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**LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS**

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**Actinide (VI) Solubility in Carbonate-free WIPP Brine:
Data Summary and Recommendations**

J. F. Lucchini, H. Khaing, M. Borkowski, M. K. Richmann, and D. T. Reed

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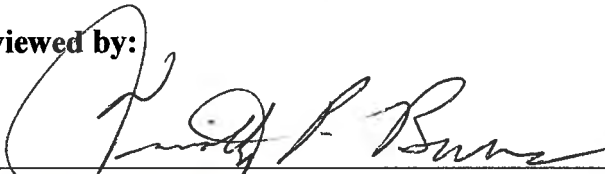


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Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations

J. F. Lucchini, H. Khaing, M. Borkowski, M. K. Richmann, and D. T. Reed

EXECUTIVE SUMMARY

The solubility of uranium (VI) in carbonate-free WIPP-relevant brine was determined as part of an overall effort to establish a more robust WIPP chemistry model to support ongoing WIPP recertification activities. This research was performed by the Los Alamos National Laboratory Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP). The solubility data in carbonate-free brine systems is the first step in understanding the relative contribution of hydrolysis and carbonate complexation to uranium (VI) solubility over a wide range of pC_{H^+} under WIPP-relevant conditions.

The Waste Isolation Pilot Plant (WIPP) Actinide Source Term Program (ASTP) did not develop a model for the solubility of actinides in the VI oxidation state. The solubility of UO_2^{2+} , in the absence of WIPP-specific data, is presently set at 10^{-3} M in the WIPP Performance Assessment (PA) for all expected WIPP conditions. This value was selected at the recommendation of the Environment Protection Agency (EPA), based on their review of the relevant data available in the literature and accounts for the potential and likely effects of carbonate complexation on the solubility of uranium (VI).

In this report, the results of experiments to establish the solubility of U(VI) in carbonate-free WIPP brines from over-saturation are presented. This is the research status in this area at the time of the 2009 Compliance Recertification Application (CRA) data cutoff. The objective of these experiments was to establish a baseline solubility to further investigate the effects of carbonate complexation. The experiments performed were done according to the DOE approved Test Plan entitled "Solubility/ Stability of Uranium (VI) in WIPP Brines" and designated LCO-ACP-02. All data reported were obtained under the LANL-Carlsbad Operations WIPP Quality Assurance Plan, which is compliant with the Department of Energy (DOE) Carlsbad Field Office, Quality Assurance Program Document (CBFO/QAPD). The data summarized in this report are supported by QA documentation that is maintained in the LANL-CO record center. A literature review on the solubility of VI actinides, and more specifically U(VI), was also done, and is reported herein.

There are a number of key results and observations from this U(VI) solubility study in carbonate-free brine systems and the literature search that was performed. The most important of these are:

- There were no WIPP-specific experimental data available in the literature on VI actinide solubility in carbonate-free brine. The two WIPP-relevant papers found in the

literature were from Yamazaki [Yamazaki 1992] and Diaz-Arocas [Diaz-Arocas 1998]. They determined the solubility of uranium (VI) in conditions close to those expected in WIPP (brine, high ionic strength, basic pH), but with a less rigorous control of a carbon dioxide free environment than in our experiments. These are not new results and have already been reflected in the WIPP conceptual approach.

- Our solubility data for uranium (VI) provides the first WIPP-relevant data for the VI actinide oxidation state that establish the solubility of uranium (VI) over an extended pC_{H^+} range for GWB and ERDA-6 brines in the absence of carbonate. These data are the first data generated at high pC_{H^+} under what we believe to be a truly carbonate-free system. They establish uranium solubility, in the absence of carbonate that is 10-100 times lower than published results. The uranium (VI) solubilities measured in our experiments were about 10^{-6} M in GWB brine at $pC_{H^+} \geq 7$ and about 10^{-8} - 10^{-7} M in ERDA-6 at $pC_{H^+} \geq 8$.
- Our solubility data for uranium (VI) demonstrate that high pC_{H^+} values lead to low uranium solubility due to hydrolysis, in carbonate-free and low carbonate content WIPP brines. At $pC_{H^+} \geq 10.5$, hydrolysis overwhelms carbonate effects, and no amphoteric effect was observed.

Overall, there are four key recommendations or conclusions with respect to the current WIPP PA position on the solubility of the VI actinides based on our experimental results and literature review:

- 1) ***Our data on uranium (VI) solubility in WIPP simulated brine are the first experimental data obtained in a truly carbonate-free system.*** They establish a uranium solubility, in the absence of carbonate, that is 10-100 times lower than published results. The uranium (VI) solubility experiments reported in the two relevant publications ([Yamazaki 1992] and [Diaz-Arocas 1998]) were performed in brines close to the WIPP brine composition, but with a less rigorous control of a carbon dioxide free environment than in our experiments. The lower uranium solubilities we report are indicative of a good experimental protocol and point towards a lower overall solubility of uranium in the WIPP.
- 2) ***The data for carbonate-free WIPP brines provide a baseline for carbonate effects on uranium (VI) solubility.*** These data, obtained from the over-saturation approach only, are the first repository-relevant data for the VI actinide oxidation state which fills a gap in experimental data in the current WIPP PA. The solubility trends observed point towards lower uranium solubilities in WIPP brine, a lack of amphotericity, an insignificant effect of borate complexation, and a predominance of hydrolysis at $pC_{H^+} > 10.5$.
- 3) ***Further investigations of the role of carbonate in the VI actinide solubility are needed.*** Given some of the relatively high uranium concentrations reported in the literature, accounting for the effect of carbonate complexation is critical to establish that the current assumption of a 1 mM U(VI) concentration is supported. Experiments are currently in progress to determine the relative contribution of carbonate complexation

over a broad range of pH, and these data are expected to support the current position on An(VI) solubility under WIPP-relevant conditions.

- 4) ***It is still not clear that an actinide (VI) solubility model is needed although this was recommended by the EPA.*** This issue cannot be fully evaluated until the effects of carbonate on U(VI) solubility under WIPP-relevant conditions are established. Given that the results of the carbonate-free brine system point to a lower overall solubility than previously thought and higher pH trends toward lower solubilities, it is likely that U(VI) solubilities under expected conditions will be well below the current 1 mM value set by the EPA. This is further supported by the continued low importance and role of the VI oxidation state in calculating the potential for actinide release from the WIPP.

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LIST AND DEFINITION OF ACRONYMS

ACRSP	Los Alamos actinide chemistry and repository science program
ACS	American Chemical Society
Ar	Argon
Am	Americium
An	Actinide
An(III)	General Actinide in the III oxidation state
An(IV)	General Actinide in the IV oxidation state
An(V)	General Actinide in the V oxidation state
An(VI)	General Actinide in the VI oxidation state
ASTP	WIPP Actinide Source Term Program
Å	Angstrom
β°	Stability constant at reference state
CaCl ₂	Calcium chloride
(DOE) CBFO	(Department of Energy) Carlsbad Field Office
CCA	Compliance Certification Application
CEMRC	Carlsbad Environmental Monitoring and Research Center
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
CRA	Compliance Recertification Application
DOE	US Department of Energy
EPA	US Environment Protection Agency
ERDA-6	(U.S.) Energy Research and Development Administration (WIPP well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
EXAFS	Extended X-ray Absorption Fine Structure
Fe	Iron
FMT	Fracture-Matrix Transport model
g	Gram
GWB	Generic Weep Brine, a synthetic brine representative of fluids in Salado brine reservoirs
H ⁺	Hydrogen ion
H ₂ O	Water

HP water	High Purity water, i.e. deionized water with a specific resistance of 18.0 megaohm-cm or greater at room temperature
I	Ionic strength
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
KCl	Potassium chloride
kDa	kiloDalton
K ₂ U ₂ O ₇	Potassium diuranate
L	Liter
LANL	Los Alamos National Laboratory
LANL-CO	Los Alamos National Laboratory - Carlsbad Operations
LiCl	Lithium chloride
mL	Milliliter
mM	Millimole
M	Mole per liter
MgCl ₂	Magnesium chloride
MgO	Magnesium oxide
Mg(OH) ₂	Brucite
MΩ·cm	Megaohm-centimeter
NaBr	Sodium bromide
Na ₂ B ₄ O ₇	Sodium tetraborate
NaCl	Sodium chloride
Na ₂ SO ₄	Sodium sulfate
nm	nanometer
NMSU	New Mexico State University
Np	Neptunium
N ₂	Nitrogen
OH ⁻	Hydroxyl ion
PA	Performance Assessment
PABC	Performance Assessment Baseline Calculation
PAVT	Performance Assessment Verification Test
pC _{H+}	Negative logarithm of H ⁺ concentration
pH	Negative logarithm of H ⁺ activity
ppb	Parts per billion
ppm	Parts per million
Pu	Plutonium

Pu(VI)	Plutonium in the VI oxidation state
QA	Quality Assurance
QAPD	Quality Assurance Program Document
QL1	Quality Level 1
SOTERM	Actinide Source Term appendix for WIPP recertification applications
T	Temperature
Th	Thorium
TRU	Transuranic (actinides higher in atomic number than uranium)
U	Uranium
U(III)	Uranium in the III oxidation state
U(IV)	Uranium in the IV oxidation state
U(V)	Uranium in the V oxidation state
U(VI)	Uranium in the VI oxidation state
UO_2^+	Uranyl ion – Aqueous form of the uranium at the V oxidation state
UO_2^{2+}	Uranyl ion – Aqueous form of the uranium at the VI oxidation state
UO_2CO_3	Uranyl carbonate
WIPP	Waste Isolation Pilot Plant
XANES	X-ray Absorption Near Edge Spectroscopy
XRD	X-Ray Diffraction

Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations

1.0 INTRODUCTION

The solubility of actinides in the VI oxidation state in Waste Isolation Pilot Plant (WIPP) brine was and continues to be considered in WIPP performance assessment (PA). Actinides that could potentially exist in the VI oxidation state are U(VI), Np(VI) and Pu(VI). Of these, only U(VI) is expected under current WIPP PA assumptions since both Np(VI) and Pu(VI) can be excluded because of the highly reducing conditions expected to predominate in the WIPP. Since the release of uranium is a relatively minor contributor to actinide release, the WIPP has not developed a VI actinide model as was done for all the other possible actinide oxidation states in the WIPP (III, IV, V) prior to the Compliance Certification Application (CCA). There are relatively few uranium (VI) solubility data published in the literature and these were not obtained under WIPP-relevant conditions.

In this context, the LANL/ACRSP team initiated uranium (VI) solubility experiments in simulated WIPP brine to provide WIPP-relevant data that help establish the degree of conservatism in current WIPP PA assumptions. The initial step in this process was the determination of the solubility of uranium in carbonate-free brine. These results represent what was completed at the time of the CRA-2009 cutoff and are summarized in this report.

The key objectives of this technical summary report are to provide the following:

- 1) An updated literature review for the solubility of uranium in the VI oxidation state under conditions that are relevant to the WIPP case.
- 2) A summary of WIPP-specific data obtained by the LANL-ACRSP team on the solubility of U(VI) in carbonate-free simulated WIPP brine. These data would also apply more generically to An(VI) solubility in the WIPP.
- 3) An assessment and comparison of the new literature data and our WIPP-specific results with the current WIPP PA position on the solubility of uranium in brine.

The WIPP is located in the Delaware Basin in southeastern New Mexico 26 miles east of Carlsbad. It is the only operating underground nuclear waste repository in the United States. It was first certified by EPA in May 1998 as a transuranic (TRU) waste repository. The regulatory guidelines for the WIPP are given in 40CFR191/194 [DOE 1996]. Based on these regulations, the WIPP is required to undergo a re-certification process by the EPA every five years. The first CRA was submitted in 2004 by DOE CBFO, and was approved in April 2006. This documentation is part of the second WIPP recertification cycle and supports CRA-2009 documentation provided to the EPA.

The WIPP relevant solubility studies summarized in this report were performed by the Los Alamos-Carlsbad Office (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) team at the New Mexico State University (NMSU) Carlsbad Environmental Monitoring and Research Center (CEMRC). The overall research goals of ACRSP are 1) to establish the conservatisms of the current WIPP Performance Assessment (PA) calculations of actinide solubility, 2) to help establish a more robust WIPP chemistry model, and 3) to extend past research to conditions that better simulate potential brine environments in the WIPP. This is being done by a combination of redox invariant analog studies and actinide studies in two simulated WIPP brines, GWB and ERDA-6 brine, that bracket the range of brine composition expected in the WIPP. All the experiments are performed under the LANL-CO Quality Assurance Program that is DOE CBFO Quality Assurance Program Document (QAPD) compliant.

