

NOTICE: The current controlled version of this document is available in the LANL-CO Document Center (<http://lcodocs.lanl.gov>). A printed copy of the document may not be the current version.

**LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS**

LCO-ACP-14, Revision 0

Uranium (VI) Solubility in WIPP Brine

J.F. Lucchini, M.K. Richmann, and M. Borkowski

Effective Date: 4-14-13

Originator:



Jean-François Lucchini, LANL-CO ACRSP

02/05/2013
Date

Reviewed by:




Donald Reed, LANL-CO ACRSP Team Leader

2/7/2013
Date



Tim Burns, LANL-CO, Technical Program Manager

2/7/2013
Date



Laurie Smith, LANL-CO Quality Assurance Manager


2/7/2013
Date

Approved by:



Donald Reed, LANL-CO ACRSP Team Leader

2/7/2013
Date



Laurie Smith, LANL-CO Quality Assurance Program Manager

2/7/2013
Date



Ned Elkins, LANL-CO Group Leader

2.7.13
Date

History of Revision

Revision Number	Effective Date	Pages Revised	Reason for Revision
0	4-16-13	All	Original Release

Uranium (VI) Solubility in WIPP Brine

J.F. Lucchini,
M.K. Richmann, and M. Borkowski

EXECUTIVE SUMMARY

The solubility of uranium (VI) in Waste Isolation Pilot Plant (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 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 WIPP brines are presented. The solubility of uranium (VI) was determined in WIPP-relevant brines as a function of pC_{H^+} and ionic strength, in the absence or presence of carbonate. A major objective of these experiments was to establish the effects of carbonate complexation on uranium (VI) solubility in WIPP brines. The experiments performed were done according to the Department of Energy (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-CO Quality Assurance Program, which is compliant with the DOE Carlsbad Field Office, Quality Assurance Program Document (CBFO/QAPD). The data summarized in this report are supported by Quality Assurance (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), under WIPP-related conditions was also conducted, and is reported herein.

There are a number of key results and observations from this U(VI) solubility study 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. The two WIPP-relevant papers found in the literature were from Yamazaki [1992] and 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 less rigorous control of a carbon dioxide free environment than in our experiments. The values reported by Yamazaki [1992] and Diaz-Arocas [1998] were in the range $10^{-7} - 3 \times 10^{-3}$ M.
- Our solubility data for uranium (VI) provide the first WIPP-relevant data for the VI actinide oxidation state and establishes the solubility of uranium (VI) over an extended pC_{H^+} range for GWB and ERDA-6 brines in the absence or in the presence of carbonate. In the absence of carbonate, 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 $pC_{H^+} \geq 8$. In the presence of carbonate, the highest uranium solubility obtained experimentally was $\sim 10^{-4}$ M, under WIPP-related conditions ($pC_{H^+} \sim 9$).
- The solubility data for uranium (VI) in WIPP brine presented in this report accomplished the following:
 - Provided the first WIPP-relevant data for the VI 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 or presence 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, and an upper limit of $\sim 10^{-4}$ M uranyl concentration at the reference pC_{H^+} WIPP case in the presence of carbonate. These are 10-100 times lower than published results.
 - Demonstrated 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. No amphoteric effect was observed in WIPP simulated brines at high pH values.
 - Demonstrated a small effect of borate complexation in the pC_{H^+} range [7.5 – 10].

The data we reported in this document showed that the 1 mM value for uranium (VI) solubility used in WIPP PA was conservative, by over a factor of 50, relative to our experimental site-specific results. Our data clearly support the current WIPP PA assumption on An(VI) solubility.

TABLE OF CONTENTS

LIST AND DEFINITION OF ACRONYMS, ELEMENTS AND CHEMICAL

	EXECUTIVE SUMMARY	3	CO MP OU ND S
	LIST AND DEFINITION OF ACRONYMS	6	
1.0	INTRODUCTION	10	
2.0	ROLE AND IMPORTANCE OF ACTINIDE (VI) SOLUBILITY IN CRA-2009.....	12	
	2.1 WIPP Position on Uranium Source Term.....	12	
	2.2 CRA-2009 WIPP Position on Actinide (VI) Solubility.....	13	
	2.3 EPA Position on Uranium (VI) Solubility.....	14	
	2.4 Need for the Development of an Actinide (VI) Solubility Model.....	16	
3.0	LITERATURE BACKGROUND: SOLUBILITY OF U(VI)	18	
	3.1 Hydrolysis of Uranium (VI).....	18	
	3.2 Solubility of Uranium (VI) in Carbonate-free Brine.....	21	
	3.3 Solubility of Uranium (VI) in Brine in the Presence of Carbonate.....	24	
4.0	WIPP-RELEVANT EXPERIMENTAL RESULTS: SOLUBILITY OF UO_2^{2+} IN SIMULATED WIPP BRINE	27	
	4.1 Experimental Goals and Test Matrices.....	27	
	4.2 Experimental Approach, Limitations, Considerations and Error Analysis	31	
	4.3 Results and Discussion	42	
	4.4 Solubility of U(VI) in the Absence of Carbonate.....	65	
	4.5 Solubility of U(VI) as a Function of Ionic Strength.....	68	
	4.6 Solubility of Uranium (VI) Solids in Carbonate-free Brines.....	71	
	4.7 Solubility of U(VI) in the Presence of Carbonate.....	74	
	4.8 Summary of Experimental Results and Conclusions	77	
5.0	CONCLUSION.....	86	
6.0	QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION.....	88	
7.0	LITERATURE REFERENCES.....	93	

°C	Degrees Celsius
%	Percent
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
C_M	Concentration of M species
CaCl ₂	Calcium chloride
CaCO ₃	Calcium carbonate
(DOE) CBFO	(Department of Energy) Carlsbad Field Office
CCA	Compliance Certification Application
CEMRC	Carlsbad Environmental Monitoring and Research Center
CO ₂	Carbon dioxide
CO ₂ (aq)	Carbon dioxide gas dissolved in solution
CO ₃ ²⁻	Carbonate ion
CRA	Compliance Recertification Application
DOE	US Department of Energy
EDS	Energy-Dispersive x-ray Spectrometer
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
HCO ₃ ⁻	Bicarbonate ion
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ CO ₃ (aq)	Carbonic acid
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
kDa	kiloDalton
K _{a1}	First dissociation constant for carbonic acid
K _{a2}	Second dissociation constant for carbonic acid
K _h	Hydrolysis constant of carbonic acid
K _w	Dissociation constant of water
KNO ₃	Potassium nitrate
K ₂ U ₂ O ₇	Potassium diuranate
KCl	Potassium chloride
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
Mg(OH) ₂	Brucite, magnesium hydroxide
MΩ·cm	Megaohm-centimeter
Na ₂ B ₄ O ₇	Sodium tetraborate
Na ₂ CO ₃	Sodium carbonate
Na ₂ SO ₄	Sodium sulfate
Na ₂ U ₂ O ₇ .xH ₂ O	Sodium diuranate hydrate
NaBr	Sodium bromide
NaCl	Sodium chloride
NIST	National Institute of Standards and Technology
nm	Nanometer

NMSU	New Mexico State University
N ₂	Nitrogen
Np	Neptunium
Np(VI)	Neptunium in the VI oxidation state
O ₂	Oxygen
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
pH _{obs}	Measured/Observed pH
pKa	Negative logarithm of the dissociation constant of an acid
ppb	Parts per billion
ppm	Parts per million
Pu	Plutonium
Pu(III)	Plutonium in the III oxidation state
Pu(IV)	Plutonium in the IV oxidation state
Pu(VI)	Plutonium in the VI oxidation state
rpm	Revolution per minute
QA	Quality Assurance
QAPD	Quality Assurance Program Document
SEM	Scanning Electron Microscopy
SOTERM	Actinide Source Term appendix for WIPP recertification applications
T	Temperature
Th	Thorium
Th(IV)	Thorium in the IV oxidation state
TRU	Transuranic (actinides higher in atomic number than uranium)
U	Uranium
U(IV)	Uranium in the IV oxidation state
U(VI)	Uranium in the VI oxidation state
UO ₂ ²⁺	Uranyl ion – Aqueous form of the uranium at the VI oxidation state
UO ₂ CO ₃	Rutherfordine, uranium (VI) carbonate
UO ₂ (CO ₃) ₂ ²⁻	Uranium (VI) carbonate ion – (1:2) complex
UO ₂ (CO ₃) ₃ ⁴⁻	Uranium (VI) carbonate ion – (1:3) complex or triscarbonato

	complex
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	Uranium (VI) carbonate ion – (3:6) complex
$(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$	Uranium (VI) carbonate hydroxide ion – (2:1:3) complex
$(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$	Uranium (VI) carbonate hydroxide ion – (11:6:12) complex
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Depleted uranium (VI) nitrate hexahydrate
$\text{UO}_2(\text{OH})^+$	Uranium (VI) hydroxide ion – (1:1) complex
$\text{UO}_2(\text{OH})_2$	Uranium (VI) hydroxide
$\text{UO}_2(\text{OH})_3^-$	Uranium (VI) hydroxide ion – (1:3) complex
$\text{UO}_2(\text{OH})_4^{2-}$	Uranium (VI) hydroxide ion – (1:4) complex
$(\text{UO}_2)_2\text{OH}^{3+}$	Dimer uranium (VI) hydroxide ion – (2:1) complex
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	Dimer uranium (VI) hydroxide ion – (2:2) complex
$(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4$	(2:2:2) uranium (VI) hydroxide chloride complex
$[(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$	(2:2:2) uranium (VI) hydroxide nitrate complex hydrated
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	Trimer uranium (VI) hydroxide ion – (3:4) complex
$(\text{UO}_2)_3(\text{OH})_5^+$	Trimer uranium (VI) hydroxide ion – (3:5) complex
$(\text{UO}_2)_3(\text{OH})_7^-$	Trimer uranium (VI) hydroxide ion – (3:7) complex
$(\text{UO}_2)_3(\text{OH})_8^{2-}$	Trimer uranium (VI) hydroxide ion – (3:8) complex
$(\text{UO}_2)_3(\text{OH})_{10}^{4-}$	Trimer uranium (VI) hydroxide ion – (3:10) complex
$(\text{UO}_2)_4(\text{OH})_6^{2+}$	Quadramer uranium (VI) hydroxide ion – (4:6) complex
$(\text{UO}_2)_4(\text{OH})_7^+$	Quadramer uranium (VI) hydroxide ion – (4:7) complex
$(\text{UO}_2)_5(\text{OH})_8^{2+}$	Pentamer uranium (VI) hydroxide ion – (4:7) complex
UO_3	Uranium (VI) trioxide
$\text{UO}_3 \cdot 2\text{H}_2\text{O}$	Schoepite
UO_4	Uranium (VI) peroxide
WIPP	Waste Isolation Pilot Plant
XANES	X-ray Absorption Near Edge Spectroscopy
XRD	X-Ray Diffraction

Uranium (VI) Solubility in WIPP Brine

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 considered in WIPP PA because its existence cannot be completely excluded, as is the case for Np(VI) and Pu(VI), under the highly reducing conditions expected to predominate in the WIPP. Since uranium is a relatively minor contributor to overall potential release of actinides from the WIPP, a VI actinide model was never developed.

