; Grambow et al., 1996; Weiner, 1996; Slater et al., 1997) have shown that iron metal and iron corrosion products reduce actinide oxidation states and actinide solution concentrations in brines.

Oversby et al. (2001) cite Haschke (1992) as providing evidence that PuO$_2$$_x$ is the stable oxide in chloride-rich solutions. However, the cited Haschke (1992) article does not mention the existence of PuO$_2$$_x$, which was identified in a later article (Haschke et al., 2000).

Oversby et al. (2001) determined that chloride did not affect Pu(OH)$_4$(s) solubility based on a comparison of the results of Nitsche et al. (1994) to the results of a group of studies cited by Haschke and Oversby (2001). However, it is questionable whether this conclusion can be reached based on experiments conducted under a variety of conditions and that may have had different plutonium solid phases in contact with the solutions.

The presence of iron in the experiments conducted by Felmy et al. (1989) is said to provide evidence that iron increases plutonium concentrations in solution (Oversby et al., 2001). However, in the low-ionic-strength solutions in the pH range (8.5 to 10) applicable to WIPP conditions, the concentrations of plutonium measured by Felmy et al. (1989) were less than or equal to the detection limits of $10^{-9}$ moles/L. This concentration is less than the concentrations shown in Figure 1 of Haschke and Oversby (2001) for Pu(OH)$_4$(am) and is comparable to the concentrations shown for PuO$_2$. Thus, in the pH range relevant to WIPP, the addition of iron alone does not appear to increase plutonium solubility.

Oversby et al. (2001) states that PuO$_2$$_x$(s) forms spontaneously at the Eh values of -250 to -350 mV, based on the analysis presented in Haschke and Oversby (2001). The analysis by Haschke and Oversby (2001) was, in turn, based on the detection of oxidized (V+VI) plutonium in the experiments conducted by Felmy et al. (1989). However, as discussed in Section 3.1, the detection of plutonium(V+VI) in these experiments was probably caused by errors inherent in the solvent extraction method used to determine...
plutonium oxidation states. Therefore, no evidence exists that PuO$_{2-}$ (s) forms spontaneously under reducing conditions.

In this article, it is stated that a slope of -3 in the Felmy et al. (1989) Pu(OH)$_2$ (s) solubility experiments when the log plutonium concentration is plotted as a function of pH implies that plutonium(V) released from the solid is reduced to Pu(III) by Fe in solution. However, as previously noted, there is no reliable evidence of plutonium(V) in the solutions from these experiments. In addition, if plutonium(V) released by PuO$_{2-}$ dissolution is reduced to plutonium(III) by iron(II) in solution, the reaction would be written:

$$\text{PuO}_{2-}(s) + (3-x) \text{H}_2\text{O(l)} + 2 \text{Fe}^{2+}(aq) = \text{Pu}^{3+}(aq) + 2 \text{Fe}^{3+}(aq) + 5 \text{OH}(aq) + (1-2x/2)\text{H}_2$$

This reaction results in a slope of -5 if the log plutonium concentration is plotted as a function of pH, which is inconsistent with the observed slope of -3. Therefore, it is unlikely that this reaction controlled plutonium concentrations in the experiments conducted by Felmy et al. (1989).

In the final paragraph of the section “Implications for Performance Assessment,” Oversby et al. (2001) states that the plutonium concentration for plutonium(IV) in Salado brine is estimated as $4.4 \times 10^{-6}$ moles/L. However, the value cited by Oversby et al. (2001) for plutonium is actually the median concentration for neptunium(IV); in Table 6-11 of the CCA, the median plutonium concentration is listed as $3.58 \times 10^{6}$ (USDOE, 1996a). The most appropriate comparisons to the concentrations calculated by Oversby et al. (2001) are the maximum plutonium(IV) concentrations of $1.11 \times 10^4$ moles/L for Salado brine and $1.51 \times 10^7$ for Castile brine (USDOE, 1996b). The maximum concentration for Salado brine is comparable to the range of concentrations predicted by Oversby et al. ($10^4$ to $2 \times 10^4$ moles/L). Because the calculations using the pyrochemical salt waste are likely to be a short-term, worst-case scenario, these results seem to indicate that the performance assessment included in the CCA conservatively addressed the likely range of plutonium concentrations.
4.0 LANL ACTINIDE CHEMISTRY INVESTIGATIONS

During the CBFO/EPA working meeting on February 6, 2002, Los Alamos National Laboratory (LANL) staff provided information on the initial WIPP actinide chemistry experimental program. The handouts from these presentations are included as Attachments A and B. The presentations included an update on the status of the New Mexico State University Carlsbad Environmental Monitoring and Research Center (CEMRC), where collaborative actinide research will be performed by Center staff and personnel from LANL and Sandia. The experimental work presented by LANL at this meeting is only scoping in nature and does not have the level of quality assurance required by the WIPP project.