2.0 SUMMARY OF THE CRA-2004 WIPP PA POSITION ON ACTINIDE (VI) SOLUBILITY

The CRA-2004 WIPP PA position on the solubility of actinides in the VI oxidation state was presented in attachment SOTERM [SOTERM 2003]. Based on this attachment, the following is an overview of the relative importance of the predominant actinides and oxidation states in the WIPP:

Importance of actinide solubility to release: $Pu \approx Am > U \gg Np \approx Th$

Importance of actinide oxidation state: $An(III) > An(IV) \gg An(VI) \gg An(V)$

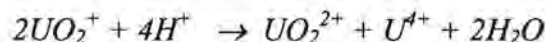
In the actinide inventory that was emplaced in the two first completed WIPP panels [Lucchini 2007], uranium is by far the most prevalent actinide (~83% by mass) and plutonium is the most prevalent TRU component (most of which is Pu-239) from the perspective of mass. From the perspective of Curie content, both plutonium and americium are approximately equal and are together by far, the most important contributors to the potential actinide release calculations. In terms of overall actinide oxidation states, III and IV are expected to predominate in the WIPP, although it is recognized that localized oxidizing zones may exist. These transient oxidizing zones will be overwhelmed by the highly reducing environment established by the waste components (e.g. Fe from the containers) and anticipated microbiology (e.g. sulfate reduction and methanogenesis).

2.1 WIPP Position on Uranium Source Term

The WIPP PA position on the uranium source term is addressed in the following excerpt from SOTERM [SOTERM 2003]:

SOTERM-4.2 Uranium

U can exist in aqueous solution in the +III, +IV, +V, and +VI oxidation states (Hobart 1990; Keller 1971; Clark et al. 1995). The predominant oxidation states for U in the natural environment are +IV and +VI. U(III) may be prepared in aqueous solution but is easily oxidized to U(IV) (Katz et al. 1986, 1139 and following). The standard reduction potential of U favors reduction of U(V) to U(IV) in aqueous solution, and the pentavalent oxidation state is the least stable oxidation state in solution. U(V) disproportionates in acidic aqueous solution by the reaction:



However, the U(VI) species UO_2^{2+} is the most stable in low concentrations in the

pH 2 to 4 range (Katz et al. 1986).

It is the disproportionation reaction of U(V) that limits it to trace level concentrations. U(VI) is a stable oxidation state, even under mildly reducing conditions, but may be reduced to U(IV) by a variety of reducing agents. In the chemically reducing environment expected in the WIPP, U(VI) will be reduced to U(IV). However, Reed et al. (1996) found that at pH 10 under anoxic conditions, U(VI) is stable as a CO_3^{2-} complex in simulated WIPP brines. U(IV) is the predominant oxidation state in half of the PA vectors, and U(VI) in the other half, due to uncertainty predicting the more stable oxidation state of U under WIPP conditions.

In summary, the CRA-2004 attachment SOTERM [SOTERM 2003] conservatively assumes that uranium speciates in the IV oxidation state in 50% of the PA vectors (reduced vectors) and speciates in the VI oxidation state in the other 50% of the PA vectors (oxidized vectors). This is a conservative assumption since U(IV) species should be predominant under the expected WIPP conditions and U(IV) species are much less soluble than U(VI) species.

2.2 CRA-2004 WIPP Position on Actinide (VI) Solubility

The VI actinides of interest to the WIPP are uranium and plutonium, and to a much lesser extent, neptunium. Plutonium (VI) is only expected as a transient oxidation state for plutonium given the reducing conditions expected in the repository. In WIPP PA, plutonium speciates as Pu(IV) in the oxidized vectors and Pu(III) in the reduced vectors. Uranium (VI), in this context, is predicted to be the only VI actinide present in the WIPP in significant concentrations. The uranyl ion UO_2^{2+} is a relatively stable form of uranium in solution and is also the most stable of the actinyl (VI) cations [Morss 2006]. This redox stability makes it the most suitable for solubility studies and uranium is used as a “redox-invariant” analog species for experimental studies of actinide (VI) species.

As a part of the WIPP Actinide Source Term (ASTP) program results, during the 1990s, a range of solubilities was assigned to each probable actinide oxidation state. The goal of the ASTP was to determine the concentration of actinides present in WIPP disposal rooms that could be mobilized by contact with brine and possibly migrate from the WIPP to the accessible environment. This program featured the development of a numerical model to predict mobile actinide concentrations with order-of-magnitude accuracy. This accuracy requirement reflected the expected precision in the WIPP Performance Assessment (PA) calculations for EPA compliance [Novak 1996].

The WIPP ASTP program, however, did not develop a model for the solubility of actinides in the VI oxidation state. Hobart and Moore estimated that the appropriate uranium (VI) concentration for Brine A and ERDA-6 brine was 1.2×10^{-5} M, based on an assessment of the limited experimental data available at the time [Hobart 1996; Brush 2003]. This selected concentration was not a conservative estimate; instead, this value was selected because it was within the range of the available experimental values.

The actinide solubilities calculated based on the data generated by the ASTP program were summarized as part of the CRA-2004 effort [Trovato 1997; Brush 2003, SOTERM 2003] and are shown in Table 2-1. The uranium (VI) solubility used in the Compliance Certification Application (CCA), the PAVT, and the CRA-2004 was $(8.8 \pm 0.1) \times 10^{-6}$ M [DOE 1996, Appendix SOTERM Table SOTERM-2; SOTERM 2003, Appendix PA Table PA-8 and Appendix PA Attachment SOTERM Table SOTERM-2]. This value corresponds to the solubility of schoepite ($UO_3 \cdot 2H_2O$), which was selected as the solubility-controlling phase [Hobart 1996].

Table 2-1. Actinide Solubilities (M) Calculated (+III, +IV, and +V) or Estimated (+VI) for the CRA-2004 PA, the 1997 PAVT and the CCA PA [DOE 2004b, Table SOTERM-2]. The CRA calculations reflect the inclusion of organic complexation and updated chemical conditions for microbial and non-microbial vectors.

Actinide Oxidation State, and Brine	CRA Solubilities, Microbial Vectors	CRA Solubilities, Non-microbial Vectors	PAVT Solubilities	CCA Solubilities
+III, Salado brine	3.07×10^{-7}	3.07×10^{-7}	1.2×10^{-7}	5.82×10^{-7}
+III, Castile brine	1.69×10^{-7}	1.77×10^{-7}	1.3×10^{-8}	1.3×10^{-8}
+IV, Salado brine	1.19×10^{-8}	1.24×10^{-8}	1.3×10^{-8}	4.4×10^{-6}
+IV, Castile brine	2.47×10^{-8}	5.84×10^{-9}	4.1×10^{-9}	6.0×10^{-9}
+V, Salado brine	1.02×10^{-6}	9.72×10^{-7}	2.4×10^{-7}	2.3×10^{-6}
+V, Castile brine	5.08×10^{-6}	2.13×10^{-5}	4.8×10^{-5}	2.2×10^{-6}
+VI, Salado brine	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}
+VI, Castile brine	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}

In the CRA-2004 Performance Assessment Baseline Calculation (PABC), which superseded the CRA-2004 PA, a value of 10^{-3} M was used as the solubility of U(VI) based on recommendations by the EPA to better account for uncertainties in the effect of carbonate on the solubility of U(VI). This value of 10^{-3} M is a fixed upper-limit value that reflects the scarcity of uranium (VI) solubility data relevant to WIPP repository conditions and the lack of a thermodynamic model for An (VI) solubility. This concentration value provides a conservative estimate of the upper limit of uranium (VI) concentrations for use in PA [EPA 2006a] for the conditions expected in the WIPP.

2.3 EPA Position on Uranium (VI) Solubility

The EPA position on uranium (VI) solubility is presented in the following excerpt from [EPA 2006b, page 7-9]:

7.4.2 Uranium(VI) Solubility

Uranium is the only +VI actinide expected to be present in significant quantities in solution at equilibrium in the WIPP repository. For the CRA PA (DOE 2004b), DOE used the same estimated +VI actinide concentration that was used in the CCA PA and PAVT (Table 7-5). The Agency noted in their review of the CRA that DOE did not re-evaluate the +VI actinide solubility used in the CRA PA based on data that had become available since the CCA. The Agency requested additional information from DOE regarding relevant actinide solubility data developed outside the WIPP program since the CCA (EPA 2004b, Comment C-23-14). In their response, DOE cited data that were included in the FMT database for the +III, +IV, and +V actinides, but did not address the +VI actinides (DOE 2004d). Because DOE did not address potential new information related to the solubility of the +VI actinides, the Agency reviewed the available literature to determine whether the assumed +VI actinide solubility should be revised (EPA 2005b). The Agency took into consideration the presence of low, but significant carbonate ion concentrations in the presence of the brucite/hydromagnesite buffer, as well as the uranium(VI) aqueous species and solid phases likely to form under WIPP repository conditions. Based on the results of this review, the Agency specified the use of a fixed upper-limit value of 10^{-3} M for the uranium(VI) concentration in the PABC (EPA 2005a and 2005b).

DOE stated that they have not developed a speciation and solubility model for calculating the solubility of uranium(VI) in the WIPP repository because of the complexity of uranium(VI) hydrolysis (DOE 2004b, Appendix PA Attachment SOTERM). However, DOE has apparently not considered the probability that carbonate complexes of uranium(VI) will dominate its aqueous speciation under expected WIPP chemical conditions. In addition, a study that provided estimated Pitzer parameters for uranium(VI) has been published since the PAVT (Plyasunov et al. 1998). DOE did not address whether these estimated Pitzer coefficients are sufficient for the development of an FMT solubility model or whether this type of approach could be used to develop a model for predicting uranium(VI) solubilities under WIPP conditions. The uranium(VI) concentration specified as a fixed, upper-limit value for the PABC is higher than the upper limit of the uncertainty for the +VI actinide solubility used in the CCA PA, PAVT, and CRA PA. This conservative, higher upper limit was necessary because of the additional experimental data available in the literature since the PAVT and DOE's decision not to develop a solubility model for the +VI actinides. The Agency chose to specify a conservative, fixed value for uranium(VI) solubility of 10^{-3} M because it is difficult to provide a technical basis for an uncertainty range for a "reasonable" solubility estimate without additional data.

This excerpt from the EPA documentation [EPA 2006b] gives the historical reasons of their recommendation for a uranium (VI) solubility of 10^{-3} M. Although this U(VI) solubility estimate takes into account some new experimental data published in the literature since the CCA, these data are not in fact WIPP-relevant and conservatively overestimate the expected solubility of uranium in the WIPP.

2.4 Need for the Development of an Actinide (VI) Solubility Model

There remains no need for an An(VI) solubility model based on current WIPP PA assumptions. This is true even though an actinide solubility model exists for each of the other possible oxidation states in the WIPP (+3, +4, +5). The data we report herein, however, are a starting point towards the development of an An(VI) model should this become needed. Much additional research would be needed to accomplish this goal.

For the CRA-2004, the following assumption in selecting the uranium (VI) concentration was used for PA: carbonate would be mostly absent from repository brines because of the presence of MgO. Consequently, U(VI) would exist in hydrolyzed forms. Because of the uncertainties regarding uranium (VI) hydrolysis species in basic solutions, DOE has stated that a satisfactory solubility model for this case is unavailable.

Since the CRA-2004, however, the EPA reviewed DOE's predictions of uranium (VI) solubilities, including the information in the CCA and supporting documents [Hobart 1996; Novak 1996], and additional information that became available after the CCA [DOE 1996]. The EPA has indicated [EPA 2006a] that the brucite-hydromagnesite reaction will control carbonate concentrations at relatively low, but non-zero levels. In this case, the EPA noted that the dominant species in the pH range relevant to the WIPP repository are likely to be carbonate complexes such as UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ [DOE 1996]. For this reason a value of 1 mM was recommended for the solubility of U(VI) and was used in the CRA-2004 PABC. There is no recommendation of need to change this assumed value for the CRA-2009 based on this data summary report.

3.0 LITERATURE BACKGROUND: SOLUBILITY OF U(VI) IN CARBONATE-FREE MEDIA

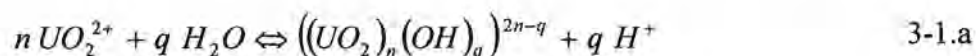
The solubility and extent of aggregation in WIPP-relevant brine are key factors that define the potentially mobile concentration of actinides from an underground repository to the environment [Clark 1995, Reed 1996, Runde 2000, Moulin 2001, Choppin 2003]. Solubility, which is the focus of this report, is governed by the oxidation state distribution and the speciation of each oxidation state.

In this report, the focus is on the uranyl cation UO_2^{2+} , as the best oxidation state analog for the actinide VI oxidation state, in carbonate-free solutions. Under these conditions, the speciation of uranium (VI) in water is dominated by hydrolysis (section 3.1). We also report on some literature experimental results that were performed to determine the solubility of uranium (VI) under conditions that approach those expected in WIPP (brine, high ionic strength, basic pH). These literature results are presented and discussed in section 3.2.

3.1 Hydrolysis of Uranium (VI)

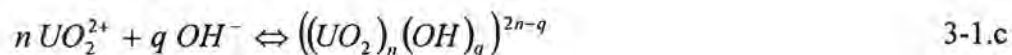
The hydrolysis of the uranyl cation, UO_2^{2+} , has been studied quite intensely, partially because it forms a wide variety of polynuclear hydrolytic species, resulting in a quite complex chemistry.