The solubility of uranium (VI) in brine systems has not been well studied and, in particular, the effect of carbonate complexation on its solubility is not well understood. For this reason, a 1 mM upper limit to its solubility is used in WIPP PA release calculations. It is in this context that the Los Alamos National Laboratory Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) team performed multi-year uranium (VI) solubility experiments in simulated WIPP brine. These data, which are summarized in this report, are the first WIPP-relevant data for the solubility of U(VI) and can in effect be used to establish the degree of conservatism in the WIPP PA modeling assumptions.

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 the WIPP-specific data obtained by the LANL-CO/ACRSP team on the solubility of U(VI) in simulated WIPP brine. These data, more generically, apply to An(VI) solubility in the WIPP.
- 3) An overall assessment of the current WIPP PA assumptions in light of the literature review and our WIPP-specific results.

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 the Environmental Protection Agency (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 Compliance Recertification Application (CRA) was submitted in 2004 by Department of Energy Carlsbad Field Office (DOE CBFO), and was approved in April 2006. The second CRA was submitted in 2009, and approved by EPA in 2010. The results summarized in this report will contribute to the third WIPP recertification application that will be submitted in 2014.

The WIPP-relevant solubility studies summarized in this report were performed by the LANL-CO/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 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 compliant with the DOE CBFO Quality Assurance Program Document (QAPD).

2.0 ROLE AND IMPORTANCE OF ACTINIDE (VI) SOLUBILITY IN CRA-2009

The role and importance of An(VI) solubility in CRA-2009 was presented in Appendix SOTERM [SOTERM 2009]. The relative importance, based on their potential to contribute to actinide release from the WIPP, of the predominant actinides and oxidation states in the WIPP is:

Importance of actinide solubility to release: Pu ≈ Am >> U > Th >> Np ≈ Cm

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

In the actinide inventory for the TRU waste emplaced in the two first WIPP panels [Lucchini 2007], uranium is indicated to be 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 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 position on the uranium source term is addressed in the following excerpt from Appendix SOTERM [SOTERM 2009]:

SOTERM-3.3 Uranium Chemistry

*U is not a TRU component, but is, by mass, expected to be the most prevalent actinide component in the WIPP. Current estimates predict that ~647 metric tons will be placed in the repository (see Table SOTERM-7) *. By mass, greater than 99% of this U will be the ²³⁸U isotope, with minor amounts of ²³³U, ²³⁴U, ²³⁵U, and ²³⁶U. U does not contribute significantly to the calculation of actinide release through cuttings/cavings and spallings because of its low specific activity. U release can occur through the Culebra in very small amounts because of its potentially high solubility in the VI oxidation state.*

U release, as the ²³⁴U isotope, was calculated in the CRA-2004 PABC. In the WIPP PA, the oxidation state distribution assumption is that U speciates as U(IV) in 50% of the PA vectors and as U(VI) in the other 50% of the vectors. The

* 647 metric tons of U estimates from [TWBIR-2004] were refined in the later PAIR-2008 document and reduced to 83 metric tons [PAIR-2008]

U concentration for this oxidation state is currently set at 1 mM (U.S. Environmental Protection Agency 2005), since there is no An(VI) model in the WIPP. U(IV) solubility is calculated using the Th(IV) speciation data reported in the FMT model. For the current WIPP PA assumptions, uranium does not contribute significantly to the overall release of actinides from the WIPP.

In summary, it is conservatively assumed in CRA-2009 Appendix SOTERM [SOTERM 2009] 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 much lower solubility U(IV) species should be predominant under the expected highly reducing anoxic WIPP conditions. The solubility of U(VI) in the WIPP was conservatively set by the EPA to be 10^{-3} M to account for the lack of reliable data on the effects of carbonate complexation [EPA 2005].

2.2 CRA-2009 WIPP Position on Actinide (VI) Solubility

The actinides of interest to the WIPP that could speciate in the VI oxidation state are uranium and plutonium, and, to a much lesser extent due to inventory limitations, 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 the most stable of the actinyl (VI) cations [Morss 2006] towards reduction in a wide range of aqueous systems. This redox stability makes it suitable for our uranium solubility studies although there are serious limitation in extending these results to other An(VI) actinides. As part of the WIPP Actinide Source Term (ASTP) program conducted in 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].

A summary of the oxidation-state specific actinide solubilities calculated for the various WIPP performance assessments is given in Table 2-1. 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 value was selected because it was within the range of the available experimental values. A somewhat lower value of 8.7×10^{-6} M that corresponds to the solubility of schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) as the controlling phase [Hobart 1996] was used in the WIPP CCA, PAVT, and CRA-2004 calculations.

Table 2-1. Actinide Solubilities (M) Calculated (+III, +IV, and +V) or Estimated (+VI) for the CRA-2009 PABC, the 2004 PABC, the CRA-2004 PA, the 1997 PAVT and the CCA PA [SOTERM 2009; Brush 2009].

Actinide Oxidation State, and Brine	CRA-2009 PABC Solubilities (Hydro-magnesite, with organics, all vectors)	CRA-2004 PABC Solubilities (Hydro-magnesite, with organics, all vectors)	CRA-2004 Solubilities (Hydro-magnesite, with organics, microbial vectors)	PAVT Solubilities (Hydro-magnesite, without organics, all vectors)	CCA Solubilities (Magnesite, without organics, all vectors)
+III, Salado brine	1.66×10^{-6}	3.87×10^{-7}	3.07×10^{-7}	1.2×10^{-7}	5.82×10^{-7}
+III, Castile brine	1.51×10^{-6}	2.88×10^{-7}	1.69×10^{-7}	1.3×10^{-8}	6.52×10^{-8}
+IV, Salado brine	5.63×10^{-8}	5.64×10^{-8}	1.19×10^{-8}	1.3×10^{-8}	4.4×10^{-6}
+IV, Castile brine	6.98×10^{-8}	6.79×10^{-8}	2.47×10^{-8}	4.1×10^{-8}	6.0×10^{-9}
+V, Salado brine	3.90×10^{-7}	3.55×10^{-7}	1.02×10^{-6}	2.4×10^{-7}	2.3×10^{-6}
+V, Castile brine	8.75×10^{-7}	8.24×10^{-7}	5.08×10^{-6}	4.8×10^{-7}	2.2×10^{-6}
+VI, Salado brine	1.0×10^{-3}	1.0×10^{-3}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}
+VI, Castile brine	1.0×10^{-3}	1.0×10^{-3}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}

In the CRA-2004 Performance Assessment Baseline Calculation (PABC) and subsequent PA calculations a value of 10^{-3} M was used as the solubility of U(VI). This was 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.

2.3 EPA Position on Uranium (VI) Solubility

The current EPA position on uranium (VI) solubility is presented in the following excerpt from [EPA 2010, page 79-81]:

6.4.4.2 Uranium

Uranium is assumed to be present in WIPP brines as uranium (IV) in 50% of the PA realizations, and as uranium (VI) in 50% of the PA realizations (see Section 5.0). The solubility of uranium (IV) is assumed equal to the thorium (IV) solubility (Section 6.1.2). Because DOE has not developed a model for calculating the solubility of uranium (VI), a fixed bounding concentration of 10^{-3} M is assumed for PA (Section 6.3.4).

DOE (2009, Appendix SOTERM-2009) addressed the solubility and speciation of uranium (VI) (Section 3.3.1.3), and provided WIPP-specific experimental results from Lucchini et al. (2009) that have become available since the PABC04. Because this report was not provided with the CRA-2009, EPA requested a copy from DOE for review (Cotsworth 2009a, Comment 1-23-2b). This report was received from DOE (Moody 2009b), but the correct citation is Lucchini et al. (2010).

Lucchini et al. (2010) investigated the solubility of uranium (VI) solid phases in brine, using sequential addition of uranium (VI) stock solution to the brines to establish oversaturation with respect to potential uranium (VI) phases. Experiments were carried out in simulated GWB from approximately pH 6 to 9 and in simulated ERDA-6 from approximately pH 8 to 12. All experiments were carried out in a nitrogen atmosphere and CO_2 was excluded from the experiments. The concentrations of uranium (VI) in the carbonate-free GWB and ERDA-6 brines were approximately 10 to 100 times lower than previously reported for carbonate-free 5 M NaCl brines by Díaz Arocas and Grambow (1998). At moderately alkaline pH values, the solubility of uranium was about one order of magnitude higher in GWB than in ERDA-6 brine (Figure 6-2 – Source: Lucchini et al. (2010), Figure 4-9).

DOE (2009, Appendix SOTERM-2009, Section SOTERM-3.3.1.3) noted the higher solubility in GWB brine compared to ERDA-6 brine, and attributed the higher solubility to complexation by higher borate and sulfate ion concentrations in GWB. In a letter sent to DOE (Cotsworth 2009a, Comment 1-23-6c), EPA observed that higher concentrations in these experiments and in neodymium solubility experiments (Section 6.4.4.5) attributable to borate complexation do not appear to be consistent with the current Dissolved Actinide Source Term conceptual model assumption that states (SC&A 2008b, Appendix A.3):

The important ions in WIPP brines are H^+ , Na^+ , K^+ , Mg^{2+} , OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} , and Ca^{2+} . Other ions such as PO_4^{3-} , F^- , Al^{3+} , Fe^{2+} , and Fe^{3+} may be important, but their effects are included only in a qualitative understanding of the chemical environment.

However, borate complexation of uranium (VI), if it occurs to a significant extent, would not substantially change the current understanding of likely uranium (VI) solubility in WIPP brines because it is expected that uranyl carbonate species are likely to dominate aqueous speciation under WIPP repository conditions. DOE clarified that the potential effects of borate complexation on actinide solubilities were still under investigation, and that different solubilities predicted in GWB and ERDA-6 brine were likely caused by the many differences between the two brines and not solely by different borate concentrations (Moody 2010a). [...].

Because of the probable importance of carbonate complexation on uranium (VI) concentrations in brine under repository conditions, the experiments reported by Lucchini et al. (2010) cannot be used to revise the upper limit of 10^{-3} M established for uranium (VI) at the time of the PABC04 (Section 6.3.4). However, these experiments provide a baseline for experiments planned by DOE for uranium solids solubility in WIPP brines with carbonate.