In the LANL presentation, a number of issues related to actinide chemistry in the WIPP repository were identified:

- Occurrence of plutonium(V) and plutonium(VI) in some of the STTP experiments;
- Effects of alpha radiolysis of WIPP-relevant brines on the oxidation states of actinides;
- Reduction of oxidized actinides by iron and aluminum metal;
- Effects of waste form reactions on brine chemistry;
- Sorption (including coprecipitation and adsorption) of actinides by backfill, borehole, and other relevant materials (MgO, cements, corrosion products);
- Effects of colloids and waste form degradation products on actinide solubility and transport;
- Microbial reduction of plutonium(V), plutonium(VI), uranium(VI), and neptunium(VI), and the effects of the repository environment on microbial activity; and
- An integrated thermodynamic and kinetic redox model for plutonium under repository conditions.

LANL provided a list of studies that may be carried out to address these issues (Attachment A). The immediate tasks planned by LANL include:

- Upgrading the existing facilities at CEMRC;
- Finalizing and implementing a quality assurance program;
- Empirical actinide stability experiments, e.g., small reaction vessel experiments with Castile brine, plutonium(VI), hypochlorite, aluminum metal, and relevant organics under a controlled atmosphere at 30°C;
- Development of the laser spectroscopy method for determination of actinide speciation in brines;

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• Immobilization of actinides by backfill and borehole fill materials under repository conditions; and
• Irradiation of brines and waste forms.

A series of scoping plutonium sorption tests have been carried out with MgO backfill (Attachment A). In addition, method development testing has been carried out to evaluate the effects of oxidizing chloride species (e.g., hypochlorite, \( \text{OCl}^- \)) and reducing species (e.g., hydrogen peroxide, \( \text{H}_2\text{O}_2 \)) on actinide chemistry in the WIPP repository environment (Attachment B). These tests included an evaluation of absorption spectra of hypochlorite in water and four different salt solutions, absorption spectra of potentially important chloride species in water and chloride solutions, and the influence of pH on the formation of hypochlorite in water and 5 M sodium chloride (NaCl). Additional experiments were carried out to test the colorimetric analysis of hypochlorite, chlorite, and chlorate mixtures using potassium iodide.

Scoping solubility experiments were also carried out using ERDA-6 (Castile) brine at pH values of 7 to 9 and plutonium(VI) stock solution (Attachment B). These experiments were carried out with and without the addition of \( 1 \times 10^{-2} \) moles/L hydrogen peroxide.

Scoping brine irradiation experiments were carried out using 5 M sodium chloride, ERDA-6 brine, 3.7 M \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \), and GWB brine. These experiments were performed using an electron linear accelerator to quantify the irradiation-induced formation of typical radiolysis byproducts at doses between 120 and 216 kGy. Additional irradiation experiments were carried out using a high-energy proton beam line to determine the effects of alpha radiation on brine chemistry.
5.0 DISCUSSION

The issues raised by the EEG papers presented at the Materials Research Society Meeting in 2001 (Haschke and Oversby, 2001; Oversby et al., 2001) include:

- The plutonium concentrations used in the WIPP performance assessment should be increased;
- Plutonium(V) and plutonium(VI) oxidation states may be present in the long-term WIPP repository;
- The applicability of the STTP experimental results to the WIPP repository; and
- Kinetically controlled processes should be used to predict actinide solubilities in the long-term WIPP repository.

In the following sections, these issues are reviewed, previous EPA responses to these issues are provided, and the status of these issues is summarized.

5.1 Potential Issue: Higher Plutonium Concentrations Should be Used in the Performance Assessment

Issue Description: EEG contends that the effects of heterogeneous repository conditions (e.g., high concentrations of plutonium associated with pyrochemical salts) have not been appropriately considered in the WIPP repository performance assessment.

USEPA's Previous Responses to This Issue: USEPA (2001) addressed the potential effects of repository heterogeneity as follows:

EEG's concern regarding the effects of waste heterogeneity in the repository is that, during a human intrusion into the repository, a drum or drums with relatively high actinide concentrations could be disturbed and could result in an unacceptable release of actinides from the repository. However, the performance assessment for the CCA was based on a probabilistic approach, rather than calculations of worst-case scenarios. This probabilistic approach has been peer-reviewed and found to be acceptable. The effects of waste heterogeneity were incorporated in the uncertainties assigned to actinide solubilities, and have been adequately addressed in the performance assessment.
**Issue Resolution Status:** The probabilistic performance assessment approach used in the CCA has been peer-reviewed and deemed appropriate. Oversby et al. (2001) calculated anticipated plutonium concentrations in contact with pyrochemical salts. However, their model does not account for the presence of strong reductants. In addition, the model was developed assuming that kinetics rather than equilibrium reactions control actinide concentrations. Thus, although this model could be applicable to reactions in localized areas of the repository early in its history, it is not applicable to expected long-term repository conditions.

### 5.2 Potential Issue: Plutonium Oxidation States

**Issue Description:** EEG questions whether plutonium in the long-term WIPP repository environment will be present only in the (III) and (IV) oxidation states.