Hydrolysis reactions occur for the f-elements in weakly acidic to alkaline solutions in the III, IV and VI oxidation states and often predominate over other complexation reactions in neutral and basic solutions. The hydrolysis reactions involving UO_2^{2+} can be expressed by the general reaction



$$^*\beta_{nq} = \frac{[((UO_2)_n(OH)_q)^{2n-q}][H^+]^q}{[UO_2^{2+}]^n} \quad 3-1.b$$

where $^*\beta_{nq}$ increases with increasing cationic charge density. Such hydrolysis reactions can also be described as hydroxide complexation reactions:



$$\beta_{nq} = \frac{[((UO_2)_n(OH)_q)^{2n-q}]}{[UO_2^{2+}]^n [OH^-]^q} \quad 3-1.d$$

with $K_w = [H^+][OH^-]$, this becomes

$$\beta_{nq} = \beta_{nq}^* / K_w^q \quad 3-1.e$$

Palmer and Nguyen-Trung established the speciation diagram for the formation of $((UO_2)_n(OH)_q)^{2n-q}$ with $[UO_2^{2+}]_{total} = 4.75 \times 10^{-4}$ M, ionic strength $I = 0.1$ M, $T = 25$ °C (Figure 3-1) [Palmer 1995]. This diagram was obtained from fitted experimental data given in Table 3-1 by the authors.

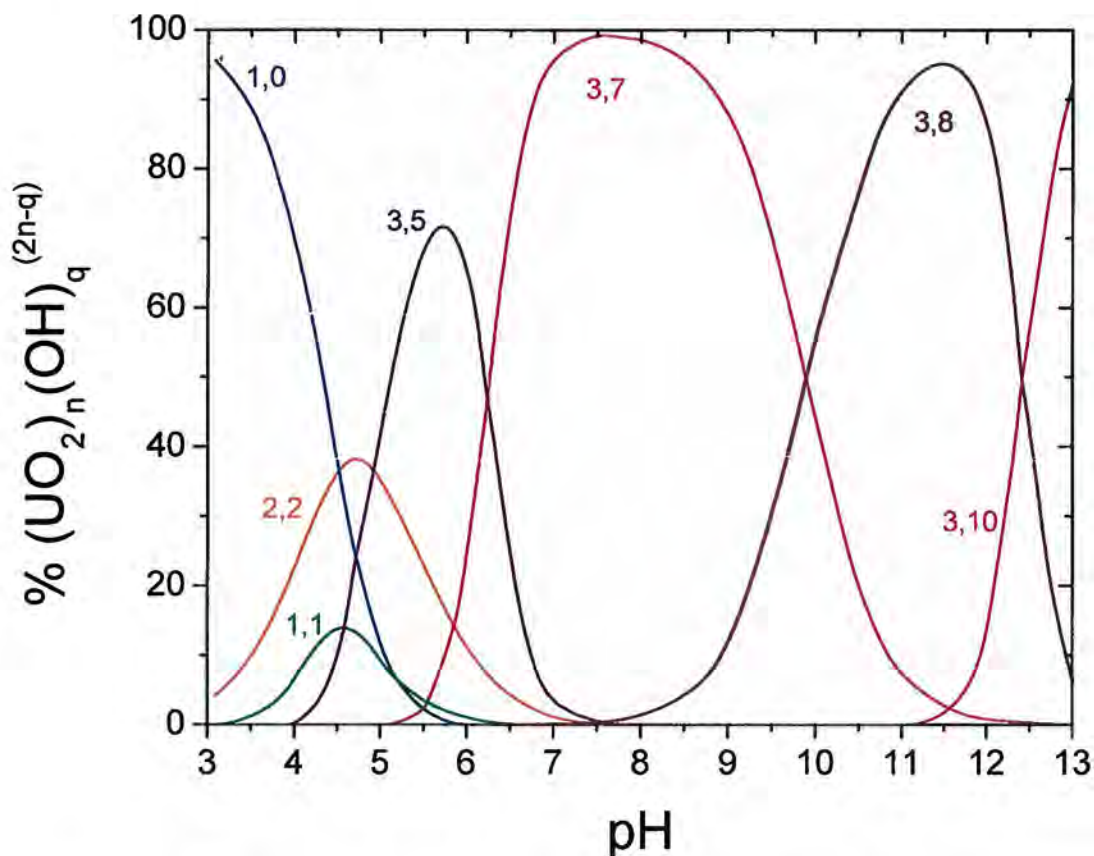


Figure 3-1: Speciation diagram for the formation of $((UO_2)_n(OH)_q)^{2n-q}$ with $[UO_2^{2+}]_{total} = 4.75 \times 10^{-4}$ M, ionic strength $I = 0.1$ M, $T = 25$ °C. The number pairs shown on the graph refer to n and q . (Based on data in Palmer 1995)

Table 3-1. Hydrolysis constants at I = 0 and 25°C for formation of $((\text{UO}_2)_n(\text{OH})_q)^{2n-q}$ species [Morss 2006].

n,q	$\log^* \beta_{nq}^0$ [Palmer and Nguyen-Trung 1995]	$\log^* \beta_{nq}^0$ [Guillaumont 2003]
1,1	-5.42 ± 0.04^a	-5.25 ± 0.24
2,2	-5.51 ± 0.04	-5.62 ± 0.04
3,5	-15.33 ± 0.12	-15.55 ± 0.12
3,7	-27.77 ± 0.09	-32.2 ± 0.8
3,8	-37.65 ± 0.14	---
3,10	-62.4 ± 0.3	---

^a For I = 0.10 M (KNO₃).

In very dilute solutions, $[\text{UO}_2^{2+}] \leq 10^{-6}$ M, the hydrolysis of UO_2^{2+} first forms mononuclear $\text{UO}_2(\text{OH})_q^{2-q}$ species, but above this concentration, UO_2^{2+} exists mainly as polynuclear species [Morss 2006]. Within wide ranges of pH and C_M (metal concentration), the predominant complex is the dimer $(\text{UO}_2)_2(\text{OH})_2^{2+}$. As the pH increases, the 3:5 complex $(\text{UO}_2)_3(\text{OH})_5^+$ becomes prominent. Between pH = 6.5 and 9.5, the uranyl cation is almost exclusively in the form of the 3:7 complex $(\text{UO}_2)_3(\text{OH})_7^-$. At $9.5 \leq \text{pH} \leq 12.5$, the uranyl cation is present in carbonate-free solution as $(\text{UO}_2)_3(\text{OH})_8^{2-}$. The uranyl complex $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$ is expected at $\text{pH} \geq 12.5$.

Other hydrolytic uranyl species were reported to exist [Morss 2006]. In chloride solutions, $(\text{UO}_2)_3(\text{OH})_4^{2+}$ is also formed. In concentrated solutions at low pH, $(\text{UO}_2)_2\text{OH}^{3+}$ may be present. Other complexes which have been proposed to form are $(\text{UO}_2)_3(\text{OH})_7^-$, $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$, $(\text{UO}_2)_4(\text{OH})_6^{2+}$, $(\text{UO}_2)_4(\text{OH})_7^+$ and $(\text{UO}_2)_5(\text{OH})_8^{2+}$. The existence of the dimer $(\text{UO}_2)_2(\text{OH})_2^{2+}$ has been confirmed by direct determination of the species present in hydrolyzed uranyl (VI) chloride solutions [Åberg 1970]. Even in the concentrated solutions ($C_M = 3\text{M}$) used in these diffraction studies, the dimer is an important species at the lower ligand-number species investigated. The average U-U distance in the species present in these concentrated solutions is 3.88 Å which is close to the distance of 3.94 Å found in the solids $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ and $[(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ [Åberg 1970, Perrin 1976].

As an example of the effect of ionic strength, the variation of the hydrolysis constant of $\text{UO}_2(\text{OH})^+$ as a function of ionic strength is given in Table 3-2. The increase in ionic strength leads to the formation of increased amounts of the uranyl complex in water.

Table 3-2. Hydrolysis constants for UO_2^{2+} at different ionic strengths; T = 25°C [Morss 2006].

I (M)	$\log^* \beta_{11}$	$\log \beta_{11}$
0 ^a	-5.88	8.12
0.1	-6.09	7.70
0.4	-6.20	7.56
0.7	-6.07	7.71
1.0	-6.20	7.82

^a Extrapolated values

3.2 Solubility of Uranium (VI) in Carbonate-free Brine

In this section, we present and discuss the uranium literature data in brine systems that were obtained in so-called carbonate-free media. Overall, there are little/no uranium (VI) solubility data that are directly relevant to WIPP-specific conditions: i.e., magnesium-sodium-chloride brines, high ionic strength ($I > 5$ M), and moderately alkaline pH. The available results in the more generic brine systems are summarized in Table 3-3 and plotted in Figure 3-2.

In contrast to the carbonate-free case, there are several WIPP-relevant studies reported in the literature that were performed in the presence of carbonate [Kramer-Schnabel 1992, Meinrath 1993, Reed 1996, Lin 1998, Yamamura 1998]. The role of carbonate in defining the solubility of uranium (VI) is indeed important [Clark 1995, Guillaumont 2003], but this will be the topic of future research and reports and is outside the scope of this data summary report.

Yamazaki et al. conducted U(VI) solubility experiments from both oversaturation and undersaturation in a synthetic brine at pC_{H^+} values ranging from 6.4 to 12.4 [Yamazaki 1992]. The composition of this synthetic brine was close to the composition of the WIPP GWB brine, with higher concentrations of NaCl, NaBr, KCl and MgCl_2 . This synthetic brine initially contained 0.1 mM of bicarbonate HCO_3^- , but the solution treatment (continuous nitrogen gas flow above the solution,) likely removed some of the carbonate from solution before the later uranium additions and prevented any CO_2 uptake during the experiment. The results obtained at the pC_{H^+} closest to WIPP repository conditions with no further carbonate additions are listed in Table 3-3 and plotted in Figure 3-2. Uranium (VI) concentrations of approximately 10^{-7} M were observed at $pC_{H^+} = 10.4$ and 12.4 when nitrogen gas was continuously passing over the solutions to minimize CO_2 uptake.

Despite extensive precipitation of brucite $\text{Mg}(\text{OH})_2$ at these high pC_{H^+} values, the solubility-controlling phase at $pC_{H^+} \geq 9.3$ was found to be potassium diuranate $\text{K}_2\text{U}_2\text{O}_7$. At $pC_{H^+} = 8.4$, good agreement was found for uranium (VI) solubility in the oversaturation and undersaturation experiments that were carried out in an air atmosphere. At this pC_{H^+} value, millimole concentrations of uranium were measured in solution. Solids obtained at $pC_{H^+} = 8.4$ were identified as poorly crystalline schoepite by X-Ray Diffraction (XRD). Yamazaki carried out some calculations to model the competition between calcium and magnesium for carbonate

complexation in order to interpret his experimental solubility data. He concluded that the uranium solubility decrease above $pC_{H^+} = 8.4$ was related to a shift from the triscarbonato uranyl complex $UO_2(CO_3)_3^{4-}$ to the uranyl hydroxide complexes $UO_2(OH)_n^{2-n}$, as precipitation of calcium carbonate ($CaCO_3$) occurred, and to the conversion of schoepite to potassium diuranate.

At $pH = 9.8$ in brine in the absence of carbonate, Palmer observed a U(VI) solubility of 2.8×10^{-6} M in equilibrium with a phase that appeared to be $UO_2(OH)_2$ (s) [Palmer 1996]. These results were privately communicated by Palmer, and reported by Hobart [Hobart 1996], but never published. For this reason they are not considered further in this report.

Diaz-Arocas and Grambow investigated uranium (VI) solubility in NaCl solutions up to 5 M at 25°C and different basic pH values, under an argon atmosphere using an oversaturation approach [Diaz-Arocas 1998]. Their uranium concentration equilibria in 5 M NaCl are presented in Table 3-3. The published values were converted from molality to molarity using a density value of 5 M NaCl equal to 1185 g/L. At $pH \geq 7.5$, poorly-crystalline sodium-uranates, identified by XRD, were formed in solutions. Diaz-Arocas and Grambow indicated that the solubility of this phase was about 3×10^{-5} M at $pC_{H^+} = 8.9$ in 5 M sodium chloride in the absence of carbonate.

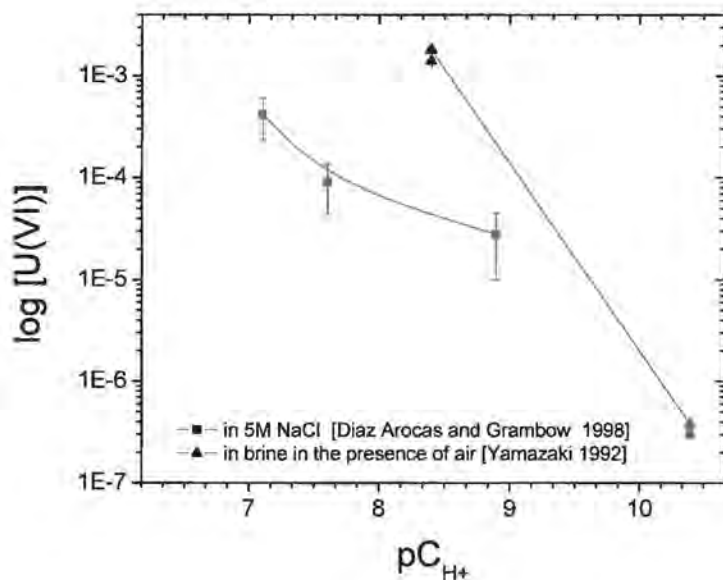


Figure 3-2: Uranium (VI) solubility data obtained in carbonate-free (otherwise mentioned) high ionic strength media at $pC_{H^+} > 7$. The full square symbols and corresponding fit line represent data obtained by Diaz Arocas and Grambow in 5 M NaCl under an argon atmosphere [Diaz Arocas 1998]. The full triangle symbols and corresponding fit line represent data obtained by Yamazaki et al. in brine with an air atmosphere [Yamazaki 1992].