This excerpt from the EPA documentation [EPA 2010] mostly discusses the data presented in [Lucchini 2010a], which were the only WIPP-relevant data on uranium (VI) solubility since the CCA. The EPA noted that borate complexation of uranium (VI) will not significantly affect uranium (VI) solubility in WIPP brine, because of the predominance of carbonate complexation. The 1 mM solubility limit for U (VI), although it takes into account some new experimental data published in the literature since the CCA, is not based on WIPP-relevant data and conservatively overestimated the expected solubility of uranium in the WIPP.

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

The WIPP project continues to successfully argue that there is no need for an An(VI) solubility model to calculate the solubility of uranium under the current WIPP PA assumptions. This is largely based on actinide release calculations that show little/no uranium (in terms of activity) release from the WIPP even with an assumed 1 mM uranium (VI) concentration. This project position continues even though the An(VI) oxidation state is the only oxidation state without a model and the EPA continues to flag the need for an An(VI) model in their reviews of the WIPP project [EPA 2010].

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 2006] 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 and in the CRA-2009 PABC.

In its review of CRA-2009 [EPA 2010], the EPA mentioned an inconsistency between experimental data obtained on uranium (VI) solubility in WIPP-relevant carbonate-free brines by Lucchini et al. [Lucchini 2010a] and the current Dissolved Actinide Source Term conceptual model assumptions, due to the discovery of borate complexation of uranium (VI). The EPA acknowledged that borate complexation of uranium (VI) would have an insignificant impact on uranium (VI) solubility, because of the bigger effect of carbonate

complexation. However, in conclusion of its most recent review of chemistry-related issues important to WIPP PA [EPA 2010], the EPA listed the “development of a uranium (VI) aqueous speciation and solubility model and [the] incorporation of this model into the FMT database” as one of the "issues related to WIPP repository chemical processes that have been identified for possible additional investigation prior to the CRA-2014".

In conclusion, the U(VI) solubility data we report herein, as will be seen in Section 4, support the WIPP position that an An(VI) model is not needed and show the 1 mM value to be conservatively high even for WIPP brine with greater-than-predicted carbonate concentration. It is important to note that these solubility data could be used as a starting point towards the development of an An(VI) model should this become needed. Significantly more experimental work would, however, be required to obtain the Pitzer interaction parameters for this U(VI) solubility model.

3.0 LITERATURE BACKGROUND: SOLUBILITY OF U(VI)

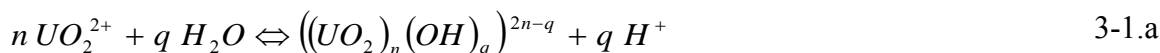
The solubility and extent of aggregation in WIPP-relevant brine are key factors that define the potentially mobile concentration of actinides from an underground repository to the environment [Clark 1995, Runde 2000, Moulin 2001, Choppin 2003]. Solubility, which is the focus of this report, is governed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

The solubility of uranium in the VI oxidation state (U(VI)) in repository conditions is dominated by the relative contribution of hydrolysis and carbonate complexation. In the absence of carbonate, 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), in the absence of carbonate. These literature results are presented and discussed in section 3.2. Section 3.3 presents the role of carbonate on the speciation and solubility of U(VI) in experimental conditions expected in an underground nuclear waste repository in salt environment like the WIPP.

3.1 Hydrolysis of Uranium (VI)

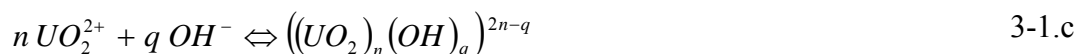
The hydrolysis of UO_2^{2+} has been studied quite intensely, partially because it forms a wide variety of polynuclear hydrolytic species, resulting in a quite complex chemistry.

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



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

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



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

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 $[UO_2^{2+}]_{\text{total}} = 4.75 \times 10^{-4}$ 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.

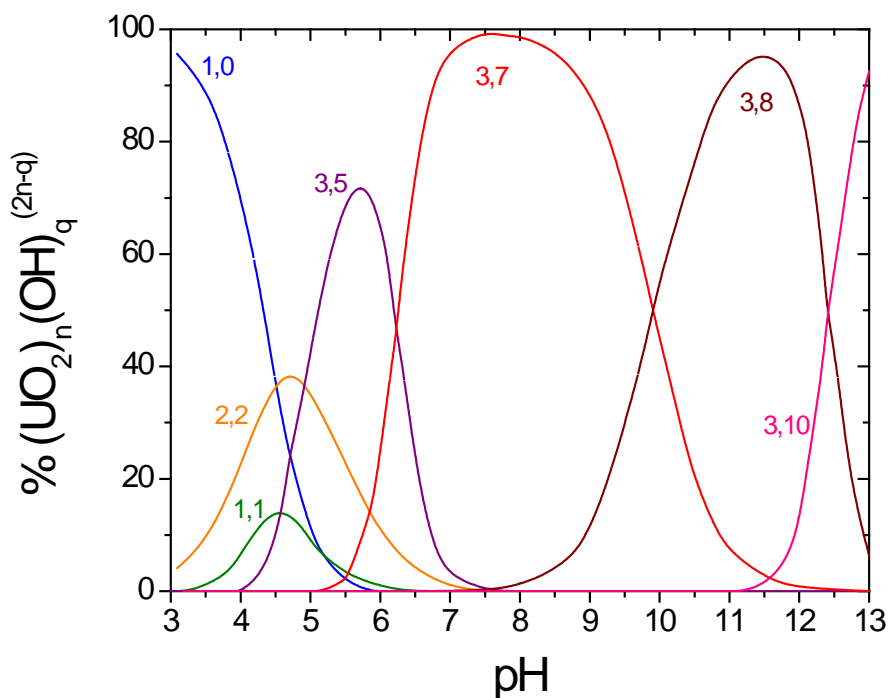


Figure 3-1: Speciation diagram for the formation of $((UO_2)_n(OH)_q)^{2n-q}$ with $[UO_2^{2+}]_{\text{total}} = 4.75 \times 10^{-4}$ M, ionic strength $I = 0.1$ M, $T = 25$ °C. The number pairs shown on the graph refer to n and q . (Based on data in Palmer 1995)

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

n,q	$\log * \beta_{nq}^{\circ}$ [Palmer and Nguyen-Trung 1995]	$\log * \beta_{nq}^{\circ}$ [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 the 3:8 complex $(\text{UO}_2)_3(\text{OH})_8^{2-}$. 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.

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
 $\beta^* = \beta / K_w$ with $K_w = [\text{H}^+] \times [\text{OH}^-]$

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 reported 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.

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 and ionic strength ~ 6 M. This synthetic brine initially contained 0.11 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 $\text{pC}_{\text{H}^+} = 10.4$ 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 $\text{pC}_{\text{H}^+} \geq 9.3$ was found to be potassium diuranate $\text{K}_2\text{U}_2\text{O}_7$.

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 $\text{UO}_2(\text{OH})_2$ (s) [Palmer 1996]. These results were privately communicated by Palmer, and reported by Hobart [1996], but never published. For this reason they are not considered further in this report.

Table 3-3. Experimental uranium (VI) solubility data in carbonate-free 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) ~6 M	100	α-schoepite (oversaturation)	[Yamazaki 1992]
$(1.81 \pm 0.01) \times 10^{-3}$	8.4	Brine (air atmosphere) ~6 M	100	α-schoepite (oversaturation)	[Yamazaki 1992]
$(1.40 \pm 0.05) \times 10^{-3}$	8.4	Brine (air atmosphere) ~6 M	244	α-schoepite (undersaturation)	[Yamazaki 1992]
$(1.80 \pm 0.05) \times 10^{-3}$	8.4	Brine (air atmosphere) ~6 M	244	α-schoepite (undersaturation)	[Yamazaki 1992]
$(3.8 \pm 0.4) \times 10^{-7}$	10.4	Brine ~6 M (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 ~6 M (initial 0.11 mM HCO ₃ ⁻)	150	Mg(OH) ₂ and K ₂ U ₂ O ₇ (oversaturation)	[Yamazaki 1992]

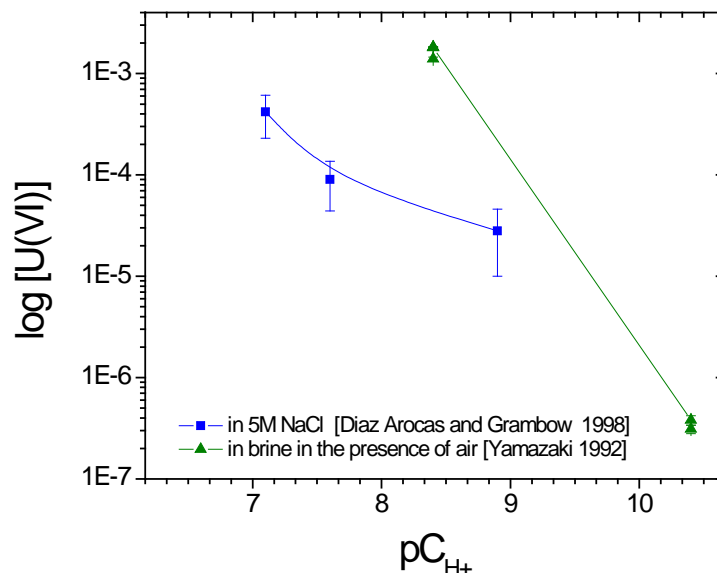


Figure 3-2: Uranium (VI) solubility data obtained in carbonate-free (otherwise mentioned) high ionic strength media at $pC_{H^+} > 7$. The full square symbols and corresponding trend line represent data obtained by Diaz Arocas and Grambow in 5 M NaCl under an argon atmosphere [Diaz Arocas 1998]. The full triangle symbols and corresponding trend line represent data obtained by Yamazaki et al. in brine (1~6 M) with an air atmosphere [Yamazaki 1992].

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.

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 uranium solubility controlling 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 reported in Diaz-Arocas' experiments.

3.3 Solubility of Uranium (VI) in Brine in the Presence of Carbonate

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, Reed 1997, Lin 1998, Yamamura 1998, Fanghanel 2002]. The role of carbonate (CO_3^{2-}) in the uranium (VI) solubility is indeed important [Clark 1995, Guillaumont 2003]. Carbonate complexes of uranium are of interest not only in nuclear waste repository chemistry, but also in the industry because of extensive applications, primarily in recovery from ores and nuclear fuel reprocessing. The alkaline leaching process for the recovery of uranium is very selective and utilizes the high stability of the soluble 1:3 complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$, as a means of selectively separating uranium from ore. Recovery of the uranium from the leach liquor is achieved by addition of hydroxide to precipitate $\text{Na}_2\text{U}_2\text{O}_7$, or by acidification to liberate carbon dioxide [Clark 1995].