**USEPA's Previous Responses to this Issue:** In its response to comments (USEPA, 1998a), USEPA stated:

...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)$_2$(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)$_2$ 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.
USEPA (1998b) stated:

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 solubilities 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.

USEPA (2001) stated:

The assumption that plutonium will be present as plutonium(III) and plutonium(IV) in the equilibrium WIPP repository environment is supported by the data obtained under conditions (low Eh and slightly alkaline pH) relevant to the WIPP repository. The USDOE is currently planning experiments to develop additional data regarding the likely oxidation states of plutonium in solution and solids in the repository environment. The results of these experiments may be useful for reducing the controversy surrounding the assumption that only plutonium(III) and plutonium(IV) oxidation state will be present in the long-term WIPP repository environment.

Issue Resolution Status: No new experimental data have been presented that invalidate the conclusion that plutonium will be present as plutonium(III) and plutonium(VI) in the equilibrium WIPP repository environment. Planned LANL experiments (Section 4.0) may provide additional data on plutonium oxidation states that will be present at equilibrium in the repository brines and may help to resolve this issue.

5.3 Potential Issue: Applicability of STTP Experiments to the WIPP Repository

Issue Description: EEG has used the results of STTP testing of pyrochemical salts to estimate plutonium concentrations in the WIPP repository, and indicates that the plutonium concentrations based on the STTP experimental results should be used in the WIPP performance assessment.

USEPA's Previous Responses to this Issue: USEPA has previously commented on the applicability of the STTP experiments to the WIPP repository (USEPA, 2000a):
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, 2000; 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).

**Issue Resolution Status:** Because the STTP experiments differed significantly from WIPP repository conditions, the results of these experiments cannot be used to predict long-term, equilibrium plutonium concentrations in repository brines.

### 5.4 Potential Issue: Kinetic Control of Actinide Solubilities in the WIPP Repository

**Issue Description:** EEG developed a model based on kinetically controlled plutonium concentrations in WIPP brines using the results of the STTP tests (Oversby et al., 2001). Consequently, EEG contends that:

Dissolution behavior is not correctly predicted by equilibrium modeling of Pu "solubility." Kinetic factors must be considered in modeling and may preclude the establishment of a true equilibrium state.

**USEPA's Previous Responses to this Issue:** USEPA, in their review of the source term conceptual model, stated (USEPA, 1998b):

...EPA also agrees that chemical equilibrium models are appropriate for predicting the solubilities and subsequent concentrations of actinides in WIPP brines.

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In a later review of this issue, USEPA stated (USEPA, 2001):

EEG contends that non-equilibrium conditions will control plutonium oxidation states. The assumption of thermodynamic equilibrium in the long-term repository environment is a key assumption in the conceptual model. This model and its underlying assumptions have been thoroughly peer-reviewed and found to be acceptable.

**Issue Resolution Status:** The model of kinetically controlled plutonium solution concentrations developed by Haschke and Oversby (2001) and Oversby et al. (2001) for the WIPP repository is based on the interpretation of experiments conducted under relatively oxidizing conditions. However, reducing conditions are expected in the long-term WIPP repository. The kinetic model development also relied on the results of the STTP tests. However, the STTP tests are not applicable to the WIPP environment because of the presence of oxidizing conditions, the absence of MgO, and high carbon dioxide pressures in these tests (Section 5.3). Oversby et al. (2001) asserted that this kinetic model is applicable to reducing conditions because higher plutonium oxidation states were observed in plutonium solubility measurements in brine that contained iron metal (Felmy et al., 1989). However, the small amounts of plutonium(VI) observed in these solutions were likely a result of error associated with the extraction method (Section 3.1), so the kinetic model developed by Haschke and Oversby (2001) and Oversby et al. (2001) does not appear to apply to reducing conditions such as those predicted for the WIPP repository, based on the available data.

The available experimental data indicate that plutonium will exist in reduced form because of the iron metal in the repository (Weiner, 1996; Felmy et al., 1989; Reed et al., in preparation). In addition, organic compounds likely to be present in the repository, such as humic acids, have been shown to cause reduction of plutonium to the (IV) oxidation state (Choppin, 1991). Therefore, the kinetic model developed by Haschke and Oversby (2001) and Oversby et al. (2001) is not applicable to the long-term WIPP repository, and the assumption of equilibrium in the long-term WIPP repository remains reasonable and appropriate for modeling long-term actinide oxidation states and solubilities.
6.0 CONCLUSIONS

EEG presented two papers at the Materials Research Society Meeting in November 2001. In these papers, EEG raised issues concerning: 1) the maximum plutonium concentrations that should be considered in WIPP performance assessment calculations, 2) the possible occurrence of plutonium(V) and/or plutonium(VI) in the long-term repository brines, 3) whether the STTP experiments are applicable to the WIPP repository, and 4) whether the assumption of equilibrium is appropriate for the actinide source term model.