The uranium solubility reported by Diaz-Arocas and Grambow was about two orders of magnitude lower than the data obtained by Yamazaki at a comparable pC_{H^+} value (8.4). It is difficult to provide an explanation for this difference since there were a number of differences between these two sets of experiments. The Yamazaki experiments may have had some residual carbonate in their system and were done in the presence of oxygen. In the Yamazaki oversaturation experiments at $pC_{H^+} = 8.4$ and an air atmosphere, a poorly crystalline solid phase, identified as α -schoepite $UO_3 \cdot 2H_2O$, was identified as the solubility controlling uranium phase [Yamazaki 1992]. He also found that the equilibration time was much longer at $pC_{H^+} = 10.4$ than at lower pC_{H^+} , which likely reflected the much slower uranium phase transformation that occurred in his experimental approach. Yamazaki's experiments were also longer in duration so a greater degree of equilibration may have occurred. This may also explain the poorly crystalline nature of the solids formed in Diaz-Arocas' experiments.

Table 3-3. Experimental uranium (VI) solubility data in carbonate-free (otherwise mentioned) high ionic strength media.

U (VI) concentration (M)	pC _{H+}	Solution	Time (days)	Solid	Reference
$(2.8 \pm 1.8) \times 10^{-5}$	8.9	5 M NaCl	≈ 50	Na _{0.68} UO _{3.34} · (2.15 ± 0.10) H ₂ O	[Diaz-Arocas 1998]
$(8.2 \pm 4.6) \times 10^{-5}$	7.6	5 M NaCl	≈ 110	Na _{0.45} UO _{3.23} · (4.5 ± 0.1) H ₂ O	[Diaz-Arocas 1998]
$(4.2 \pm 1.9) \times 10^{-4}$	7.1	5 M NaCl	≈ 170	Na _{0.29} UO _{3.15} · (2.9 ± 0.2) H ₂ O	[Diaz-Arocas 1998]
$(2.8 \pm 0.9) \times 10^{-3}$	6.5	5 M NaCl	≈ 170	Na _{0.14} UO _{3.07} · (2.5 ± 0.1) H ₂ O	[Diaz-Arocas 1998]
2.8×10^{-6}	9.8	WIPP brine	Not specified	UO ₂ (OH) ₂	[Palmer 1996]
$(1.82 \pm 0.01) \times 10^{-3}$	8.4	Brine (air atmosphere)	100	α-schoepite (oversaturation)	[Yamazaki 1992]
$(1.81 \pm 0.01) \times 10^{-3}$	8.4	Brine (air atmosphere)	100	α-schoepite (oversaturation)	[Yamazaki 1992]
$(1.40 \pm 0.05) \times 10^{-3}$	8.4	Brine (air atmosphere)	244	α-schoepite (undersaturation)	[Yamazaki 1992]
$(1.80 \pm 0.05) \times 10^{-3}$	8.4	Brine (air atmosphere)	244	α-schoepite (undersaturation)	[Yamazaki 1992]
$(3.8 \pm 0.4) \times 10^{-7}$	10.4	Brine (initial 0.11 mM HCO ₃ ⁻)	150	Mg(OH) ₂ and K ₂ U ₂ O ₇ (oversaturation)	[Yamazaki 1992]
$(3.1 \pm 0.3) \times 10^{-7}$	10.4	Brine (initial 0.11 mM HCO ₃ ⁻)	150	Mg(OH) ₂ and K ₂ U ₂ O ₇ (oversaturation)	[Yamazaki 1992]

4.0 WIPP-RELEVANT EXPERIMENTAL RESULTS: SOLUBILITY OF UO_2^{2+} IN CARBONATE-FREE SIMULATED WIPP BRINE

The LANL/ACRSP team performed experiments to determine the solubility of uranium (VI) in simulated WIPP brines in the absence of carbonate. The experimental approach was established in the Test Plan entitled “Solubility/ Stability of Uranium (VI) in WIPP Brines” designated LCO-ACP-02. The data obtained from these experiments are summarized in this section. These data are the first of their kind generated under an approved WIPP Quality Assurance Program for the solubility of uranium (VI) in simulated WIPP brine under repository conditions.

4.1 Experimental Goals and Test Matrix

The most important goals of the solubility studies were:

- Evaluate the effective long-term solubility of U(VI) in brine under experimental conditions that simulate the expected environment in the WIPP.
- Strengthen, and make more robust, the current WIPP position on the VI actinide solubility under WIPP-relevant conditions.
- Establish a baseline to evaluate the importance and relative contribution of hydrolysis and carbonate complexation to the solubility of uranium (VI) over a broad range of pH.

The experiments described herein were performed under the Test Plan entitled “Solubility/ Stability of Uranium (VI) in WIPP Brines” designated LCO-ACP-02. This Test Plan consisted of the following three tasks:

- Task 1: Solubility of U(VI) in WIPP brine
- Task 2: Redox stability of U(VI) in WIPP brine
- Task 3: Effect of radiolytic products on uranium speciation

Task 1 included three subtasks: U(VI) solubility under oxic conditions (Subtask 1), U(VI) solubility under anoxic conditions (Subtask 2), and Carbonate effects study on U(VI) solubility (Subtask 3).

The solubility experiments discussed herein pertain to experiments identified in Subtasks 1 and 2 of Task 1. These experiments were performed in a nitrogen controlled atmosphere, so under anoxic conditions. The glovebox atmosphere was free of oxygen and carbon dioxide. Carbonate is known to have a significant impact on U(VI) solubility in the environment, whereas oxygen has no direct impact at all on the aqueous speciation of U(VI), although the possibility that this affects solid phase formation is an open question.

Table 4-1 shows the experimental matrix for the U(VI) solubility studies in simulated WIPP brine, that are presented in this report.

Table 4-1. Experimental matrix for uranium (VI) solubility studies in anoxic atmosphere.

pC _{H+}	Brine and experimental conditions	
	GWB anoxic	ERDA-6 anoxic
~6.0	TI-GW-6.x	
~7.0	TI-GW-7.x	
~8.0	TI-GW-8.x	TI-ER-8.x
~9.0	TI-GW-9.x	TI-ER-9.x
~10.0		TI-ER-10.x
~11.0		TI-ER-11.x
~12.0		TI-ER-12.x

Where x = 1, 2 denotes the numbering of replicate experiments.

4.2 Experimental Approach, Limitations, Considerations and Error Analysis

The experimental approach used in these U(VI) solubility studies is described in detail in section 4.2.1. There were a number of limitations and constraints on the experiments performed. The most important of these are outlined in section 4.2.2. Because experimental errors are always associated with any experimental data, an error analysis on the experimental results of this study is performed in section 4.2.3.

4.2.1 Experimental Approach

The general experimental approach was to investigate uranium (VI) solubility from over-saturation, as described by Nitsche [Nitsche 1992]. This consisted of sequentially adding dissolved uranium, as a function of experimental conditions, e.g., brine and pC_{H+}, until precipitation was observed. Subsequently, the uranium concentration was monitored until a steady state concentration was achieved.

The general conditions of the study were:

- pC_{H^+} between 6 and 12
- Carbonate-free
- Temperature of 25 ± 4 °C

The overall experimental protocol used in the U(VI) solubility experiments was the following:

- 1) Two simulated brines (GWB and ERDA-6) were prepared according to procedure ACP-EXP-001. These were 95% of initial composition to prevent salt precipitation during the solubility experiments.
- 2) The pH of the brine was varied as a parameter. pC_{H^+} in brines was determined according to procedure ACP-EXP-010: "Determination of Hydrogen Ion Concentration in Brines".
- 3) The uranyl stock solution was prepared with high oxidation-state purity in aqueous solution at pH ~ 3.
- 4) All controlled-atmosphere experiments were performed in a nitrogen glove box to eliminate any possible carbon dioxide uptake in the system. The gas phase environment (nitrogen) was monitored throughout the experiment by an oxygen analyzer (detection limit: 0.1 ppmO₂).
- 5) Throughout the solubility experiments, the uranium concentration was analyzed by ICP-MS to establish its steady state concentration as a function of time and size distribution was established by sequential filtration.
- 6) The subsequent additions of uranyl eventually led to its precipitation as a solid. The characterization of these uranium solid phases is a difficult task and is still in progress.

A more detailed description of key aspects of the experimental approach is provided in the following sections.

Carbonate-free simulated WIPP brines

Two simulated WIPP brines were used in our studies. The Generic Weep Brine that is designated as GWB brine is based on high magnesium content, and the Energy Research and Development Administration Well 6 brine that is designated as ERDA-6 is based on low magnesium content. The initial composition of these two simulated WIPP brines was established by Brush [Brush 1990]. We prepared and used these two brines at 95% of their initial formulation to minimize salting and simplify the sampling process. The composition and the density of the simulated brines are given in Table 4-2.

All chemicals in these experiments were reagent-grade certified ACS (> 99% purity) purchased from Fisher, with the exception of sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$ from Acros Organics. They were used without further purification. Appropriate amounts of salts were dissolved in high purity (HP) 18 $\text{M}\Omega\text{-cm}$ water to prepare GWB brine and ERDA-6 brine.

Table 4-2. Composition and density of GWB and ERDA-6 simulated WIPP brines (95% initial formulation).

Component	GWB brine [M]	ERDA-6 brine [M]
NaCl	2.874	4.254
MgCl ₂	0.953	0.018
Na ₂ SO ₄	0.166	0.159
NaBr	0.025	0.010
Na ₂ B ₄ O ₇	0.037	0.015
KCl	0.437	0.092
CaCl ₂	0.013	0.011
LiCl	0.004	-
Density (g/mL)	1.216	1.183
Ionic strength (M)	6.839	4.965

Significant care was taken to establish carbonate-free conditions. Polypropylene bottles were placed in an anoxic carbon dioxide-free glovebox for two weeks to remove residual carbon dioxide (CO_2) adsorbed on the bottle walls. The removal of carbonate from the brines was a two-step process. The first step consisted of acidification of the brines to $\text{pC}_{\text{H}^+} \sim 3$, which converted carbonate into bicarbonate, in equilibrium with carbonic acid, then into dissolved carbon dioxide gas. The second step was to place the solutions in a vacuum chamber for a slow pump-down process to smoothly remove all dissolved gas from the brines. The vacuum chamber was placed in a low-flow-through high-purity-nitrogen glove box to maintain low levels of carbon dioxide. The oxygen level in this nitrogen glove box was continuously monitored, and was always lower than 10 ppmO_2 .

After more than 10 days of degassing in the vacuum chamber, the solutions were transferred to our MBraun[®] nitrogen glove box with an anoxic carbon dioxide-free atmosphere (high purity nitrogen) that was controlled by a recirculating closed loop oxygen purification system for the duration of the solubility experiment. The bottles were kept sealed except for the minimal contact with nitrogen controlled atmosphere that occurred when the solutions were sampled.

pC_{H^+}

In our brines, the measurement of the hydrogen ion concentration is difficult because of their high ionic strength that affects the activity coefficients and because of the presence of a high sodium concentration that introduces junction potentials. However, reliable hydrogen ion concentrations can be calculated from the measured/observed pH (pH_{obs}) by the following equation based on the modified Gran titration method [Rai 1995]:

$$pC_{H^+} = pH_{obs} + K \tag{4-2.a}$$

where pC_{H^+} is the negative logarithm of the hydrogen concentration in molarity (mol/L or M) units, and K is an experimentally determined constant. The values of K were found to be proportional to the ionic strength of the solutions (Figure 4-1). The values of K for the two WIPP brines used in the present work were determined (table in Figure 4-1) according to the procedure adapted from Rai *et al.* [Rai 1995]. The correction factors K were (1.23 ± 0.01) for GWB brine and (0.94 ± 0.02) for ERDA-6 respectively.