In the absence of other complexing ligands, carbonate complexation will dominate the speciation of the uranyl ion under near-neutral pH conditions as long as there is ample carbonate-bicarbonate available [Clark 1995]. Complexation constants for binary U(VI) carbonate complexes at $I = 0$ M and 25°C are listed in Table 3.4 [Guillaumont 2003]. Three monomeric complexes, $\text{UO}_2(\text{CO}_3)$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are predicted to be present. There is also evidence from redox, solubility, and spectroscopy data supporting the existence of polymeric solution species of formulas $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, and $(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$ which can form only under conditions of high metal ion concentration or high ionic strength [Clark 1995]. At uranyl concentrations above 10^{-3} M, the trimeric cluster $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ is present in significant concentrations. When the uranyl ion concentration exceeds the carbonate concentration, hydrolysis competes with carbonate complexation and plays an increasingly important role [Clark 1995].

Table 3-4. Complexation constants for binary U(VI) carbonate complexes at $I = 0$ M and 25°C [Guillaumont 2003].

Reaction and Solubility product for $\text{UO}_2\text{CO}_3(\text{cr})$	
$\text{UO}_2\text{CO}_3(\text{cr}) \rightleftharpoons \text{UO}_2^{2+} + \text{CO}_3^{2-}$	$\text{Log } K_{\text{SP}(\text{cr})}^0 = -14.76 \pm 0.02$
Reactions and Formation constants β_{nq}^0 for $(\text{UO}_2)_n(\text{CO}_3)_q^{2n-2q}$	
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{UO}_2\text{CO}_3(\text{aq})$	$\text{Log } \beta_{11}^0 = 9.94 \pm 0.03$
$\text{UO}_2^{2+} + 2 \text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{Log } \beta_{12}^0 = 16.61 \pm 0.09$
$\text{UO}_2^{2+} + 3 \text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{Log } \beta_{13}^0 = 21.84 \pm 0.04$
$3 \text{UO}_2^{2+} + 6 \text{CO}_3^{2-} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	$\text{Log } \beta_{36}^0 = 54.0 \pm 1.0$

The major uranyl carbonato complex in solution at low ionic strength and high carbonate concentration is $\text{UO}_2(\text{CO}_3)_3^{4-}$ [Kramer-Schnabel 1992, Peper 2004]. However, at $I = 0.5 \text{ M}$ and $I = 3 \text{ M}$, the polynuclear species $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ becomes an important competitor of $\text{UO}_2(\text{CO}_3)_3^{4-}$. Grenthe *et al.* indicated that the formation of $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ is favored at high ionic strengths due to possible stabilization of the complex by ions of the background electrolyte [Grenthe 1984]. The experimental curve of the solubility of UO_2CO_3 obtained by Kramer-Schnabel *et al.* is displayed in Figure 3-3, together with two curves obtained at higher ionic strengths by Grenthe *et al.* [Grenthe 1984]. The experimental points from Kramer-Schnabel *et al.* were obtained in the region $3 < \text{pH} < 6$ and $-11 < \log[\text{CO}_3^{2-}] < -6$ where UO_2CO_3 is the solid phase. These experimental data were fit using the stability constants of three carbonate complexes: UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. Including additional uranyl-carbonate complexes did not improve the fit obtained. An important observation from Figure 3-3 is that uranium concentration in solution exhibited an increasingly complex dependency on ionic strength with increasing carbonate concentrations.

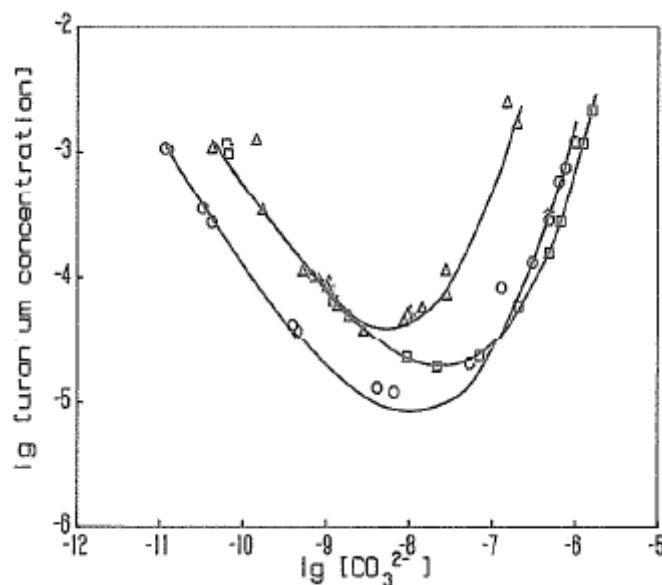


Figure 3-3: Experimental (symbols) and theoretical (lines) solubility curves of UO_2CO_3 at 25°C and $I = 0.1 \text{ M}$ (triangles, [Kramer-Schnabel 1992]), $I = 0.5 \text{ M}$ (squares, [Grenthe 1984]) and $I = 3 \text{ M}$ (circles, [Grenthe 1984]).

At high pH, Yamamura *et al.* demonstrated that hydrolysis overwhelms carbonate complexation when carbonate source is limited [Yamamura 1998]. The solubility of U(VI) was measured in highly basic solutions ($11 \leq \text{pH} \leq 14$) at different ionic strengths ($0.5 - 2 \text{ M}$) over a wide range of carbonate concentrations ($10^{-3} - 0.5 \text{ M}$) using both oversaturation and undersaturation approaches. In the oversaturation experiments, the solubility of U(VI) decreased with increasing equilibration time from 1 week to 1 year, suggesting an increase in

the crystallinity of the solid phase with aging. The solid phase was identified as $\text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ by X-ray diffraction. The undersaturation experiments conducted for 1 month with the solid phase indicated a rapid equilibrium. These data were well interpreted by considering the formation of $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_4^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ [Yamamura 1998].

The influence of carbonate on U(VI) solubility in highly saline solutions was investigated by Yamazaki *et al.* [1992], Lin *et al.* [1998] and Reed *et al.* [1997].

A few U(VI) solubility experiments performed by Yamazaki *et al.* were conducted in a synthetic brine and an air atmosphere [Yamazaki 1992]. This implies that some carbonate was present in solution, as a result of the equilibrium with carbon dioxide from the above atmosphere. The results obtained at $\text{pC}_{\text{H}^+} = 8.4$ using both oversaturation and undersaturation approaches are listed in Table 3-3 and plotted in Figure 3-2. A 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 $\text{pC}_{\text{H}^+} = 8.4$ were identified as poorly crystalline schoepite ($\text{UO}_3 \cdot x\text{H}_2\text{O}$) 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 $\text{pC}_{\text{H}^+} = 8.4$ was related to a shift from the triscarbonato uranyl complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ to the uranyl hydroxide complexes $\text{UO}_2(\text{OH})_n^{2-n}$, as precipitation of calcium carbonate (CaCO_3) occurred, and to the conversion of schoepite to potassium diuranate.

Lin *et al.* [1998] evaluated uranium (VI) solubilities with up to 5 M NaCl in a range of carbonate concentrations. At carbonate ion concentrations greater than 10^{-7} M, $\text{UO}_2(\text{CO}_3)_3^{4-}$ was the dominant U(VI) complex in solution. At higher carbon dioxide partial pressures, the solubility-controlling solid phase was found to be $\text{UO}_2\text{CO}_3(\text{s})$, whereas at lower partial pressures, sodium uranate was identified as the solid phase in NaCl-saturated solutions. The reported solubility of $\text{UO}_2\text{CO}_3(\text{s})$ at a carbonate ion concentration of 10^{-5} M was approximately 5×10^{-3} M. However, in this study, the pH of the solution was not reported.

The only U(VI) solubility values available in the literature that were obtained in the presence of carbonate and that are relevant to the WIPP were featured in the fiscal year 1997 year-end report by Reed *et al.* titled, "Actinide Stability/Solubility in Simulated WIPP Brines." [Reed 1997]. The experiments were carried out in ERDA-6 brine at pH 8 and 10, and in G-Seep brine at pH 5 and 7. U(VI), Np(VI), and Pu(VI) were added to the brine samples. CO_3^{2-} (10^{-4} M) was also added to some of the samples. The experiments were conducted under a hydrogen atmosphere at 25 ± 5 °C. Concentrations and oxidation states of the actinides were monitored over time. The U(VI) concentration was stable at approximately 1×10^{-4} M when measured as a function of time in ERDA-6 brine at pH 10 in the presence of CO_3^{2-} [Reed 1997].

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

The LANL-CO/ACRSP team performed experiments to determine the solubility of uranium (VI) in simulated WIPP brines. 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 Matrices

The most important goals of the solubility studies were:

- Establish 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 An (VI) solubility under WIPP-relevant conditions.
- 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 |

The solubility experiments discussed herein pertain to experiments identified in Task 1. Results from Task 2 and Task 3 are not discussed in this report.

Task 1 initially included three subtasks: U(VI) solubility under anoxic conditions (Subtask 1), U(VI) solubility under oxic conditions (Subtask 2), and carbonate effects study on U(VI) solubility (Subtask 3). The experiments identified in Subtask 2 were initiated, but subsequently discontinued because they were not WIPP-relevant and no data from these preliminary experiments are included in this report. Additionally, three subtasks were added to Task 1: U(VI) solubility in diluted WIPP brine (Subtask 4), and U(VI) solubility in carbonate-free brine using the undersaturation approach (Subtask 8). All the experiments described herein 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

should not impact the aqueous speciation of U(VI), although there is a possibility that the presence of oxygen may affect solid phase formation.

In sections 4.1.1 to 4.1.4, the experimental goals and experimental matrices associated with each subtask of Task 1 are presented.

4.1.1 Subtask 1: U(VI) solubility in an anoxic atmosphere

In Subtask 1, the solubility of U(VI) was investigated in carbonate-free simulated WIPP brines GWB and ERDA-6, as a function of pC_{H^+} , under an anoxic atmosphere, and from over-saturation. The goal of these experiments was to evaluate the effect of hydrolysis on the uranium solubility. These results defined a “baseline” carbonate-free uranium solubility that was used to evaluate the effect of carbonate on uranium (VI) solubility in subsequent studies.

Table 4-1 shows the experimental matrix for Subtask 1.

Table 4-1. Experimental matrix for carbonate-free uranium (VI) solubility studies in anoxic atmosphere using the over-saturation approach (Subtask 1).

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 $x = 0, 1$ denotes the numbering of replicate experiments.