EEG’s analysis of these issues is based on information that has already been considered by the USEPA, and these issues have been addressed a number of times (USEPA, 1998a; USEPA, 1998b; USEPA, 2000a; USEPA, 2000b; USEPA, 2001). The available scientific evidence is consistent with the uncertainty ranges used for plutonium solubilities in the WIPP performance assessment. In addition, experimental data obtained at WIPP-relevant conditions indicate that plutonium will be present as either plutonium(III) or plutonium(IV) in the equilibrium WIPP repository environment, although higher plutonium oxidation states may be found initially in localized areas of the repository because of waste heterogeneity. The STTP experiments have been previously reviewed (USEPA, 2000a; USEPA, 2000b) and the results of these tests are not applicable to the WIPP environment. Finally, the assumption of equilibrium in the actinide source term model has been thoroughly peer-reviewed and found to be appropriate.

The predicted plutonium concentrations in the long-term WIPP repository brines used in the ASTM appear to remain in dispute because of the relatively limited amount of data used to demonstrate the stability of plutonium(III) and plutonium(IV) oxidation states in the long-term WIPP repository brines. Further controversy has been associated with the use of the oxidation-state analogy for predicting the solubility of plutonium(III) and plutonium(IV) solids from americium(III) and thorium(IV) solids data. The USDOE has proposed experiments that could provide additional data regarding the equilibrium plutonium oxidation states and solids solubility under WIPP-relevant conditions. Successful completion of these experiments could help to resolve the issues associated with expected plutonium concentrations in the repository brines.

15 March 26, 2002
7.0 REFERENCES


Rai, D. 1984. Solubility Product of Pu(IV) Hydrous Oxide and Equilibrium Constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), and Pu(V)/Pu(VI) Couples. Radiochimica Acta 35:97-106.


<table>
<thead>
<tr>
<th>Study</th>
<th>Solution</th>
<th>Experiment Duration</th>
<th>Solid Phases and Aqueous Species Identified</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rai et al. (1980)</td>
<td>0.0015 M CaCl₂ solution in contact with air, pH 3.8 to 7.85, Eh values of approximately 275 to 625 mV</td>
<td>90 to 250 days</td>
<td>PuO₂(s) and Pu(OH)₃(s); Pu(V) believed to be present in solution</td>
<td>pH of solutions decreased with time due to radiolysis; Pu(OH)₃(s) maintained a higher plutonium concentration in solution than PuO₂(s)</td>
</tr>
<tr>
<td>Rai and Ryan (1982)</td>
<td>Deionized water in contact with air, pH 3 to 5</td>
<td>4 to 1,300 days</td>
<td>Partially crystalline PuO₂·xH₂O(s) and PuO₂(s); Pu(V) observed in solution above pH 3.5</td>
<td>Solubility of ²³⁹PuO₂·xH₂O(s) decreased upon aging to concentrations near the solubility of ²³⁹PuO₂(s); interaction of solids with radiolysis products of water was believed to affect solid crystallinity</td>
</tr>
<tr>
<td>Newton et al. (1986)</td>
<td>Ionic strengths up to 1 M NaCl or LiClO₄, pH 1 to 3.4</td>
<td>191 to 618 days</td>
<td>Colloidal Pu(IV); Pu(IV), Pu(V) and Pu(VI) observed in solution</td>
<td>Initial solutions contained Pu(IV), Pu(V), or Pu(VI), changes in oxidation states were observed due to radiolysis effects</td>
</tr>
<tr>
<td>Nitsche et al. (1993)</td>
<td>I-13 groundwater from Yucca Mountain, pH 5.9 to 8.5</td>
<td>--</td>
<td>Pu(V) &gt; Pu(VI) &gt; Pu(IV) &gt; Pu(III+polymer) in solution</td>
<td>Experiments conducted from oversaturation. No trend observed in concentration as a function of pH</td>
</tr>
<tr>
<td>Nitsche et al. (1994)</td>
<td>Synthetic WIPP brine H-17, operational pH of 7.08 to 7.15, Eh 394 to 490 mV</td>
<td>252 to 680 days</td>
<td>Pu(IV) polymer, unidentified crystalline solids, and sodium ploutony(V) in solid phase; predominantly Pu(VI) in solution</td>
<td>Experiments conducted in oxidizing conditions under a fixed carbon dioxide overpressure; plutonium oxidation states measured by solvent extraction; alpha radiolysis may have caused high plutonium oxidation states in solution</td>
</tr>
</tbody>
</table>
Table 1 (continued)

Experimental Data Included in Haschke and Oversby (2001)

<table>
<thead>
<tr>
<th>Study</th>
<th>Solution</th>
<th>Experiment Duration</th>
<th>Solid Phases and Aqueous Species Identified</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efurd et al.</td>
<td>J-13 groundwater from Yucca Mountain, pH 6 to 8.5, under an</td>
<td>Up to 400 days</td>
<td>Color of precipitate and diffraction patterns were characteristic of Pu(IV) solids, with diffuse diffraction peaks</td>
<td>Experiments conducted from oversaturation</td>
</tr>
<tr>
<td>(1998)</td>
<td>argon/carbon dioxide gas mixture, Eh of 430 mV at pH 7, ionic strength of 3.7 mmol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2