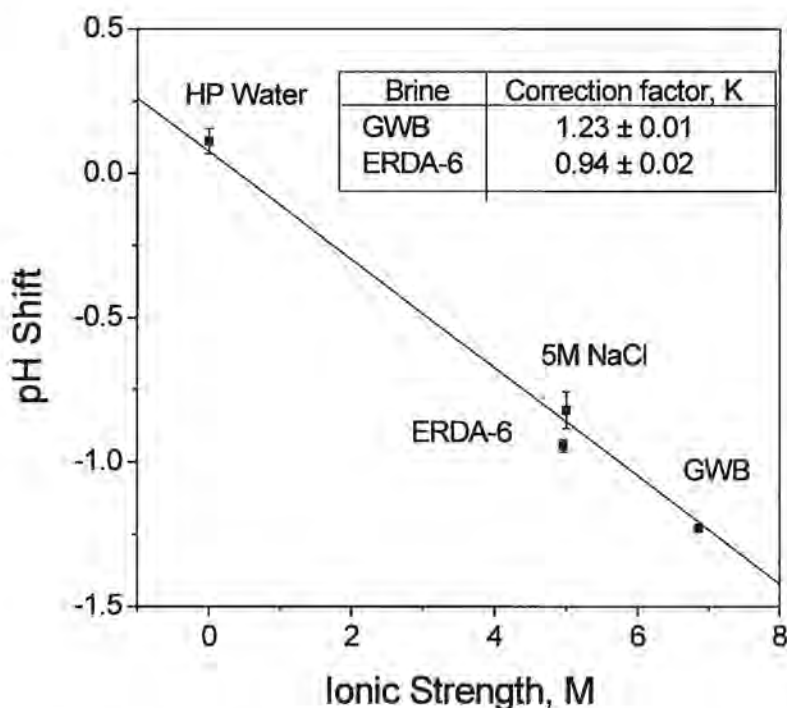


Figure 4-1: Correlation between the pH shift (ΔpH) and the ionic strength (I) of the two simulated WIPP brines, GWB and ERDA-6, 5 M NaCl brine and high purity (HP) water. The opposite value of ΔpH corresponds to the correction factor K. The correction factors for WIPP brines we used, based on this graph, are given in the table insert.

The pH of the brine solutions was measured with a sealed Orion-Ross combination glass electrode calibrated against NIST-certified pH buffers. Adjustments of pH were made with low carbonate sodium hydroxide (50 weight%) to minimize the re-introduction of carbonate in solution (errors in pH measurements were within 0.1 pH unit). This was done in the anoxic carbon dioxide-free glovebox. The following desired pC_{H^+} values were selected, according to the experimental matrix (Table 4-1): 6, 7, 8 and 9 for GWB brine in nitrogen atmosphere; and 8, 9, 10, 11 and 12 for ERDA-6 brine in nitrogen atmosphere. 50 mL-duplicates were prepared for each pC_{H^+} -adjusted brine.

From this point, all brine solutions were kept in polypropylene bottles, tightly capped, in the atmosphere of the experiment (nitrogen).

Uranyl solution

Our source of uranyl ion in this experiment was a uranium chloride stock solution (~ 0.15 M) that was prepared with high oxidation-state purity. Depleted uranium (VI) nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, was converted to a nitrate-free hydrochloric acid solution by the following consecutive steps:

- dissolution of the uranyl nitrate salt in 1 M hydrochloric acid and taking to dryness three times,
- precipitation of a uranyl hydroxide with sodium hydroxide,
- washing of the precipitate with hydroxide base to remove the residual nitrate impurities,
- and finally re-dissolution of the precipitate in 1 M hydrochloric acid.

Prepared this way, the uranium stock solution (~ 0.15 M) had an oxidation-state purity of greater than 99% for UO_2^{2+} (Figure 4-2). Appropriate amounts of this U(VI) stock solution were volumetrically pipetted into an aliquot of each brine at a pH of ~ 3-4 and checked for precipitation. This step led to properly diluted carbonate-free solutions to use as uranyl spikes in the pC_{H^+} -adjusted brines.

The uranyl stock solution was stored in a polypropylene bottle, tightly capped, in room atmosphere. Considering the high acidity of the solution, no uptake of carbon dioxide occurred over time in the uranyl stock solution.

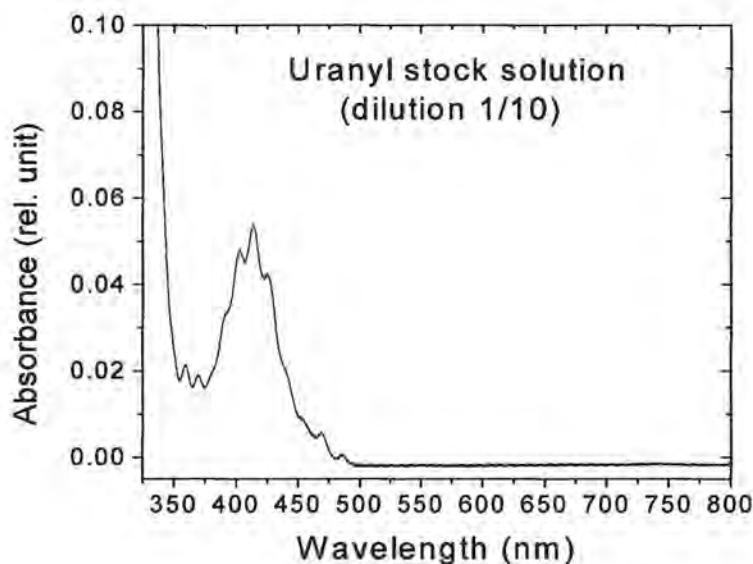


Figure 4-2: Absorption spectrum of the prepared uranyl stock solution diluted 1/10 (so $[U] = 15 \text{ mM}$). The absence of spectral features above 500 nm confirmed that there was no significant amounts of U(IV) present.

U(VI) solubility experiments

The U(VI) solubility experiments were initiated by the addition of uranyl spiked brine into corresponding pC_{H^+} -adjusted brine solutions, designated in the experimental matrix (Table 4-1). The initial uranyl concentration in all of the brine experiments was $(1.7 \pm 0.3) \times 10^{-5} \text{ M}$. This was approximately the expected solubility of uranium in ERDA-6 brine as established by our developmental experiments. All the experiments were carried out at $(25 \pm 4)^\circ\text{C}$ in an anoxic carbon dioxide-free glovebox (MBraun Labmaster 130 with a nitrogen atmosphere and with an oxygen purification system).

Once underway, aliquots were periodically removed (0.3 mL) and centrifuged at 8000 or 13500 rpm for 13 or 15 minutes. Supernatants were filtered through Microcon[®] Millipore centrifugal filters with a nominal molecular weight limit of 30,000 Daltons corresponding approximately to a 5 nm pore size. The filtration step removed potential uranium colloids or particulates bigger than 5 nm from the sample aliquots.

Filtrates were analyzed for uranium content using an inductively coupled plasma mass spectrometer (ICP-MS) Elan model 6000. Aliquots of the filtrates were diluted 50 or 100 times in nitric acid due to the high salt concentration and to establish uranium concentrations within

the range of the ICP-MS calibration. The detection limit by ICP-MS for uranium was $\sim 5 \times 10^{-12}$ M, which was effectively $\sim 2.5 \times 10^{-10}$ M or $\sim 5 \times 10^{-10}$ M for our experiments due to the sample dilutions made.

After 216 days of experiment, steady-state concentrations of uranium were observed in all the investigated solutions. At this time, a second uranyl spike was added to every solution to re-establish over-saturation with respect to uranium concentration. This second uranium addition was $(8.6 \pm 1.7) \times 10^{-5}$ M, which was about 5 times the initial uranium spike.

4.2.2 Experimental Limitations and Considerations

There were a number of limitations and constraints on the experiments performed. The most important of these are described in this section. Some considerations to specific experimental aspects are also developed in this section.

pC_{H+} range of the brines

Both brines, GWB and ERDA-6, contain significant concentrations of magnesium and calcium cations. At high pH, these cations form insoluble hydroxide phases. The precipitation “cloud” point for each brine solution was established by titration with sodium hydroxide. The addition of acid, conversely, was done to establish the point where there is a transition in the buffering agent – indicated by the point where a sudden pH decrease was noted.

For titration with base, the cloud point observed was at $pC_{H^+} = 8.7$ in GWB brine and at $pC_{H^+} = 10.8$ in ERDA-6 brine. In acid titrations, the sharp decrease in pH was observed at $pC_{H^+} \sim 5.5$ in both brines and corresponded to the end point of titration with borate (a component of each simulate brine). A good correlation was found between the amount of acid added and the concentration of borate for each brine titrated.

The working pC_{H^+} range was established between 6.0 and 8.7 for GWB brine, and between 7.0 and 10.8 for ERDA-6 brine (Figure 4-3).

For each brine, the higher pC_{H^+} value corresponded to the “cloud” point where significant precipitation was observed. Above these values, the brine composition effectively changed. In the experimental matrix for the present study in carbonate-free brines (Table 4-1), the U(VI) solubility was investigated beyond the domain of stability of the brines in the high pC_{H^+} values. However, the pC_{H^+} boundaries for the chemical stability of the WIPP simulated brines, which are presented in Figure 4-3, have an uncertainty of ± 0.5 pH unit.



Figure 4-3: Chemical stability of GWB and ERDA-6 brines versus pC_{H^+} . The lower pC_{H^+} value is defined by the buffering capacity and range of borate in the brines. The higher pC_{H^+} value corresponds to the “cloud” point when precipitation occurs. The pC_{H^+} boundaries have an accuracy of ± 0.5 pH unit.

Constant pC_{H^+} values during the experiments

Before the second uranium spike addition, we checked the pC_{H^+} of all the experimental solutions. After 214 days of experiment, no significant pC_{H^+} drift (defined as < 0.3 pH units) from initial values were measured in the experimental solutions in nitrogen-controlled atmosphere. The pC_{H^+} values were again checked after 369 days of experiment. Once again, no significant shift was observed with the exception of the lowest selected pC_{H^+} in ERDA-6. In this case, the initial pC_{H^+} decreased from 6.9 to 6.2 after the second uranyl addition. This occurred despite the small volume of uranyl added to the solution (about 1% of the total volume) due to the acidity of the second uranyl addition in the brine when it was at the lower range of its buffer capacity. Despite these exceptions, our overall observation was that the high buffer capacities of the simulated WIPP brines led to high pH stability.

Potential effect of filtration

A potential experimental complexity was the potential effect of the Microcon[®] Millipore centrifugal filters (nominal molecular weight limit: 30,000 Daltons) used in this study on the measured uranium concentration. There was a possibility that the filter membrane selected for the experiments could retain uranium species smaller than 5nm by chemical affinity or adsorption and then lower the concentrations measured. This potential effect was evaluated to confirm our experimental approach.

Figure 4-4 displays the time profiles of uranium concentration in GWB brine at $pC_{H^+} = 6.3$ and in ERDA-6 brine at $pC_{H^+} = 8.1$ in a nitrogen-controlled atmosphere and up to 369 days of experiments. For each brine case, two time profiles are represented. In the first profile, the

sampled aliquots were filtered through a 30kDa filter. In the second profile, extra aliquots were sampled but not filtered. The difference between unfiltered and filtered data for the same brine and experimental conditions is generally within the calculated uncertainty of the data (see section 4.2.3). The 30kDa filter membrane used in the experiments did not show any significant (>10%) retention of uranium during the filtration of the aliquots. This confirmed that there was no significant impact of the nature of the filter membrane used during the uranium filtration step.

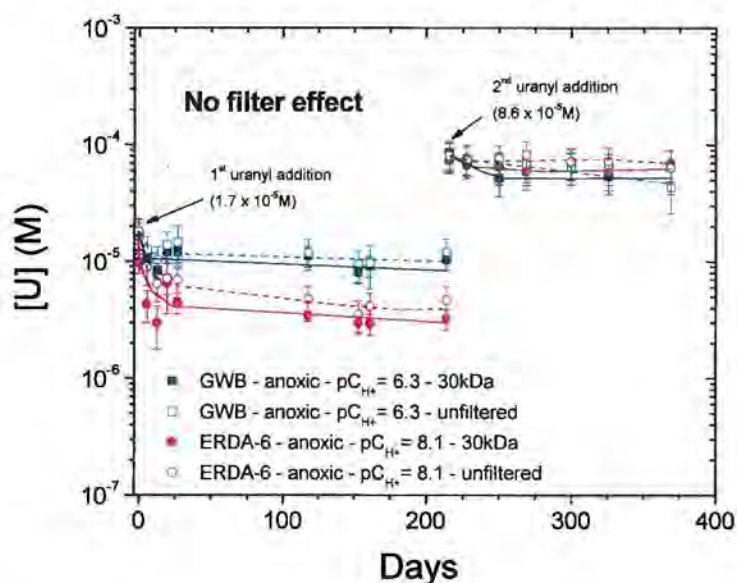


Figure 4-4: Time profiles of uranium concentration in GWB brine at $pC_{H^+} = 6.3$ (square scatter) and in ERDA-6 brine at $pC_{H^+} = 8.1$ (circle scatter) in the nitrogen-controlled atmosphere and up to 369 days of experiments. For each brine case, the sampled aliquots were filtered through a 30kDa filter (filled scatter), and extra aliquots were sampled but not filtered (open scatter). The difference between unfiltered and filtered data for the same brine and experimental conditions is generally within the calculated uncertainty of the data. The 30kDa filter used in the experiments did not exhibit any significant retention of uranium during the filtration of the aliquots.