The initial results for Subtask 1 were already presented and discussed in the LCO-ACP-10 report entitled: Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations [Lucchini 2010a]. They are reproduced herein (section 4.3.1), and discussed more extensively in the context of the other data obtained.

4.1.2 Subtask 3: Carbonate effects study on U(VI) solubility

The effect of carbonate on U(VI) solubility was investigated in Subtask 3. Experiments were performed in simulated WIPP brines GWB and ERDA-6 containing a defined amount of carbonate, at different pC_{H^+} values, under an anoxic atmosphere and from over-saturation. The goal of these experiments was to evaluate the effect of carbonate on uranium (VI) solubility as a function of pC_{H^+} .

Table 4-2 shows the experimental matrix for Subtask 3. The experimental matrix takes into consideration the chemical stability of the brines as a function of pC_{H^+} (see Section 4.2.2).

Table 4-2. Experimental matrix to evaluate the effect of carbonate on uranium (VI) solubility (Subtask 3).

pC_{H^+}	GWB			ERDA-6		
	Carbonate concentration (M)			Carbonate concentration (M)		
	Zero	$\sim 10^{-4}$	$\sim 10^{-3}$	Zero	$\sim 10^{-4}$	$\sim 10^{-3}$
~ 7.5	T3-GW-CO-7.x	T3-GW-C4-7.x	T3-GW-C3-7.x			
~ 9.0	T3-GW-CO-9.x	T3-GW-C4-9.x	T3-GW-C3-9.x	T3-ER-CO-9.x	T3-ER-C4-9.x	T3-ER-C3-9.x
~ 12.0				T3-ER-CO-12.x	T3-ER-C4-12.x	T3-ER-C3-12.x

Where $x = 0, 1$ denotes the numbering of replicate experiments.

4.1.3 Subtask 4: U(VI) solubility in diluted WIPP brine

The effect of the very high ionic-strengths present in WIPP brine on the speciation and solubility of uranium is usually difficult to determine because of the lack of high ionic-strength thermodynamic and kinetic data and the inherent difficulty/limitations in modeling at $I > 3$ M. For this reason, the U(VI) solubility in diluted WIPP brine was investigated as Subtask 4. These experiments were performed in carbonate-free diluted GWB and ERDA-6 brines, at three different pC_{H^+} values, under an anoxic atmosphere and from over-saturation. In this Subtask, three ionic strengths were investigated: $I \sim 0.1$ M, $I \sim 1$ M and $I \sim 3.4$ M.

The goal of the Subtask 4 experiments was to evaluate the effect of ionic strength on the uranium (VI) solubility at different pC_{H^+} values.

Table 4-3 shows the experimental matrix for Subtask 4.

Table 4-3. Experimental matrix to determine uranium (VI) solubility in diluted WIPP brine (Subtask 4).

pC_{H^+}	50% GWB (I ~ 3.4 M)	15% GWB (I ~ 1 M)	1.5% GWB (I ~ 0.1 M)	50% ERDA (I ~ 3 M)	17% ERDA (I ~ 1 M)	1.7% ERDA (I ~ 0.1 M)
~7.5	T4-G34-7.x	T4-G10-7.x	T4-G01-7.x			
~9.0	T4-G34-9.x	T4-G10-9.x	T4-G01-9.x	T4-E30-9.x	T4-E10-9.x	T4-E01-9.x
~12.0				T4-E30-12.x	T4-E10-12.x	T4-E01-12.x

Where $x = 0, 1$ denotes the numbering of replicate experiments.

4.1.4 Subtask 8: U(VI) solubility in brine under under-saturation

Solubility data are strengthened when the two experimental approaches, over-saturation and under-saturation, give similar results. Experiments in Subtask 1 were performed using the over-saturation approach. Complimentary experiments were performed in Subtask 8 in carbonate-free simplified WIPP brine, as a function of pC_{H^+} , under anoxic atmosphere, but using the under-saturation approach. Four different uranium solid phases were used: uranium peroxide, uranium trioxide, uranium hydroxide and precipitates from the over-saturation experiments.

The goal of the experiments planned in Subtask 8 was to confirm the data obtained in Subtask 1 on the uranium (VI) solubility in carbonate-free brines at different pC_{H^+} values, and to investigate the solubility of various uranium solid phases in those experimental conditions.

Table 4-4 shows the experimental matrix for Subtask 8.

Table 4-4. Experimental matrix for uranium (VI) solubility studies in an anoxic atmosphere using the under-saturation approach (Subtask 8).

pC _{H+}	GWB brine			
	Uranium peroxide	Uranium trioxide	Uranium hydroxide	Experimental uranium precipitate
~6	T8-GWP-6.x	T8-GWT-6.x	T8-GWH-6.x	T8-GWE-6.x
~7	T8-GWP-7.x	T8-GWT-7.x	T8-GWH-7.x	T8-GWE-7.x
~8	T8-GWP-8.x	T8-GWT-8.x	T8-GWH-8.x	T8-GWE-8.x
~9	T8-GWP-9.x	T8-GWT-9.x	T8-GWH-9.x	T8-GWE-9.x
pC _{H+}	ERDA-6 brine			
	Uranium peroxide	Uranium trioxide	Uranium hydroxide	Experimental uranium precipitate
~7	T8-ERP-7.x	T8-ERT-7.x	T8-ERH-7.x	T8-ERE-7.x
~8	T8-ERP-8.x	T8-ERT-8.x	T8-ERH-8.x	T8-ERE-8.x
~10	T8-ERP-10.x	T8-ERT-10.x	T8-ERH-10.x	T8-ERE-10.x
~11	T8-ERP-11.x	T8-ERT-11.x	T8-ERH-11.x	T8-ERE-11.x
~12	T8-ERP-12.x	T8-ERT-12.x	T8-ERH-12.x	T8-ERE-12.x

Where $x = 0, 1$ 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 Section 4.2.1. The limitations and constraints on the experiments performed and overall experimental error are discussed in Sections 4.2.2 and 4.2.3 respectively.

4.2.1 Experimental Approach

In Subtasks 1, 3, 4 and 5, the general experimental approach was to investigate uranium (VI) solubility from over-saturation, as described by Nitsche [1992]. This consisted of sequentially adding dissolved uranium until precipitation was observed. Subsequently, the uranium concentration was monitored over-time until a steady-state concentration was achieved.

In Subtask 8, the general experimental approach was to investigate uranium (VI) solubility from under-saturation. This consisted of sequentially adding a pre-determined amount of uranium solid phase, until a steady state concentration of uranium in solution was observed.

The general initial conditions of the study were:

- WIPP simulated brines and simplified brines
- pC_{H^+} between 6 and 12
- Absence or presence of a defined amount of carbonate in the brine
- Anoxic and carbonate-free atmosphere in a nitrogen glovebox
- 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 prepared at a 95% strength to minimize salt precipitation during the solubility experiments, at least before the pH adjustment.
- 2) The pH of the brine was varied as a parameter. pC_{H^+} was determined according to procedure ACP-EXP-010: "Determination of Hydrogen Ion Concentration in Brines".
- 3) In Subtask 3, the addition of carbonate in the matrix solutions was performed using an appropriate volume of a carbonate intermediate solution.
- 4) Concerning the over-saturation experiments, the uranyl stock solution was prepared with high oxidation-state purity in aqueous solution at $pH \sim 3$. For the under-saturation experiments, the uranium solid phases used in the experiments were also prepared in the laboratory using similar high oxidation-state purity uranyl stock solution.
- 5) 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).
- 6) Throughout the solubility experiments, the uranium concentration was analyzed by

ICP-MS to establish its steady state concentration as a function of time. Size distribution was established by sequential filtration.

- 7) The subsequent additions of uranyl eventually led to its precipitation as a solid. The characterization of these uranium solid phases is a difficult task due to the low amount of solid formed and the multiphase complexity and usually amorphous nature of the precipitates given the complexity of the simulated brines.

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

Simulated brines used and their preparation

Two simulated WIPP brines were used in our studies. Generic Weep Brine (GWB) is a high magnesium brine that simulates the weep brine observed in the WIPP and is considered the most relevant to repository interactions due to the MgO content. Energy Research and Development Administration Well 6 brine (ERDA-6) is a low magnesium brine that simulates brine from the Castile Formation underlying the WIPP. The nominal composition of these two simulated WIPP brines was established by 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 4-5.

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 $\text{M}\Omega\cdot\text{cm}$ water to prepare GWB brine and ERDA-6 brine.

Table 4-5. 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

Carbonate-free simulated WIPP brines

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 (CO₂). The removal of carbonate from the brines was a two-step process. The first step consisted of acidification of the brines to pC_{H+} ~ 3, which converted carbonate into carbonic acid, in equilibrium with small amount of bicarbonate, 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 less than 10 ppmO₂.

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 and only opened to take samples in the glovebox.

Hydrogen ion concentration and pC_{H+}

In our high ionic-strength brines (I>5 M), the measurement of the hydrogen ion concentration is problematic due to activity coefficient effects and high sodium content. This is circumvented, somewhat, by using a Gran titration approach as suggested by Rai [Rai 1995] leading to the following relationship:

$$pC_{H^+} = pH_{obs} + K \quad 4-1.a$$

where pC_{H+} is the negative logarithm of the hydrogen concentration in molarity (mol/L or M) units, pH_{obs} is the measured/ observed pH, and K is an experimentally determined constant. The values of K were linearly proportional to the solution ionic strength (Figure 4-1). The values of K for the two WIPP brines used in the present work were (1.23 ± 0.01) for GWB brine and (0.94 ± 0.02) for ERDA-6 respectively [Borkowski 2009]. The pH correction values (K) for diluted brines used in the different subtasks were determined by interpolation of the linear fitting curve on Figure 4-1 and are reported in Table 4-6.

The pH of the brine solutions was measured in the nitrogen glovebox with a sealed Orion-Ross combination glass electrode calibrated against NIST-certified pH buffers. Adjustments of pH to obtain the desired pC_{H+} were made with ACS certified hydrochloric acid and/or low carbonate sodium hydroxide (50 weight %) to minimize the re-introduction of carbonate (the uncertainty in the pH measurements was ± 0.1 pH unit). 50 mL-duplicates were prepared for each pC_{H+}-adjusted brine.

From this point, all brine solutions were kept in polypropylene bottles and tightly capped throughout the experiment except for sampling.