Results of Solvent Extraction Tests (Average Percentages) Conducted with Stock Plutonium(IV), Plutonium(V) and Plutonium(VI) Solutions (Schramke et al., 1989)

<table>
<thead>
<tr>
<th>Tested Solution</th>
<th>Plutonium (IV)</th>
<th>Plutonium (V)+(VI)</th>
<th>Nonextracted Plutonium</th>
<th>Total Plutonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plutonium(IV) in Deionized Water</td>
<td>88.0 ± 0.7</td>
<td>7.5 ± 0.1</td>
<td>0.2 ± 0.1</td>
<td>96.0 ± 6.2</td>
</tr>
<tr>
<td>Plutonium(IV) in PBB1 Brine</td>
<td>85.0 ± 1.4</td>
<td>11.0 ± 1.4</td>
<td>0.3 ± 0.1</td>
<td>96.3 ± 2.0</td>
</tr>
<tr>
<td>Plutonium(IV) in PBB3 Brine</td>
<td>81.0 ± 1</td>
<td>13.0 ± 1</td>
<td>0.0 ± 1</td>
<td>94.0 ± 1</td>
</tr>
<tr>
<td>Plutonium(V) in Deionized Water</td>
<td>2.2 ± 1.2</td>
<td>84.5 ± 4.7</td>
<td>7.7 ± 1.9</td>
<td>94.4 ± 5.2</td>
</tr>
<tr>
<td>Plutonium(V) in PBB1 Brine</td>
<td>4.1 ± 0.1</td>
<td>78.5 ± 0.7</td>
<td>6.5 ± 0.7</td>
<td>89.1 ± 1.0</td>
</tr>
<tr>
<td>Plutonium(V) in PBB3 Brine</td>
<td>6.5 ± 0.7</td>
<td>78.0 ± 2.8</td>
<td>7.0 ± 1.4</td>
<td>91.5 ± 3.2</td>
</tr>
<tr>
<td>Plutonium(VI) in Deionized Water (no oxidant added)</td>
<td>2.8 ± 0.4</td>
<td>85.4 ± 5.9</td>
<td>10.6 ± 6.6</td>
<td>98.8 ± 8.9</td>
</tr>
<tr>
<td>Plutonium(VI) in PBB1 Brine (no oxidant added)</td>
<td>1.5 ± 0.7</td>
<td>88.0 ± 4.2</td>
<td>2.5 ± 2.1</td>
<td>92.0 ± 4.7</td>
</tr>
<tr>
<td>Plutonium(VI) in PBB3 Brine (no oxidant added)</td>
<td>1.5 ± 0.7</td>
<td>95.1 ± 0.4</td>
<td>1.9 ± 0.2</td>
<td>98.5 ± 0.8</td>
</tr>
<tr>
<td>Plutonium(VI) in Deionized Water (10^{-3} M KMnO_{4} added)</td>
<td>2.3 ± 0.6</td>
<td>65.0 ± 2.6</td>
<td>24.7 ± 2.5</td>
<td>92.0 ± 3.7</td>
</tr>
<tr>
<td>Plutonium(VI) in PBB1 Brine (10^{-3} M KMnO_{4} added)</td>
<td>0.9 ± 0.1</td>
<td>88.5 ± 0.7</td>
<td>2.9 ± 0.3</td>
<td>92.3 ± 0.8</td>
</tr>
<tr>
<td>Plutonium(VI) in PBB3 Brine (10^{-2} M KMnO_{4} added)</td>
<td>0.7 ± 0.1</td>
<td>86.7 ± 0.1</td>
<td>4.0 ± 0.7</td>
<td>91.4 ± 0.7</td>
</tr>
</tbody>
</table>

'Single measurements'
ATTACHMENT A

LANL/CARLSBAD EXPERIMENTAL PROGRAM
MEETING HANDOUTS
LANL/Carlsbad Experimental Program

CBFO-EPA Working Meeting
February 6, 2002
Carlsbad, NM

Jim Conca, Patricia Paviet-Hartmann, Thomas Hartmann, Ningping Lu, Betty Strietelmeier

Los Alamos National Laboratory
E-Division, Carlsbad Operations
LANL/Carlsbad Experimental Program

- Validate various performance assessment assumptions concerning Pu chemistry

- Obtain additional information on Pu chemistry for various components or parameters of the repository to support potential modifications to the WIPP baseline.
LANL/Carlsbad Experimental Program

The New Mexico State University Carlsbad Environmental Monitoring and Research Center (CEMRC) will be the center for WIPP actinide chemistry and radiological studies.