Limitations in the detection of U using ICP-MS

The concentration of uranium in all of the solubility experiments was determined using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS Elan 6000). To obtain good consistency and to account for matrix effects, an internal standard (Indium-115) was used in the analyses. The range of recovery for this standard recommended by the manufacturer was 60% to 120%. To get a recovery within the recommended range, each brine solution sample was diluted

by a factor of 100 (or in some cases 50). This dilution also helped to avoid the plugging of the capillary tubing and nebulizer during the analysis. High purity nitric acid (99.9999% purity, Alfa Aesar) and water (18 MΩ·cm) were used to dilute the brine samples to ~0.5% nitric acid for ICP-MS analysis. Uranium standards (High Purity Standards) that are NIST traceable were used for instrument calibration. The actual detection limit of the instrument for uranium under these conditions was $\sim 5 \times 10^{-12}$ M. This led to an effective detection limit of $\sim 5 \times 10^{-10}$ M in the brines due to the necessary dilutions made in sample preparations, or in the few cases of a 50 times dilution, $\sim 2.5 \times 10^{-10}$ M.

4.2.3 Error Analysis

The measurement of uranium concentration was the main experimental goal in these solubility studies. There are a number of sources of error that could potentially contribute to the uncertainty in the uranium concentrations measured.

The most significant contribution to the uncertainty in the uranium concentration determination was the ICP-MS analysis. This was especially true when the concentrations measured approached the instrument detection limit. The estimated error on the uranium concentration measured by ICP-MS increased by approximately 100% at the working detection limit (5×10^{-10} M); about 70% at 10^{-8} M, and about 20% at 10^{-6} M uranium. The accuracy of the ICP-MS measurements was determined by the linear response of the instrument to a dilution series of seven (or eight depending on the sampling series) uranium standards in the concentration range of 5 ppb to 1000 ppb or 2000 ppb. The correlation coefficient of the response of the instrument to this calibration process was always equal or better than 0.99. Replicate samplings were performed to confirm the precision of the ICP-MS measurements (Table 4-1).

The experimental error attributed to pipetting was approximately 1%. Due to the high ionic strength, each sample was 100-times diluted and this operation contributed about 10% to the error in the ICP-MS analysis.

The overall uncertainty, given the sources of uncertainty just described, in the uranium concentration determination were evaluated to be about 20% at 10^{-5} M or higher, about 30% at 10^{-6} M, about 40% at 10^{-7} M, about 80% at 10^{-8} M, and 100% for uranium concentrations below 5×10^{-10} M.

The pC_{H^+} measurements also had experimental error. The pC_{H^+} was measured with an uncertainty of 0.1 pH unit. These errors on pC_{H^+} , although present, are not included in the graphs to preserve their clarity.

4.3 Results and Discussion

The results of our U(VI) solubility study using the over-saturation approach for our experimental matrix (Table 4-1) are summarized and discussed in this section.

The U(VI) concentration in carbonate-free GWB brine and ERDA-6 brine at different pC_{H^+} are presented respectively in section 4.3.1 and 4.3.2. These data correspond to the 19 samplings performed in each brine and pC_{H^+} investigated in a nitrogen-controlled atmosphere throughout the 705 days of the experiments.

These data led to the determination of the solubility of uranium (VI) in the range of pC_{H^+} investigated. The resulting U(VI) solubility in carbonate-free GWB brine and in carbonate-free ERDA-6 brine is discussed respectively in section 4.3.4 and section 4.3.5.

4.3.1 Evolution of U(VI) concentration with time in carbonate-free GWB brine

Figure 4-5 shows the uranium concentration data measured as a function of time in carbonate-free GWB brine placed in nitrogen-controlled atmosphere throughout the 705 days of the experiments.

These data show that steady state uranium concentrations were rapidly achieved (less than 20 days) in GWB brine at the start of the experiments. These concentrations were confirmed by the second uranium addition in all the investigated pC_{H^+} values with the exception of the lowest pC_{H^+} (6.3). At that pC_{H^+} , the steady state uranium concentration established after the first uranyl addition was about 10^{-5} M, but this value was not re-established at the time of the last sampling (day 705), that is 489 days after the second uranyl addition in solution. At all the other investigated pC_{H^+} values (≥ 7), steady state uranium concentrations were re-established in about 50 days, so a somewhat slower equilibration time was noted.

The steady state uranium concentration in solution depended on pC_{H^+} , as expected. The concentration of uranium decreased with lower pC_{H^+} . The uranium concentration achieved a steady state in carbonate-free GWB brines when it reached about 10^{-5} M at $pC_{H^+} = 6.3$, and about 10^{-6} M at $pC_{H^+} = 9.2$. At the investigated intermediate pC_{H^+} values (7.4 and 8.2), the results didn't follow the expected trend on the graph (Figure 4-5): the uranium concentration at $pC_{H^+} = 7.4$ was lower than the uranium concentration at $pC_{H^+} = 8.2$. However, there was only a factor two between the two concentrations: about 2×10^{-6} M at $pC_{H^+} = 7.4$, and about 4×10^{-6} M at $pC_{H^+} = 8.2$. This difference appears clearly on Figure 4-5, because the semi-logarithm scale, but it is not significant in reality.

After the second uranium addition, yellow precipitates were observed in all GWB solutions at $pC_{H^+} \geq 7$. These precipitates were presumably due to the formation of uranyl hydroxide phases. An attempt to characterize the solids formed in our experiments was made. XANES analysis performed at the Argonne Advanced Photon Source confirmed that we didn't

get reduction of uranium (VI) in these systems. EXAFS analysis could not be performed on these samples because they were amorphous. No precipitate was observed at the lowest $pC_{H^+} = 6.3$. Also, the solution at $pC_{H^+} = 9.2$ didn't exhibit any clearly visible precipitation from brine components before the second uranyl addition, even though this pC_{H^+} value is beyond the stability domain of GWB (Figure 4-3). As a reminder, the pC_{H^+} boundaries for the chemical stability of the WIPP simulated brines, which are presented in Figure 4-3, can have an uncertainty of ± 0.5 pH unit.

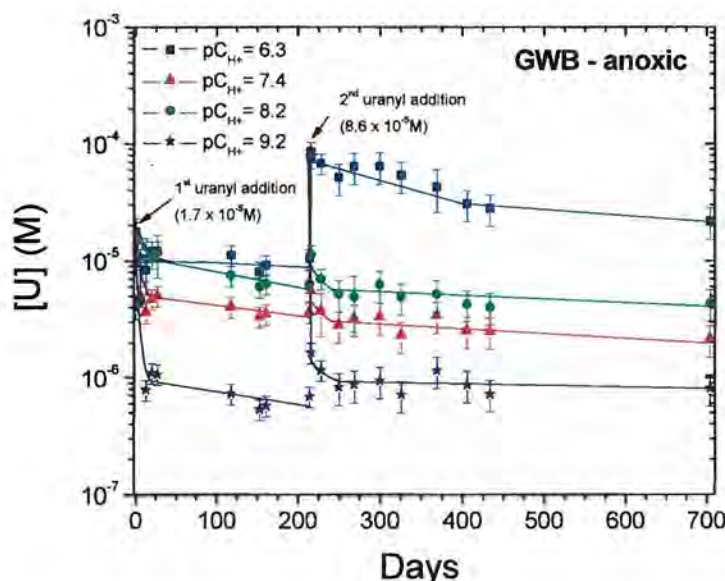


Figure 4-5: Uranium concentration in carbonate-free GWB brine in a nitrogen-controlled atmosphere as a function of time. Time profiles correspond to $pC_{H^+} = 6.3, 7.4, 8.2$ and 9.2 from top to bottom of the legend. These data correspond to 19 samplings performed throughout 705 days of the experiments.

4.3.2 Evolution of U(VI) concentration with time in carbonate-free ERDA-6 brine

The uranium concentration data measured as a function of time in carbonate-free ERDA-6 brine placed in a nitrogen-controlled atmosphere throughout the 705 days of the experiments are shown on Figure 4-6.

As with GWB, the later uranium additions had a somewhat slower equilibration time. It took about 20 days to reach steady state after the initial uranyl spike addition, and about 50 days after the second uranyl addition. These rates in ERDA-6 are similar to the rates obtained in GWB, because the ionic strength of both brines is quite high (5 M for ERDA-6, 6.8 for GWB).

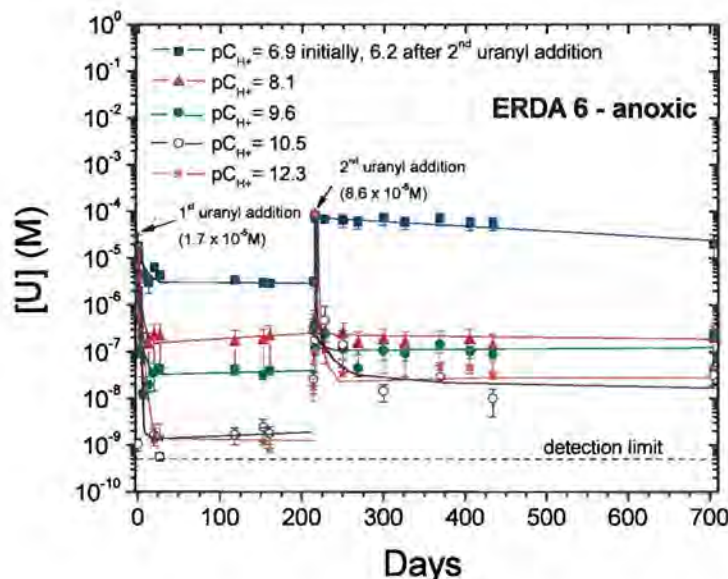


Figure 4-6: Uranium concentration in carbonate-free ERDA-6 brine in a nitrogen-controlled atmosphere as a function of time. Data shown are for $pC_{H^+} = 6.2$ (initially 6.9), 8.1, 9.6, 10.5 and 12.3 from top to bottom of the legend. These data correspond to 19 samplings performed throughout 705 days of the experiments.

The uranium steady state concentrations were not all reproducible after the first and the second uranyl addition. Only at $pC_{H^+} = 8.1$ and, to some extent at $pC_{H^+} = 9.6$, the steady state uranium concentrations were the same after the first and after the second uranyl additions. At $pC_{H^+} = 8.1$, the uranium concentration found in solution was established at about $2 \times 10^{-7} M$, whatever the uranium addition was. At $pC_{H^+} = 9.6$, the steady state uranium concentration was about $1 \times 10^{-7} M$ after the second uranyl addition, that is only two times more than the concentration established before the second uranyl addition.

Discrepancies in the steady state uranium concentrations were noticed at the lowest pC_{H^+} values and the two highest pC_{H^+} values investigated. At the lowest pC_{H^+} value, the steady state

uranium concentration was about 2×10^{-6} M after the initial uranyl addition, but about one order of magnitude higher after the second uranyl addition. However, the pC_{H^+} value of the solution changed between the two conditions: it was set initially at 6.9, but dropped to 6.2 after the second uranyl addition. This pC_{H^+} drift explains the difference in the steady state uranium concentrations measured.

In the case of the two highest pC_{H^+} solutions investigated (10.5 and 12.3), one order of magnitude difference was found between the steady state uranium concentrations obtained before the second uranyl concentration ($\sim 10^{-9}$ M) and after the second uranyl addition ($\sim 2 \times 10^{-8}$ M). These values of pC_{H^+} are on the edge of or beyond the brine stability range of ERDA-6, so there are slight compositional changes in the brine that were the likely cause of the increased concentrations. There was no change in the pC_{H^+} measured after the second uranyl addition.

Yellow precipitates were generated in all ERDA-6 solutions at $pC_{H^+} \geq 8$ a few days after the second uranyl addition. These were initially uranium hydroxide phases that were undergoing phase transformations over time. For example, the precipitate observed at $pC_{H^+} = 10.5$ turned from yellow to white about 40 days after the addition of the second uranyl spike.

4.3.3 Solubility of U(VI) in GWB brine

The overall uranium (VI) solubility measured is plotted in Figure 4-7 as a function of pC_{H^+} . This plot is based on the time-dependent experimental data given in sections 4.3.1.

It is important to note that the steady state concentrations measured are estimates of the true U(VI) solubility since they represent the results obtained using an over-saturation approach only, and phase equilibration may have not yet been fully confirmed.

The solubility values corresponding to $pC_{H^+} \leq 7$ are put in the figure as preliminary data, since the over-saturation conditions were not completely fulfilled (no precipitation in solution). The solubility data for $pC_{H^+} \geq 7$ are more reliable, because steady state uranium concentrations and precipitates in solutions were observed.

At $7 \leq pC_{H^+} \leq 9.2$, the solubility of uranium (VI) in carbonate-free GWB brine was found to be approximately 10^{-6} M (between 8×10^{-7} M and 5×10^{-6} M). The variation of the solubility with pC_{H^+} was small in the range of pC_{H^+} where steady state concentrations were established (7-9.2). The slight increase in the middle of this pC_{H^+} range (~ 8.1) is not significant, but may reflect a small effect of borate complexation.

It is important to note that, when carbonate was rigorously excluded from our brine systems, the uranium solubilities measured were 10-100 times lower than any reported in the literature [Yamazaki 1992; Diaz-Arocas 1998].