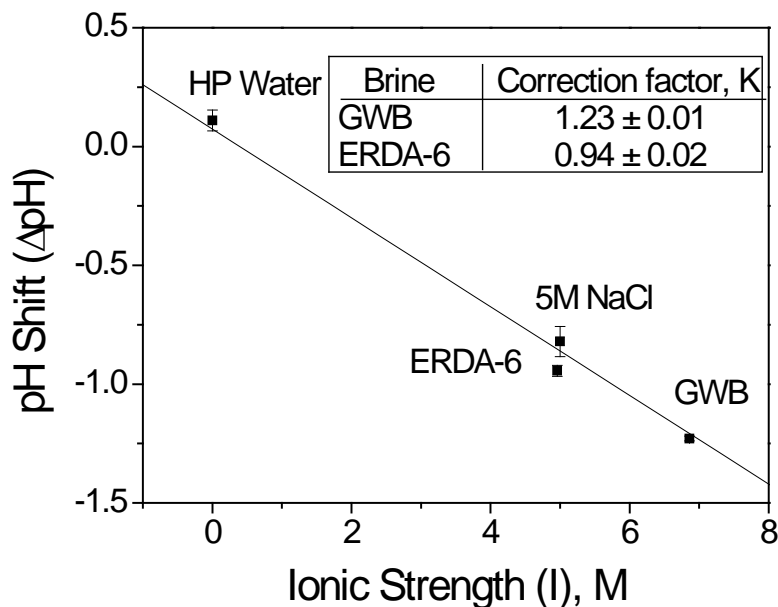


Figure 4-1: Correlation between the pH shift (ΔpH) and the ionic strength (I) of the two simulated WIPP brines, GWB and ERDA-6, 5 M NaCl brine and high purity (HP) water. The opposite value of ΔpH corresponds to the correction factor K . Based on this graph, the correction factors for WIPP brines, GWB and ERDA-6, are given in the table insert [Borkowski 2009].

Table 4-6. Correction factor K as a function of ionic strength I (M).

Ionic strength (I), M	GWB brine [M]
6.839	1.23
5	0.88
4.965	0.87
3.4	0.56
3	0.48
1	0.09
0.1	-0.08

Addition of carbonate (Subtask 3 only)

The addition of carbonate to the GWB or ERDA-6 brine in Subtask 3 was performed using a spike volume of a concentrated carbonate solution. This intermediate carbonate solution was prepared by dissolving a known amount of sodium carbonate (Na_2CO_3 - Fisher) in a determined volume of brine. An appropriate volume of the intermediate carbonate solution was then added to the GWB or ERDA-6 brine in Subtask 3 to achieve the desired carbonate concentration in solutions (see experimental matrix – Table 4-2). This way, the addition of carbonate in the Subtask 3 solutions was about 1% in volume, so dilution effects were negligible.

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, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 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.

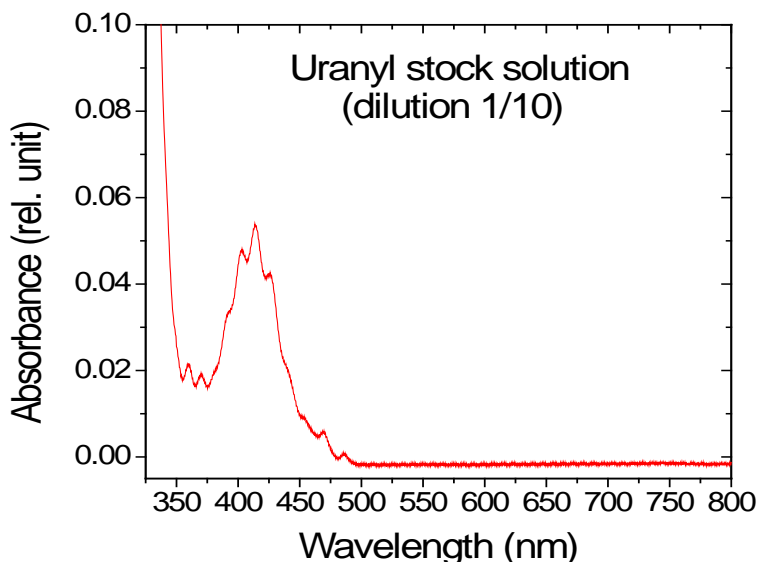


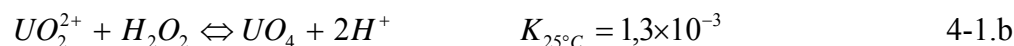
Figure 4-2: Absorption spectrum of the prepared uranyl stock solution diluted 1/10 (so $[U] = 15 \text{ mM}$). The absence of spectral features above 500 nm confirmed that there was no significant amount of U(IV) present.

Preparation of uranium (VI) solids (Subtask 8)

Four different uranium solid phases were used in the experiments conducted in Subtask 8 (see Section 4.1.4): uranium peroxide (UO_4), uranium trioxide (UO_3), uranium hydroxide ($UO_2(OH)_2$), and uranium precipitates obtained in brine from over-saturation in similar experimental conditions (same brine, about the same pH value, etc.). These solids represent a range of likely precipitates in an irradiated oxic to anoxic carbonate-free brine systems with U(VI). These different uranium (VI) solids were all generated in the ACRSP laboratory. Following is a description of their preparation.

- Uranium peroxide (UO_4)

Uranium peroxide was generated according to the following reaction [Brady 1948]:



According to Cahill's work, uranium peroxide readily precipitates when uranyl ion is in the presence of an excess of hydrogen peroxide at $pH < 5$ [Cahill 1990].

A known amount of our uranyl stock solution was then mixed with an excess of hydrogen peroxide (H_2O_2) 30% (ACS certified – Fisher). A bright yellow precipitate of uranium peroxide was readily generated. The precipitate was separated from the solution and recovered by centrifugation at room temperature.

- Uranium trioxide (UO_3)

It is well known that uranium peroxide loses an oxygen atom at 400°C [Katz 1986, p.267]. For our experiments, uranium peroxide was placed in an oven at 400°C for 5 hours. This led to a red coloration in the uranium solid that is characteristic of uranium trioxide.

- Uranium hydroxide ($\text{UO}_2(\text{OH})_2$)

Uranium hydroxide precipitate was generated by adding a known concentration of our uranyl stock solution into an excess of low carbonate-content sodium hydroxide (50 weight% - ACS certified) in a nitrogen controlled atmosphere. The precipitate was recovered by centrifugation and dried in the same nitrogen controlled atmosphere.

- Uranium precipitates

The uranium precipitates were generated at the same experimental conditions (same brine, about the same pH value, etc.) described in the Subtask 1 over-saturation experiments in carbonate-free brine.

U(VI) solubility experiments

For the over-saturation approach (Subtasks 1, 3, 4 and 5), the U(VI) solubility experiments were initiated by the addition of uranyl spiked brine into the corresponding pC_{H^+} -adjusted brine solutions, designated in the experimental matrices: Table 4-1 for Subtask 1, Table 4-2 for Subtask 3, and Table 4-3 for Subtask 4. For the under-saturation approach (Subtask 8), the U(VI) solubility experiments were initiated by the addition of a pre-determined amount of uranium solid phase into the corresponding pC_{H^+} -adjusted brine solutions, designated in the experimental matrix (Table 4-4).

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 ~10 nm pore size. The filtration step removed potential uranium colloids or particulates bigger than 10 nm from the sample aliquots.

Filtrates were analyzed for uranium content using an inductively coupled plasma mass spectrometer (ICP-MS) Elan model 6000 or Agilent 7500. 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 to $\sim 5 \times 10^{-10}$ M for our experiments.

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 addressed.

Effect of pC_{H^+} on brine stability

Both brines, GWB and ERDA-6, contain significant concentrations of magnesium and calcium cations. At $pC_{H^+} > 8.5$, these cations form insoluble hydroxide phases. The precipitation “cloud” point for each brine solution was established by titration with sodium hydroxide. Towards lower pH, acid was added to operationally establish the buffering-range of the brine (point where pH change is accelerated).

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 ~ 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).

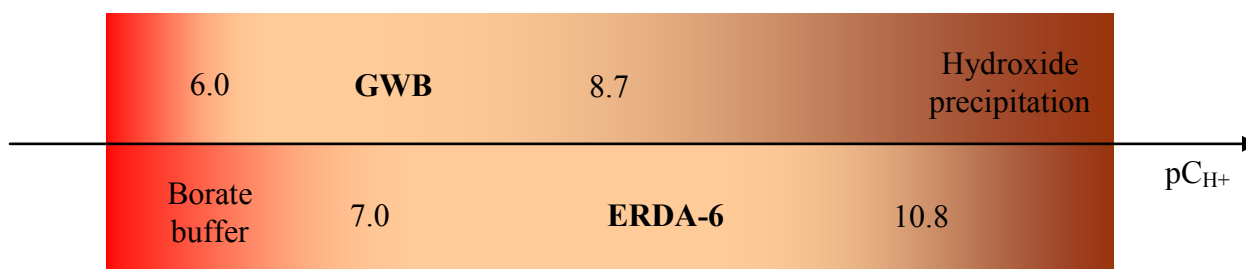


Figure 4-3: Chemical stability of GWB and ERDA-6 brines versus pC_{H^+} . The lower pC_{H^+} value is defined by the buffering capacity and range of borate in the brines. The higher pC_{H^+} value corresponds to the “cloud” point when precipitation occurs. The pC_{H^+} boundaries have an accuracy of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

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 our experimental matrix in carbonate-free brines (Table 4-1), the U(VI) solubility was investigated at pC_{H^+} values above the respective cloud points.

Constant pC_{H^+} values during the experiments performed in carbonate-free simulated brines (Subtask 1)

The stability of the pC_{H^+} values in carbonate-free simulated brines over time was investigated using some experiments of Subtask 1. Before the second uranium spike addition, the pC_{H^+} of all the experimental solutions of Subtask 1 was re-checked. After 214 days, no significant pC_{H^+} drift (defined as < 0.3 pH units) from its initial value were observed. These pC_{H^+} values were again checked after 369 days. 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 since 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. This was only true for the carbonate-free simulated WIPP brines ERDA-6 and GWB. In the presence of carbonate, the pC_{H^+} values tend to drift. In diluted brines and/or in simplified brine (e.g. NaCl), the lower ionic strength and/or the lack of buffer capacity from other brine components make the pC_{H^+} unstable over time. It was necessary to adjust the pH during the experiment when carbonate was present.

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 10nm by chemical affinity or adsorption and then lower the concentrations measured. This potential effect was evaluated using some experiments in Subtask 1 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 in Subtask 1. For each brine case, two time profiles are represented. In the first profile, the sampled aliquots were filtered through a 30 kDa 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 30 kDa filter membrane used in the experiments did not show any significant ($>10\%$) retention of uranium during the filtration of the aliquots.