- CEMRC permit has been raised to 2 Ci
- New capabilities being installed and facility will be enlarged and enhanced
- Contractual and administrative vehicles in place for collaborative work between LANL and CEMRC, and in process for SNL and the rest of the WIPP family, anticipated completion this fiscal year.
WIPP Actinide Chemistry

Issues that have been identified as important include:

- Occurrence of Pu(V,VI) in some of the STTP experiments
- Effects of alpha-radiolysis of WIPP-relevant brines on the oxidation states of actinides
- Reduction of oxidized actinides by iron-based metals and Al metal
- Effects of waste form reactions on brine chemistry
- Sorption (co-precipitation, adsorption) of actinides by backfill, borehole and other relevant materials (MgO, cements, corrosion products)
- Effects of colloids and waste form degradation products on actinide solubility and transport
- Microbial reduction of Pu(V,VI), U(VI) and Np(V), and the effects of the repository environment on microbial activity
- An integrated thermodynamic and kinetic redox model for Pu under repository conditions

LANL/Carlsbad
WIPP Actinide Chemistry

Program will involve experiments concerning both fundamental aspects of system and empirical behavior

Potential studies include (not in order of importance):
- Dose/concentration relationships for by-products in each brine
- Cumulative dose effects for waste/brine components
- Hypochlorite and hydrogen peroxide chemistry in brines
- Redox kinetics of Pu in brines
- Pu sequestration in secondary phases
- Method development, e.g., laser spectroscopy under high ionic strength (WIPP brines)
- ERDA-6, GWBrine, MgO backfill, reductants, actual waste forms, containers, concretes
- Controlled atmospheric conditions, in situ water contents
- Pu stability in WIPP brines in the presence of various components
- Pu sorption along flow paths
- Irradiation of actual waste components
LANL/Carlsbad Initial Tasks

- Upgrading of the existing facilities at CEMRC
- Finalize and implement QA Program
- Empirical actinide stability experiments
e.g., small reaction vessel with Castile brine, Pu(VI), hypochlorite, Al-metal, and relevant organics under a controlled atmosphere at 30°C
- Development of the laser spectroscopy method for determination of actinide speciation in brines
- Demobilization of actinides by backfill an borehole fill materials under repository conditions
- Irradiation of brines and waste forms
Experiments in Method Development - in situ water content

The magnitude of the water flux through the repository and the water:solid may have an effect on Pu chemistry
Pu sorption tests were run with MgO backfill and GWBrine and ERDA-6 at various water contents (brine:backfill by volume)

Pre-equilibrated for 36 days and free brine extracted

Reinfused with GWBrine and ERDA-6 with $10^{-7} M$ Pu(VI)

Equilibrated for 26 days before extraction

Desorption in clean brine for 52 days before extraction
Pu content (nCi/g) in solution with MgO backfill after sorption tests over 26 days

<table>
<thead>
<tr>
<th>Brine</th>
<th>initial brine (no backfill)</th>
<th>traditional batch tests</th>
<th>fully indurated</th>
<th>partially indurated</th>
</tr>
</thead>
<tbody>
<tr>
<td>GWBrine</td>
<td>11.9 nCi/g</td>
<td>7.32 nCi/g</td>
<td>0.357 nCi/g</td>
<td>0.036 nCi/g</td>
</tr>
<tr>
<td>$K_d$ (ml/g)</td>
<td>--</td>
<td>7.4</td>
<td>19.5</td>
<td>137</td>
</tr>
<tr>
<td>ERDA-6</td>
<td>10.8 nCi/g</td>
<td>1.53 nCi/g</td>
<td>&lt; 0.001 nCi/g</td>
<td>0.009 nCi/g</td>
</tr>
<tr>
<td>$K_d$ (ml/g)</td>
<td>--</td>
<td>69.9</td>
<td>2,630</td>
<td>356.5</td>
</tr>
</tbody>
</table>

LANL/Carlsbad
Pu desorption over 52 days using backfill from sorption tests in a traditional batch desorption test with brine:solid of 10:1

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Pu desorbed relative to total Pu sorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>GWBrine (fully indurated)</td>
<td>3.5 %</td>
</tr>
<tr>
<td>GWBrine (batch)</td>
<td>12.8 %</td>
</tr>
<tr>
<td>ERDA-6 (fully indurated)</td>
<td>0.3 %</td>
</tr>
<tr>
<td>ERDA-6 (batch)</td>
<td>0.04 %</td>
</tr>
</tbody>
</table>

LANL/Carlsbad
ATTACHMENT B

INTEGRATED REPOSITORY SCIENCE, AN OVERVIEW
MEETING HANDOUTS
Integrated Repository Science
An Overview

Actinide Chemistry Technical Exchange
6th of February 2002
Patricia Paviet-Hartmann
Los Alamos National Laboratory
The situation of a salt repository for actinide solubility and actinide speciation is rather complex and reducing effects are in competition with oxidizing effects. It is important to obtain experimental results on radiolysis under repository conditions.

Plausible inundation scenario of salt repository will allow chloride brines to access waste and be exposed to radiation from the waste.