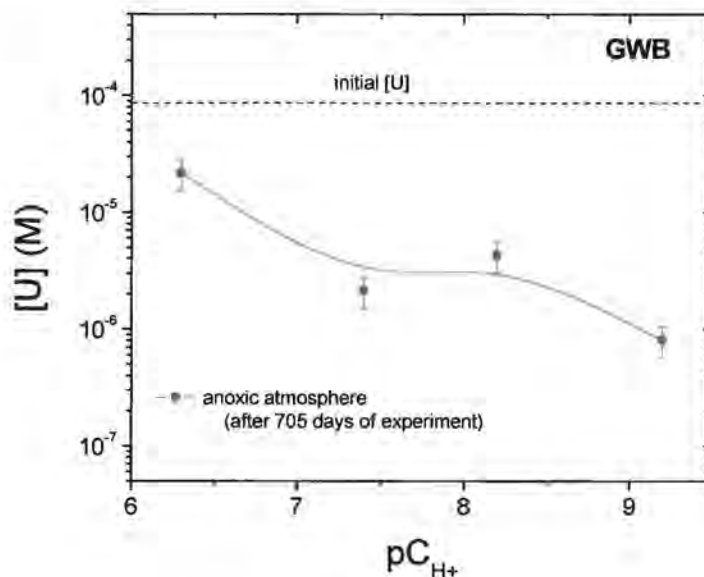


Figure 4-7: Uranium (VI) solubility in carbonate-free GWB brine solutions versus pC_{H^+} . The curve compiles data obtained from the solutions kept in a nitrogen-controlled atmosphere throughout the 705 days of the experiment.

4.3.4 Solubility of U(VI) in ERDA-6 brine

Figure 4-8 gives the U(VI) solubility estimates obtained experimentally in initially carbonate-free ERDA-6 brine solutions in the nitrogen-controlled atmosphere experiments (section 4.3.2). These data are only estimates, because the experiments were performed using the over-saturation approach for now, and the results will need to be confirmed using the under-saturation approach. However, the data obtained are considered reliable when the concentration reached a steady state over time and precipitation occurred in solution.

Because the over-saturation conditions were not completely fulfilled (no precipitation) in the solutions at $pC_{H^+} < 8$, the corresponding data in Figure 4-8 are preliminary and not yet complete. However, these preliminary solubility data were more than two orders of magnitude higher than the data obtained at $pC_{H^+} \geq 8$ in the anoxic nitrogen atmosphere.

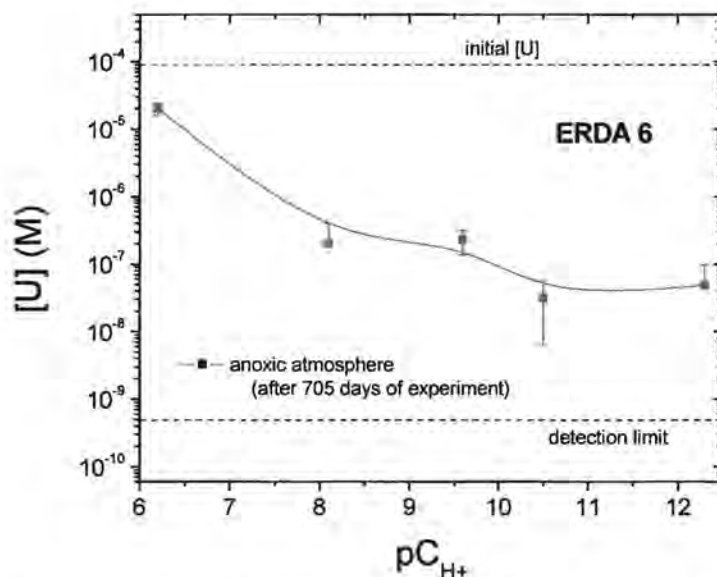


Figure 4-8: Uranium (VI) solubility estimates in carbonate-free ERDA-6 brine solutions versus pC_{H+}. The curve compiles data obtained from the solutions kept in a nitrogen-controlled atmosphere throughout the 705 days of the experiment.

In all the experimental solutions at pC_{H+} ≥ 8 and a nitrogen-controlled atmosphere, steady state uranium concentrations and precipitates were observed in solutions. From pC_{H+} 8 to 11, the solubility of uranium (VI) in carbonate-free ERDA-6 brine was in the range 10⁻⁸ to 10⁻⁷ M, specifically this was between 3.1 × 10⁻⁸ M and 2.3 × 10⁻⁷ M. This solubility decreased slightly from pC_{H+} ~ 8 to pC_{H+} ~ 11.

At pC_{H+} ~ 12.3, which is beyond the chemical stability of ERDA-6, the solubility of uranium (VI) in carbonate-free solution was ~4.8 × 10⁻⁸ M. This solubility was within the range of the data measured at pC_{H+} ≥ 8. The presence of a precipitate from the brine components prior to the beginning of the experiments and the first addition of uranium in solution did not enhance the solubility of uranium (VI). Under these experimental conditions we did not see evidence for significant amphotericity and there was no significant effect of borate complexation on the solubility trends observed.

Overall uranium concentrations when carbonate was carefully excluded were 10-100 times lower than any reported in the literature [Yamazaki 1992; Diaz-Arocas 1998].

4.4 Summary of Experimental Results and Conclusions

The uranium (VI) solubility data obtained in carbonate-free WIPP brines using the over-saturation approach and based on the 705-day sampling are summarized in Figure 4-9 for both simulated brines. The measured solubilities were about 10^{-6} M in GWB brine at $pC_{H^+} \geq 7$ and about 10^{-8} - 10^{-7} M in ERDA-6 at $pC_{H^+} \geq 8$. These results definitively put an upper bound of $\sim 10^{-5}$ M for the solubility of uranyl in the carbonate-free WIPP brines under the investigated range of experimental conditions. At the expected pC_{H^+} in the WIPP (~ 9.3), the measured uranium solubility approaches $\sim 10^{-7}$ - 10^{-6} M.

At the same pC_{H^+} , the solubility of uranium was about one order of magnitude higher in GWB than in ERDA-6 (Figure 4-9). This is likely due to the differences in ionic strength and complexant concentration in the two brines (Table 4-2). The uranium concentration trends observed over time at pC_{H^+} values up to 10.5 in carbonate-free ERDA-6 brine indicated that uranium (VI) did not exhibit amphoteric behavior under the conditions investigated.

Our experimental data were compared with the most similar published work, performed by Diaz-Arocas and Grambow [Diaz-Arocas 1998]. They performed uranium (VI) solubility experiments in 5 M NaCl at 25°C and different basic pH values, under an argon atmosphere using an over-saturation approach. Their equilibrated uranium concentration data in 5 M NaCl are presented in Table 4-3, along with our WIPP-specific data. The published values were converted from molality to molarity using a density value of 5 M NaCl equal to 1185 g/L. Diaz-Arocas and Grambow reported a uranium solubility of $(2.8 \pm 1.8) \times 10^{-5}$ M at $pC_{H^+} = 8.9$ in 5 M sodium chloride with a similar experimental approach using argon bubbling to remove carbonate. In contrast to this, the solubility of uranium in our carbonate-free ERDA-6 brine was $(2.0 \pm 2.0) \times 10^{-7}$ M at $pC_{H^+} = 8.1$ in ERDA-6 brine (containing 4.25 M NaCl). Our data obtained in a nitrogen glovebox with a carbonate-free atmosphere, are more than two orders of magnitude lower than Diaz-Arocas and Grambow's data (Figure 4-9). The lower uranium concentrations reported in our experiments primarily reflects the greater extent that carbon dioxide was removed from the brine solutions at the beginning of the experiments, along with a better control of the carbon dioxide-free environment throughout our experiment.

Our data are less comparable to the experimental data obtained by Yamazaki in brine with a nitrogen cover gas [Yamazaki 1992]. At $pC_{H^+} = 10.4$, where carbonate effects are much less significant, he measured a U(VI) solubility of $(3.8 \pm 0.4) \times 10^{-7}$ M that is ten times higher than our experimental value in ERDA-6 at about the same pC_{H^+} (Table 4.3). The difference in our results can be explained by the fact that Yamazaki did not remove CO₂ from the brines before initiating his experiments, and there was likely some residual carbonate present in solution. Consequently, our experimental results suggest that Yamazaki's data were not generated in a carbonate-free system.

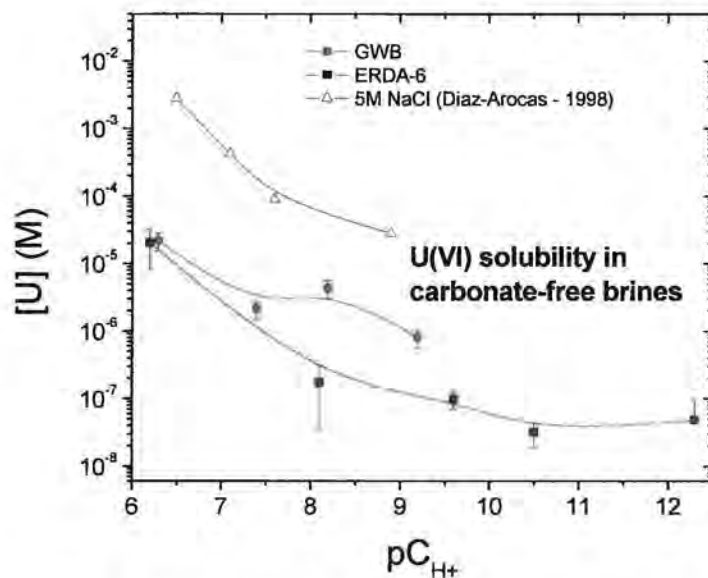


Figure 4-9: Uranium (VI) solubility in carbonate-free brines versus pC_{H^+} . The two curves at the bottom the graph are from data obtained from our 705-day solubility experiments in GWB (curve in the middle of the graph) and in ERDA-6 (curve at the bottom of the graph) using the over-saturation approach. The top curve is based on the Diaz-Arocas' data in 5 M NaCl [Diaz-Arocas 1998].

Table 4.3 Uranium (VI) solubility in chloride-based brines (I~5 M) at 25°C and different basic pH values, under controlled atmosphere (Ar or N₂) using over-saturation approach. Data from published work [Diaz-Arocas 1998] and [Yamazaki 1992], and these experiments.

Medium	pC_{H^+}	Atmosphere	Equ. [U] (M)	Reference
5 M NaCl	6.5	Ar	$(2.8 \pm 0.9) \times 10^{-3}$	[Diaz-Arocas 1998]
5 M NaCl	7.1	Ar	$(4.2 \pm 1.9) \times 10^{-4}$	[Diaz-Arocas 1998]
5 M NaCl	7.6	Ar	$(8.2 \pm 4.6) \times 10^{-5}$	[Diaz-Arocas 1998]
5 M NaCl	8.9	Ar	$(2.8 \pm 1.8) \times 10^{-5}$	[Diaz-Arocas 1998]
Brine	8.4	Air	$(1.80 \pm 0.05) \times 10^{-3}$	[Yamazaki 1992]
Brine	10.4	N ₂	$(3.8 \pm 0.4) \times 10^{-7}$	[Yamazaki 1992]
ERDA-6	8.1	N ₂	$(1.7 \pm 1.4) \times 10^{-7}$	This work
ERDA-6	9.6	N ₂	$(9.9 \pm 3.0) \times 10^{-8}$	This work
ERDA-6	10.5	N ₂	$(3.1 \pm 1.3) \times 10^{-8}$	This work

5.0 SUMMARY OF OBSERVATIONS AND RECOMMENDATIONS

The solubility of uranium (VI) was determined in carbonate-free WIPP simulated brines as a function of pC_{H^+} using the over-saturation approach. Additionally, a literature review on the solubility of uranium (VI) in carbonate-free media under WIPP-related conditions was conducted.

The solubility data for uranium (VI) in WIPP brine presented in this report accomplished the following:

- Provided the first WIPP-relevant data for the +6 actinide oxidation state that established the solubility of uranium (VI) over an extended pC_{H^+} range for GWB and ERDA-6 brines in the absence of carbonate
- Established an upper limit of $\sim 10^{-5}$ M uranyl concentration at the reference pC_{H^+} WIPP case (in the absence of carbonate)
- Demonstrated a lack of amphotericity in that higher pH values led to low uranyl solubility due to hydrolysis, in carbonate-free WIPP brines.

These data on solubility of uranium (VI) in WIPP simulated brines are the first at high pC_{H^+} under what we believe to be a truly carbonate-free system. They establish uranium solubility, in the absence of carbonate that is 10-100 times lower than published results. The uranium (VI) solubilities measured in our experiments were about 10^{-6} M in GWB brine at $pC_{H^+} \geq 7$ and about 10^{-8} - 10^{-7} M in ERDA-6 at $pC_{H^+} \geq 8$. At the expected pC_{H^+} in the WIPP (~ 9.5), measured uranium solubility approached $\sim 10^{-7}$ - 10^{-6} M.

The results from these 705-day experiments defined a “baseline” carbonate-free uranium solubility that will be used to evaluate the effect of carbonate on uranium (VI) solubility in subsequent studies.

Overall, there are four key recommendations or conclusions with respect to the current WIPP PA position on the solubility of the VI actinides based on our experimental results and literature review:

- 1) ***Our data on uranium (VI) solubility in WIPP simulated brine are the first experimental data obtained in a truly carbonate-free system.*** They establish a uranium solubility, in the absence of carbonate, that is 10-100 times lower than published results. The uranium (VI) solubility experiments reported in the two relevant publications ([Yamazaki 1992] and [Diaz-Arocas 1998]) were performed in brines close to the WIPP brine composition, but with a less rigorous control of a carbon dioxide free environment than in our experiments. The lower uranium solubilities we report are indicative of a good experimental protocol and point towards a lower overall solubility of uranium in the WIPP.