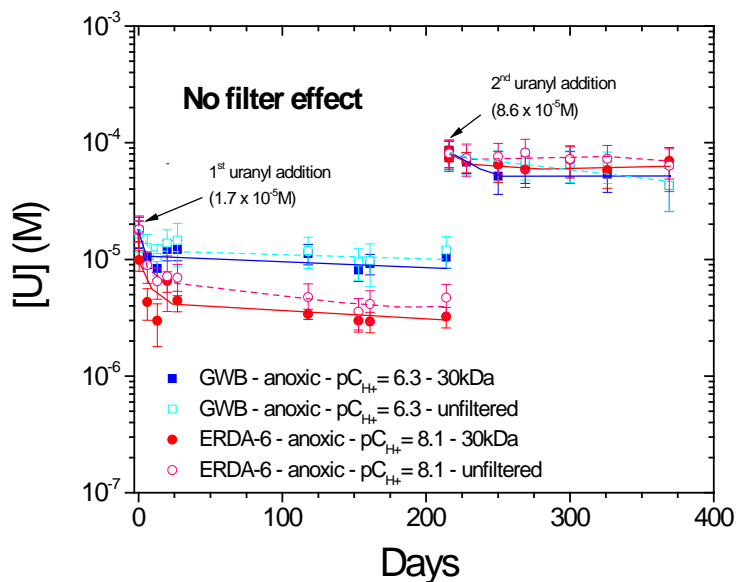


Figure 4-4: Time profiles of uranium concentration in GWB brine at $pC_{H^+} = 6.3$ (square scatter) and in ERDA-6 brine at $pC_{H^+} = 8.1$ (circle scatter) in the nitrogen controlled atmosphere and up to 369 days of Subtask 1 experiments. For each brine case, the sampled aliquots were filtered through a 30 kDa 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 30 kDa 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 or Agilent 7500). 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 ($18 \text{ M}\Omega \cdot \text{cm}$) were used to dilute the brine samples to $\sim 0.5\%$ 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 to Table 4-4).

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 are summarized and discussed in this section.

The experimental data are given in Sections 4.3.1 to 4.3.4. In Section 4.3.1, we report the data from the experiments on U(VI) solubility in carbonate-free brines using the over-saturation (Subtask 1). These data were already presented and discussed in the LCO-ACP-10 report entitled: Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations [Lucchini 2010a]. The results on the investigation of the effect of

carbonate on U(VI) solubility are presented in Section 4.3.2 (Subtask 3). Data on the U(VI) solubility in diluted brines (Subtask 4) are reported in Sections 4.3.3. The results obtained in the under-saturation experiments (Subtask 8) are given in Section 4.3.4.

The experimental data are then discussed in Sections 4.4 to 4.8.

4.3.1 Subtask 1: U(VI) solubility under anoxic conditions in carbonate-free brine

The results of our U(VI) solubility in carbonate-free brines study using the over-saturation approach for our Subtask 1 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 sections 4.3.1.1 and 4.3.1.2. These data correspond to the 19 samplings performed in each brine and pC_{H^+} investigated in a nitrogen controlled atmosphere over 705 days.

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 in section 4.4, in the light of the data obtained in the experiments using the under-saturation approach (Subtask 8).

4.3.1.1 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 and four different pC_{H^+} values in carbonate-free GWB brine placed in nitrogen controlled atmosphere throughout the 705 days of experiments.

The initial uranyl concentration was $(1.7 \pm 0.3) \times 10^{-5}$ M. The data in Figure 4-5 show that steady state uranium concentrations were rapidly achieved (less than 20 days) in GWB brine. 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). This second uranium addition that took place after 216 days of experiment was $(8.6 \pm 1.7) \times 10^{-5}$ M, which was about 5 times the initial uranium spike. At $pC_{H^+} = 6.3$, 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. For 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.

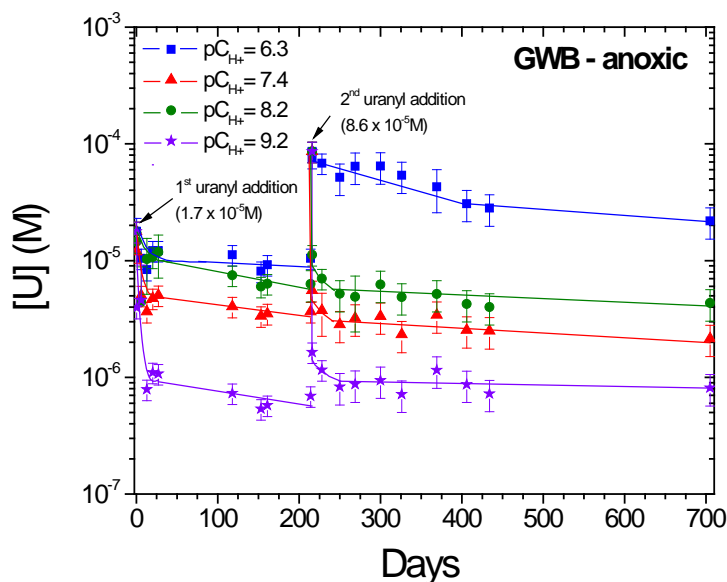


Figure 4-5: Uranium concentration in carbonate-free GWB brine in a nitrogen controlled atmosphere as a function of time. Time profiles correspond to $pC_{H^+} = 6.3, 7.4, 8.2$ and 9.2 from top to bottom of the legend. These data correspond to 19 samplings performed over 705 days.

The steady-state uranium concentration in solution depended on pC_{H^+} , as expected. The concentration of uranium increased 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 in Figure 4-5, because the semi-logarithm scale, but it is not in actuality significant.

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. Characterization of the solids is ongoing. 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).

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

The uranium concentration data measured as a function of time and five different pC_{H^+} values in carbonate-free ERDA-6 brine placed in a nitrogen controlled atmosphere throughout the 705 days of experiments are shown on Figure 4-6.

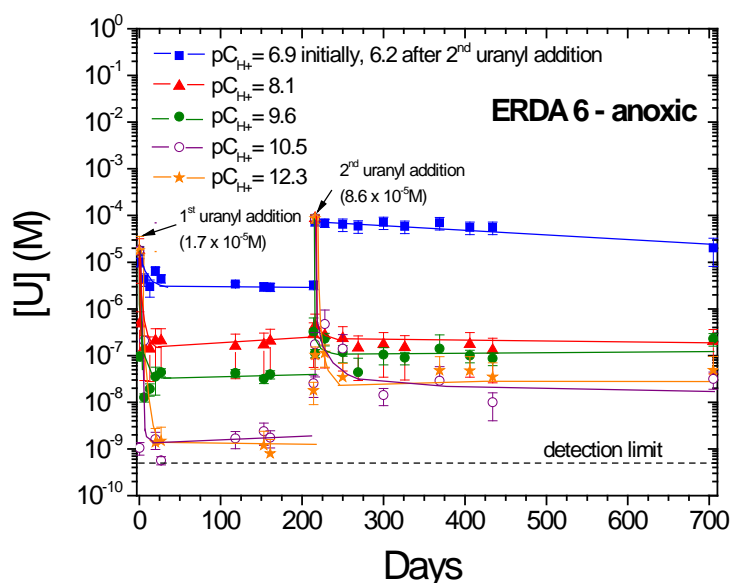


Figure 4-6: Uranium concentration in carbonate-free ERDA-6 brine in a nitrogen controlled atmosphere as a function of time. Data shown are for $pC_{H^+} = 6.2$ (initially 6.9), 8.1, 9.6, 10.5 and 12.3 from top to bottom of the legend. These data correspond to 19 samplings performed over 705 days.

The initial uranyl concentration in the ERDA-6 brine experiments was $(1.7 \pm 0.3) \times 10^{-5}$ M. This was approximately the expected solubility of uranium in ERDA-6 brine as established in our developmental experiments. Similar to the experiments in GWB, a second uranyl spike was added to every solution at day 216 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. 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 were similar to the rates obtained in GWB.

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 about 2×10^{-7} M, regardless of the uranium addition. At $pC_{H^+} = 9.6$, the steady state uranium concentration was about 1×10^{-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 for the lowest pC_{H^+} values and the two highest pC_{H^+} values investigated. At the lowest pC_{H^+} value, the addition of uranium stock led to a decrease in pC_{H^+} from 6.9 to 6.2 leading to an order of magnitude increase in the measured steady-state uranium concentration (2×10^{-6} M to 2×10^{-5} M).

The two highest pC_{H^+} brines investigated (10.5 and 12.3) showed an order of magnitude increase between the steady state uranium concentrations obtained before and after the second uranyl addition ($\sim 10^{-9}$ M to $\sim 2 \times 10^{-8}$ M). There was no change in the pC_{H^+} measured after the second uranyl addition so the cause of this change in steady-state concentration is not clear yet. 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 may have gone through 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 [Lucchini 2010b].

An attempt to characterize the solids formed in these Subtask 1 uranium (VI) solubility experiments was made. X-ray Absorption Near Edge Spectroscopy (XANES) analysis was performed at the Argonne Advanced Photon Source on the precipitates from the following three samples: ERDA-6 at $pC_{H^+} = 12.3$, ERDA-6 at $pC_{H^+} = 10.5$, and GWB at $pC_{H^+} = 9.3$. Three uranium (VI) solids prepared in our laboratory (see section 4.2.1) were also analyzed as references. The XANES spectra of these five solid samples taken at the uranium L_3 thresholds are shown in Figure 4-7 [Lucchini 2011]. These results confirm the uranium oxidation state to be primarily U(VI) but did not permit EXAFS due to the high disorder in the samples – presumably due to the amorphous nature and the likely presence of several phases in the precipitates.

Some solid characterization was also carried out by Scanning Electron Microscopy (SEM) using a Hitachi model S-3400N Type II scanning electron microscope equipped with an Energy-Dispersive x-ray Spectrometer (EDS - Thermo Electron NORAN System Six 300). Figure 4-8 shows a SEM images of the precipitate obtained in ERDA-6 solution at $pC_{H^+} = 10.5$. The presence of uranium in the bright “white” aggregates on the SEM image could be detected by EDS but we could not identify the phase present. These uranium aggregates were found among other solid phases containing mostly sodium, magnesium, oxygen and chloride (brine-related phases) although the samples were washed [Lucchini 2011].