There is a possibility that radiolysis will enhance aqueous concentration of actinides and radionuclides in the near field.

The goal is to demonstrate how the main oxidizing chloride species such as hypochlorite and reducing species such as hydrogen peroxide caused by radiolysis may affect the overall behavior of actinides under repository conditions.

Following results are from method development tests.
Hypochlorite Chemistry
The formation of OCl⁻ as a function of the medium
Influence of pH on the formation of Hypochlorite

Plutonium stability in Synthetic WIPP Brines and Chloride Solutions
- Kinetics of the Reduction of Pu(VI) by hydrogen peroxide in four different salts 5 M NaCl, 3.7 M MgCl₂·6H₂O, ERDA-6, GWB at pH 7,8,9,10
- Kinetics of the Reduction of Pu(VI) by hydrogen peroxide in different concentrations of HCl, NaCl, HClO₄, HNO₃ solutions

Irradiation Experiments on Brines
INCT, Poland Linear Accelerator of Electrons 13/9 MeV
IBML, LANL, Proton/He²⁺ ions source

H₂ Gas generated by the irradiation of simulated sludges

Los Alamos
Effects of $\alpha$-Radiolysis in a TRU Waste Drum

- Pu is an $\alpha$-emitter, $\alpha$-particle irradiation of 5 M NaCl results in the formation of transitory equilibrium system of $\text{Cl}_3^-$, $\text{Cl}_2$, $\text{HClO}$, $\text{ClO}^-$, $\text{Cl}^-$
  - pH<7, the formation of chlorine gas is favored.
  - $4<\text{pH}<7$, the formation of hypochlorous acid (HClO) is observed.
  - pH>7, the formation of hypochlorite ($\text{ClO}^-$) is formed.
UV Vis absorption spectra of hypochlorite in water and in four different salt solutions

![Absorption Spectra](image)
Several chloride species have been identified in the literature.

The generation of Cl₂ may be well distinguished by a relatively broad absorption band at 332.5 nm. ClO₂ formed by disproportionation radiolysis has also easy to detect, a broad absorption band at 360 nm.

Chlorite ion ClO₂⁻ exhibits a peak at 260 nm and hypochlorite ion ClO⁻ at 292 nm in water.
Spectroscopic characteristics of important radiolysis products in water and chloride solutions

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>Absorption Band (nm)</th>
<th>( \varepsilon ) (l.mol(^{-1}).cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}_2 )</td>
<td></td>
<td>332.5</td>
<td>65</td>
<td>Buser 1952</td>
</tr>
<tr>
<td>( \text{Cl}_3^- )</td>
<td></td>
<td>325</td>
<td>190</td>
<td>Bueppelmann 1988</td>
</tr>
<tr>
<td>( \text{HClO} )</td>
<td></td>
<td>235</td>
<td>100</td>
<td>Bueppelmann 1988</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in ( \text{H}_2\text{O} ),</td>
<td>7</td>
<td>290</td>
<td>163</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in ( \text{H}_2\text{O} ),</td>
<td>13</td>
<td>292</td>
<td>345</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in 5 m NaCl</td>
<td>6.87</td>
<td>291</td>
<td>324</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in 3.7 m MgCl(_2)</td>
<td>4.42</td>
<td>284</td>
<td>197</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in GWBrine</td>
<td>7.43</td>
<td>370</td>
<td>60</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}^- ) in ERDA-6</td>
<td>8.23</td>
<td>330</td>
<td>49</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}_2^- )</td>
<td></td>
<td>260</td>
<td>98</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}_2^- ) in 5m NaCl,</td>
<td>6.87</td>
<td>259</td>
<td>108</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}_2^- ) in 3.7m MgCl(_2)</td>
<td>4.42</td>
<td>256</td>
<td>101</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{ClO}_2^- ) in ( \text{H}_2\text{O} )</td>
<td></td>
<td>360</td>
<td>1000</td>
<td>Buser 1952</td>
</tr>
</tbody>
</table>
Influence of pH on the formation of Hypochlorite in water
Influence of pH on the formation of Hypochlorite in 5 M NaCl
Stability of Pu(VI) in Synthetic Brines and Chlorite Solutions as Affected by Hydrogen Peroxide and Solution pH

Solutions:
- 95% ERDA (without CO$_3^{2-}$ or HCO$_3^-$), pH 8.25
- 95% GWB, pH 7.36
- 5 M NaCl, pH 7.02
- 3.7 M MgCl$_2$$

Pu(VI)-239 Stock:
- 0.01 M HCl solution, pH 2
- Radioactivity of Pu(VI): 1.87 x 10$^8$ pCi/g
- Concentration: 1.26 x 10$^{-2}$ M

Analytical Methods:
- UV Vis-NIR Spectrophotometer
- Liquid Scintillation Counting (LSC)
95% ERDA pH 7/pH 8

Yellow-brown precipitates started to form slowly at 1 day after Pu(VI) was added.