- 2) ***The data for carbonate-free WIPP brines provide a baseline for carbonate effects on uranium (VI) solubility.*** These data, obtained from the over-saturation approach only, are the first repository-relevant data for the VI actinide oxidation state which fills a gap in experimental data in the current WIPP PA. The solubility trends observed point towards lower uranium solubilities in WIPP brine, a lack of amphotericity, an insignificant effect of borate complexation, and a predominance of hydrolysis at $pC_{H^+} > 10.5$.
- 3) ***Further investigations of the role of carbonate in the VI actinide solubility are needed.*** Given some of the relatively high uranium concentrations reported in the literature, accounting for the effect of carbonate complexation is critical to establish that the current assumption of a 1 mM U(VI) concentration is supported. Experiments are currently in progress to determine the relative contribution of carbonate complexation over a broad range of pH, and these data are expected to support the current position on An(VI) solubility under WIPP-relevant conditions.
- 4) ***It is still not clear that an actinide (VI) solubility model is needed although this was recommended by the EPA.*** This issue cannot be fully evaluated until the effects of carbonate on U(VI) solubility under WIPP-relevant conditions are established. Given that the results of the carbonate-free brine system point to a lower overall solubility than previously thought and higher pH trends toward lower solubilities, it is likely that U(VI) solubilities under expected conditions will be well below the current 1 mM value set by the EPA. This is further supported by the continued low importance and role of the VI oxidation state in calculating the potential for actinide release from the WIPP.

6.0 QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION

All the data presented in Section 4 were generated under the LANL-CO QA Program which is compliant with the CBFO-QAPD. The research was performed as a part of Task 1 of the Test Plan entitled “Solubility/ Stability of Uranium (VI) in WIPP Brines” and designated LCO-ACP-02 (section 3.1). The documentation for the experiments performed is found in three Test Plan-specific scientific notebooks designated ACP-TIP-002/1, ACP-TIP-002/3 and ACP-TIP-002/4 and in a series of 21 data packages designated U0 to U20. Table 6.0 gives the title of these 21 data packages. Copies of the scientific notebooks and the data packages are kept at the LANL-CO record center. Linkage of the figures published in section 4 of this document is included in data package U20. Any other figures included in this report are based on literature data, and the associated references are mentioned in the caption of the figures.

Table 6.0 Titles of the data packages U0 to U20 associated to this document.

Data package	Title
U0	LCO-ACP-02 Task 1 – U0 – U stock
U1	LCO-ACP-02 Task 1 – U1 – Sampling #1
U2	LCO-ACP-02 Task 1 – U2 – Sampling #2
U3	LCO-ACP-02 Task 1 – U3 – Sampling #3
U4	LCO-ACP-02 Task 1 – U4 – Sampling #4
U5	LCO-ACP-02 Task 1 – U5 – Sampling #5
U6	LCO-ACP-02 Task 1 – U6 – Sampling #6
U7	LCO-ACP-02 Task 1 – U7 – Sampling #7
U8	LCO-ACP-02 Task 1 – U8 – Sampling #8
U9	LCO-ACP-02 Task 1 – U9 – Sampling #9
U10	LCO-ACP-02 Task 1 – U10 – Sampling #10
U11	LCO-ACP-02 Task 1 – U11 – Sampling #11
U12	LCO-ACP-02 Task 1 – U12 – Sampling #12
U13	LCO-ACP-02 Task 1 – U13 – Sampling #13
U14	LCO-ACP-02 Task 1 – U14 – Sampling #14
U15	LCO-ACP-02 Task 1 – U15 – Sampling #15
U16	LCO-ACP-02 Task 1 – U16 – Sampling #16
U17	LCO-ACP-02 Task 1 – U17 – Sampling #17
U18	LCO-ACP-02 Task 1 – U18 – Sampling #18
U19	LCO-ACP-02 Task 1 – U19 – Sampling #19
U20	LCO-ACP-02 Task 1 – U20 – Figures 4-4 to 4-9

7.0 LITERATURE REFERENCES

- [Åberg 1970] Åberg M., Structure of the predominant hydrolysis products of uranyl (VI) in solution, *Acta Chemica Scandinavica*, **24** (1970) 2901-2915
- [Brush 1990] Brush L.H., Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant, Report SAND90-0266, Sandia National Laboratories. Albuquerque, NM. 1990
- [Brush 2003] Brush L.H., Y. Xiong, Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Sandia National Laboratories Carlsbad Programs Group, Carlsbad, NM, May 8, 2003, ERMS 529131
- [Choppin 2003] Choppin G.R., Actinide Speciation in the Environment, *Radiochimica Acta*, **91** (2003) 645
- [Clark 1995] Clark D.L., D.E Hobart., and M.P.Neu, Actinide Carbonate Complexes and their Importance in Actinide Environmental Chemistry, *Chemical Reviews*, **95** (1995) 25- 48
- [Diaz-Arocas 1998] Diaz Arocas, P., B.Grambow, Solid-liquid Phase Equilibria of U(VI) in NaCl Solutions, *Geochimica et Cosmochimica Acta*, **62/2** (1998) 245
- [DOE 1996] Title 40 CFR Part 1991 Compliance Certification Application for the Waste Isolation Pilot Plant, DOE/CAO-1996-2184, October 1996, DOE Carlsbad Field Office, Carlsbad, NM
- [DOE 2004b] Title 40 CFR Part 1991 Subparts B and C Compliance Recertification Application 2004, Appendix PA, Attachment SOTERM, November 10 (2003) DOE Carlsbad Field Office, Carlsbad, NM
- [DOE 2004d] Partial Response to Environmental Protection Agency September 2, 2004, Letter on Compliance Recertification Application. Letter from R.P. Detwiler, U.S. Department of Energy Carlsbad Field Office, to E. Cotsworth, U.S. Environmental Protection Agency Office of Radiation and Indoor Air, Washington DC, December 23, 2004
- [EPA 2004b] CRA Completeness Comments – 3rd set – August 2004, Letter (with enclosure) from E. Cotsworth, U.S. Environmental Protection Agency Office of Radiation and Indoor Air, Washington DC, to R.P. Detwiler, U.S. Department of Energy Carlsbad Field Office, September 2, 2004
- [EPA 2005a] Performance Assessment Issues. Letter from E. Cotsworth, U.S. Environmental Protection Agency Office of Radiation and Indoor Air, Washington DC, to Ines Triay, U.S. Department of Energy Carlsbad Field Office, March 4, 2005
- [EPA 2005b] Technical Support Document for Section 194.24 Evaluation of the Compliance Recertification Actinide Source Term and Culebra Dolomite Distribution Coefficient Values. Draft Final, U.S. Environmental Protection Agency Office of Radiation and Indoor Air, Washington DC, July 2005

- [EPA 2006a] Evaluation of the Compliance Recertification Actinide Source Term and Culebra Dolomite Distribution Coefficient Values, Technical Support Document for Section 194.24, March 2006, U.S. Environmental Protection Agency Office of Radiation and Indoor Air
- [EPA 2006b] Review of the 2004 Compliance Recertification Performance Assessment Baseline Calculation, Technical Support Document for Section 194.23, March 2006, U.S. Environmental Protection Agency Office of Radiation and Indoor Air
- [Guillaumont 2003] Guillaumont R., T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, and M. H. Rand, Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, ed., Mompean, F.I., Illemassene, M., Domenech-Orti, C., Ben Said, K., Nuclear Energy Agency, Organization for Economic Co-operation and Development, vol. 5, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands (2003)
- [Hobart 1990] Hobart D.E., Actinides in the Environment, Proceedings of the Robert A. Welch Foundation Conference on Chemical Research, No. XXXIV: 50 Years With Transuranium Elements, Houston, TX, October 22-23, 1990, **34** (1990) 378-436
- [Hobart 1996] Hobart D.E., R.C. Moore, Analysis of Uranium (VI) Solubility Data for WIPP Performance Assessment, Sandia National Laboratories, unpublished report, May 28, 1996. Albuquerque, NM
- [Keller 1971] Keller C., The Chemistry of Transuranium Elements, Weinheim, Germany: Verlag Chemis, GmbH
- [Katz 1986] Katz J.J., G.T. Seaborg, and L.R. Morss, The Chemistry of the Actinide Elements, 2nd eds., New York, NY: Chapman and Hall. Vols. 1-2 (1986)
- [Kramer-Schnabel 1992] Kramer-Schnabel U., H. Bischoff, R.H. Xi, and G. Marx, Solubility products and complex formation equilibria in the systems uranyl hydroxide and uranyl carbonate at 25°C and I=0.1M, *Radiochimica Acta* **56** (1992) 183-188
- [Lin 1998] Lin M.R., P. Paviet-Hartmann, Y. Xu, and W.H. Runde, Uranyl Compounds in NaCl Solutions: Structure, Solubility and Thermodynamics, American Chemical Society, Division of Environmental Chemistry, Preprints of Extended Abstracts. 216th ACS National Meeting, Boston Massachusetts, August 23-27, 1998, 38:208
- [Lucchini 2007] Lucchini J-F, M. Borkowski, M.K. Richmann, S. Ballard, and D.T. Reed, Solubility of Nd³⁺ and UO₂²⁺ in WIPP brine as oxidation-state invariant Analogs for Plutonium, *Journal of Alloys and Compounds*, **444-445** (2007) 506-511
- [Meinrath 1993] Meinrath G., T. Kimura, Carbonate complexation of the uranyl (VI) ion, *Journal of Alloys and Compounds* **202** (1993) 89-93
- [Morss 2006] Morss L.R., N. Edelstein, and J. Fuger, The Chemistry of the Actinide and Transactinide Elements, 3rd Ed., Springer, Volume 4 (2006)
- [Moulin 2001] Moulin V., C. Moulin, Radionuclide Speciation in the Environment: a Review, *Radiochimica Acta*, **89** (2001) 773-778
- [Nitsche 1992] Nitsche H., A. Muller, E.M. Standifer, R.S. Deinhammer, K. Becraft, T. Prussin, and R.C. Gatti, Dependence of Actinide Solubility and Speciation on Carbonate

- Concentration and Ionic-Strength in Groundwater, *Radiochimica Acta* **58/59** (1992) 27-32
- [Novak 1996] Novak C.F., R.C. Moore, Estimates of Dissolved Concentrations for III, IV, V, and VI Actinides in Salado and Castile Brine Under Anticipated Repository Conditions, Sandia National Laboratories Technical Memorandum, March 28, 1996
- [Palmer 1995] Palmer D.A., C. Nguyen-Trung, Aqueous Uranyl Complexes. 3. Potentiometric Measurements of the Hydrolysis of Uranyl (VI) Ion at 25°C, *Journal of Solution Chemistry*, Vol. **24**, No.12 (1995) 1281- 1291
- [Palmer 1996] Palmer C.E., Private Communication to R. Van Bynum (SAIC/SNL) from C. Palmer (LLNL), dated February 27, 1996, reported by Hobart and Moore (1996)
- [Perrin 1976] Perrin A., Structure Cristalline du Nitrate de Dihydroxo Diuranyle Tetrahydrate, *Acta Crystallographica* **B32** (1976) 1658-1661
- [Plyasunov 1998] Plyasunov A., T. Fanghanel, and I. Grenthe, Estimation of the Pitzer Equation Parameters for Aqueous Complexes. A Case Study for Uranium at 298.15 K and 1 atm, *Acta Chemica Scandinavica*, **52** (1998) 250-260
- [Rai 1995] Rai D., A.R. Felmy, S.P. Juracich, and L.F.Rao, Estimating the Hydrogen Ion Concentration in Concentrated NaCl and Na₂SO₄ electrolytes, Report SAND94-1949, Sandia National Laboratories, Albuquerque, NM. 1995
- [Reed 1996] Reed, D.T., D. G. Wygmans, and M.K. Richmann, Actinide Stability/Solubility in Simulated WIPP Brine, Interim Report under SNL WIPP Contract AP-2267 (1996)
- [Runde 2000] Runde W. The Chemical Interactions of Actinides in the Environment. Los Alamos Science, **26** (2000) 330
- [SOTERM 2003] Title 40 CFR Part 1991 Subparts B and C Compliance Recertification Application 2004, Appendix PA, Attachment SOTERM, November 10 (2003) DOE Carlsbad Field Office, Carlsbad, NM
- [Trovato 1997] Trovato E.R., Untitled letter from E.R. Trovato to G. Dials, April 25, 1997. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air
- [Yamamura 1998] Yamamura, T., A. Kitamura, A. Fukui, S. Nishikawa, T. Yamamoto., and H. Moriyama, Solubility of U(VI) in highly basic solutions, *Radiochimica Acta* **83** (1998) 139-146
- [Yamazaki 1992] Yamazaki H., B. Lagerman, V. Symeopoulos, and G.R. Choppin, Solubility of Uranyl in Brine, *Radioactive Waste Management*, **1992** (1992) 1607-1611