95% ERDA pH 7/pH 8

+ $10^{-2}$ M of $\text{H}_2\text{O}_2$

Brown precipitates formed immediately, the color of the precipitates turned to green in less than 1 hr.
95% ERDA pH 7/pH 8/pH 9

No H₂O₂

✓ In the absence of H₂O₂, yellow-brown precipitates were slowly formed at all pH levels during the 64 days.

✓ In the absence of H₂O₂, the concentration of the Pu(VI) reduced by 28% to 92%, 64 days after Pu(VI) was added.
♦ In the presence of H$_2$O$_2$, over 99% of added $^{239}$Pu(VI) was precipitated immediately regardless of pH level of solutions.

♦ The color of precipitates turned from brown to green in less than 1 hour.

♦ In the absence of H$_2$O$_2$, yellow-brown precipitates were slowly formed at all pH levels during the 64 days.

♦ In the absence of H$_2$O$_2$, the concentration of the Pu(VI) reduced by 28% to 92% at 64 days after Pu(VI) was added.
Irradiation Experiments on Brines

We attempt to quantify the irradiation-induced formation of typical radiolysis by-products such as OCl⁻ by using a 13/9 MeV LAE with doses between 120 kGy to 216 kGy.

Radiolysis set-up based on the 13 MeV Electron Linear Accelerator (LAE 13/9)

Los Alamos
Colorimetric analysis of ClO$_x$ mixture in water; reaction with KI in pH~7

\[
\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}
\]

\[
\text{I}_2 + \text{I}^- \leftrightarrow \text{I}_3^-
\]

\[
\text{ClO}_2^- + \text{I}^- \rightarrow \text{no reaction for 30 -60 min}
\]

\[
\text{ClO}_3^- + \text{I}^- \rightarrow \text{no reaction for 30 -60 min}
\]
Colorimetric analysis of ClO$_x$ mixture in 4N H$_2$SO$_4$; reaction with KI in pH~2

\[
\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}
\]

\[
2\text{ClO}_2^- + 4\text{I}^- + 6\text{H}^+ \rightarrow \text{Cl}_2\text{O} + 2\text{I}_2 + 3\text{H}_2\text{O}
\]

or

\[
\text{ClO}_2^- + 4\text{I}^- + 4\text{H}^+ \rightarrow \text{Cl}^- + 2\text{I}_2 + 2\text{H}_2\text{O}
\]

\[
\text{I}_2 + \text{I}^- \leftrightarrow \text{I}_3^-
\]

\[
\text{ClO}_3^- + \text{I}^- \rightarrow \text{no reaction for 30 -60 min}
\]
The formation of OCl⁻ in 5 M NaCl featuring high energy proton beam line experiments

- The perspective of these preliminary experiments is to be able to determine accurately the effects of α-activities up to kCi/L.
- Two preliminary experiments were performed: (1) A 4 mL quartz cuvette containing 5 M NaCl solution, pH 13 was attached to the 3 MV Tandem ion accelerator and irradiated by 4-6 MeV protons for three hours to reach a total absorbed dose of about 30 kGy. The temperature was (24 ± 2 °C). After irradiation, a UV Vis absorption spectrum of the irradiated brine was taken to identify the formation of hypochlorite.
- (2) A 20 mL polyethylene test cell containing 5 M NaCl solution, pH 13 was attached to the 3 MV Tandem ion accelerator and irradiated with incremental step of 6, 12, 18, 24, and 30 micro Coulomb of 4.939 MeV protons producing absorbed doses of 1.48 kGy to 7.41 kGy. The temperature was (24 ± 2 °C). After each irradiation step, a UV Vis absorption spectrum of the irradiated brine was taken to monitor the formation of hypochlorite as a function of the absorbed dose.
Beam distribution to the individual application chambers
UV-Vis Absorption spectrum of 5 M NaCl, pH 13, after 4.4 MeV proton irradiation, achieving an absorbed dose of 30 kGy
UV Vis absorption spectra of 5 M NaCl (pH 13) after introducing radiation doses of 1.48 kGy each producing a total absorbed dose of 7.4 kGy.
We have quantified significant formation of hypochlorite at rather low dose and dose rate.

The measured G-value for ClO⁻ formation in a 20 mL quartz cell containing 5 M NaCl solution, irradiated by proton ions is estimated to be 0.0949 molecules /100 eV, which is in fairly good agreement with the data published by Kelm et al. (1999) of 0.0965 for alpha-self-irradiation using plutonium solutions of 3.7 GBq/L (1Ci/L).

Therefore this technique shows promise for being able to provide cumulative dose effects under repository conditions without the need for large quantities of plutonium.
UV Vis absorption spectra of 3.7 M MgCl$_2$.6H$_2$O (pH 4.42) after introducing radiation doses of 1.20 kGy each producing a total absorbed dose of 7.20 kGy.
UV Vis absorption spectra of 95% GWB (pH 7.11) after introducing radiation doses of 1.26 kGy each producing a total absorbed dose of 5.04 kGy.