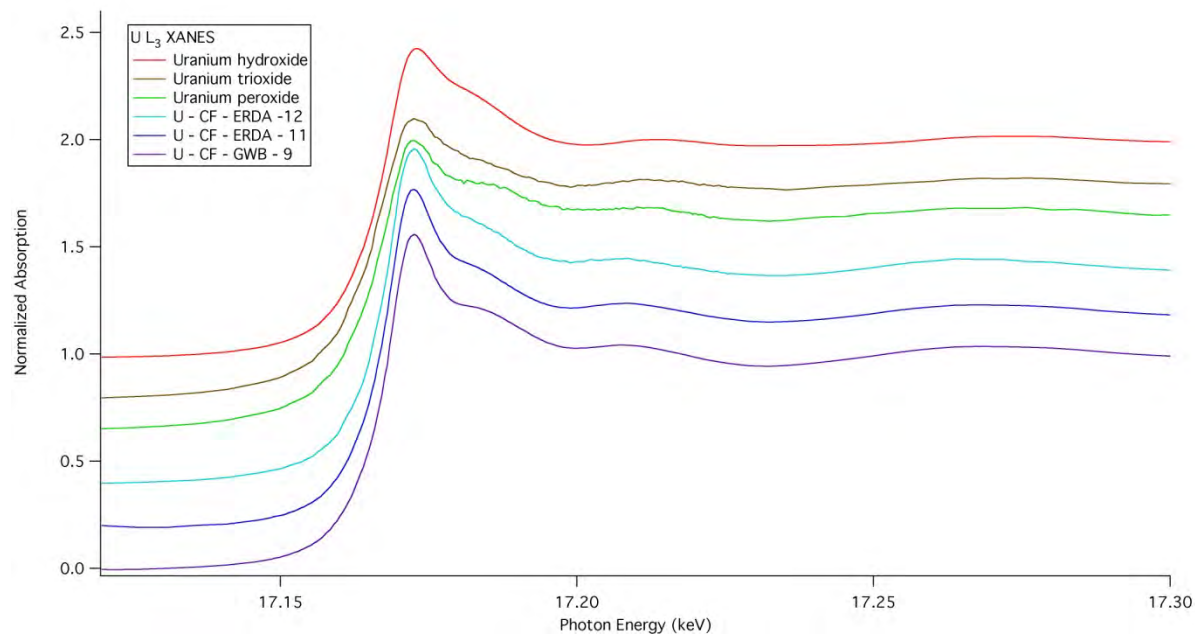


Figure 4-7: XANES spectra of five uranium solid samples taken at the uranium L_3 thresholds. From the top to the bottom, the spectra are from the following solid samples: uranium hydroxide, uranium trioxide, uranium peroxide, ERDA-6 at $pC_{H^+} = 12.3$, ERDA-6 at $pC_{H^+} = 10.5$ and GWB at $pC_{H^+} = 9.3$ [Lucchini 2011].

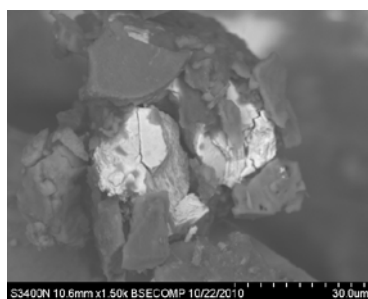


Figure 4-8: Scanning Electron Microscopy image of the precipitates obtained in ERDA-6 solution at $pC_{H^+}=10.5$ (magnification: 1500 \times). The bright white solids were the uranium phases. The surrounding solids were composed of sodium, magnesium, oxygen and chloride [Lucchini 2011].

4.3.2 Subtask 3: Carbonate effects study on U(VI) solubility

The effect of carbonate on the solubility of uranium (VI) was investigated in Subtask 3. Experiments were performed in simulated WIPP brines, GWB and ERDA-6, and involved three different initial concentrations of carbonate in the solutions (no carbonate, 2×10^{-3} M and 2×10^{-4} M) at two different pC_{H^+} values for both simulated WIPP brines. They were initiated when uranyl ion, at a concentration of 1.48×10^{-5} M, was added to all the solutions. A second uranyl-spike addition (1.0×10^{-4} M) was performed at day 231, and a third uranyl-spike addition (1.2×10^{-3} M) was done at day 675. The solutions were kept in a nitrogen controlled atmosphere throughout the experiment. Eighteen samples were taken to analyze the uranium concentration over a 1073 day period.

Experimental data obtained in GWB and ERDA-6 brines are presented herein, respectively in sections 4.3.2.1 and 4.3.2.2. The uranium concentration over time for the experiments in a nitrogen controlled atmosphere, in the absence or presence of two different initial concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) are given for the following specific conditions: in GWB at $pC_{H^+} \sim 7.5$ (Figure 4-9) and at $pC_{H^+} = 9$ (Figure 4-10) in section 4.3.2.1, and in ERDA-6 at $pC_{H^+} \sim 8.7$ (Figure 4-11) and at $pC_{H^+} \sim 12$ (Figure 4-12) in section 4.3.2.2.

4.3.2.1 Evolution of U(VI) concentration with time in GWB brine in the presence of carbonate

The uranium concentration data measured as a function of time in GWB at $pC_{H^+} \sim 7.5$ and $pC_{H^+} = 9$ in the absence or presence of two different initial concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) over the 994 days of experiments are shown in Figure 4-9 and Figure 4-10 respectively.

In GWB at $pC_{H^+} \sim 7.5$ (Figure 4-9), steady-state uranium concentrations were rapidly achieved (less than 20 days) at the start of the experiments. However, after the second addition of uranyl in the experimental solutions, the equilibration time was much longer (about 120 days), especially for the solutions with high carbonate content. After the third and last addition of uranyl, steady state uranium concentrations were re-established very quickly, in a few days.

The difference in time for steady state uranium concentrations to be achieved after uranyl additions is probably due to the precipitation of solids in the GWB solutions at $pC_{H^+} \sim 7.5$. Solid precipitation occurred in all the GWB solutions after the second uranyl-spike addition. Both the slow decrease of uranium in solutions and the formation of yellow precipitates indicated that uranium precipitates were generated over time. We noticed that the precipitates got thicker after the third uranyl-spike addition, but the time to get steady state concentration of uranium in the solutions was much shorter. Ultimately, we observed that the steady-state uranium concentrations ($\sim 2 \times 10^{-6}$ M) approached those obtained in the analogous carbonate-free GWB brine systems investigated (see Section 4.3.1.1).

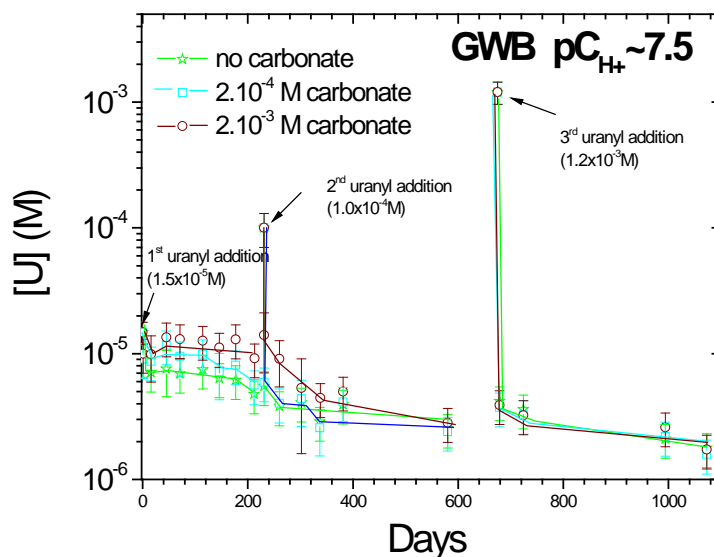


Figure 4-9: Uranium concentration in GWB as a function of time, at $pC_{H^+} \sim 7.5$, in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments. These data correspond to 18 samplings performed over 1073 days.

At $pC_{H^+} = 9$ in GWB solutions however (Figure 4-10), steady-state concentrations of uranium were systematically and rapidly achieved after each addition of uranyl-spike solution. In all solutions, we observed a bright yellow precipitate after the second uranyl-spike addition. The precipitates were thicker after the third uranyl-spike addition. Moreover, the concentrations of uranium measured in the solutions were reproducible. This indicated that steady state concentrations of uranium were achieved in all the solutions in these experiments at $pC_{H^+} = 9$ using the over-saturation approach.

A significant impact of carbonate on uranium solubility was observed at the highest initial concentration of carbonate (2×10^{-3} M) investigated. The uranium solubility was then about 10^{-4} M, which was two orders of magnitude higher than the uranium solubility values at no or low carbonate.

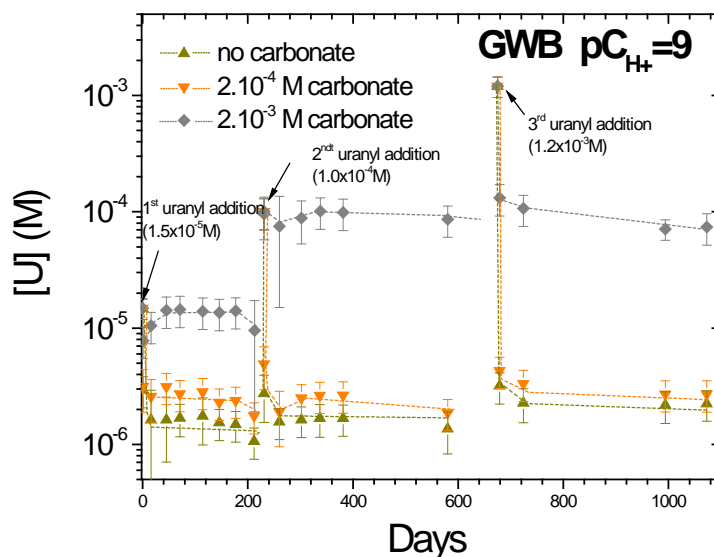


Figure 4-10: Uranium concentration in GWB as a function of time, at $pC_{H^+} = 9$, in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments. These data correspond to 18 samplings performed over 1073 days.

Similar to the $pC_{H^+} \sim 7.5$ case, we got excellent agreement between the data obtained here (Subtask 3) in carbonate-free GWB at $pC_{H^+} = 9$ and the data obtained in similar conditions in Subtask 1 (see section 4.3.1.1): a concentration of about 2×10^{-6} M was found in the two experiments.

4.3.2.2 Evolution of U(VI) concentration with time in ERDA-6 brine in the presence of carbonate

In Figure 4-11 and Figure 4-12, we show the uranium concentration data measured as a function of time in ERDA-6 respectively at $pC_{H^+} \sim 8.7$ and $pC_{H^+} \sim 12$ in the absence or presence of two different initial concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) throughout the 994 days of experiments.

In ERDA-6 at $pC_{H^+} \sim 8.7$ (Figure 4-11), steady state uranium concentrations were not achieved in all cases. In carbonate-free brine, the same concentration of uranium was measured after each uranyl-spike addition. In addition, a yellow precipitate was formed after the second uranyl-spike addition, and got thicker after the third uranyl-spike addition. Consequently, we concluded that a steady-state uranium concentration of about 2×10^{-7} M was obtained at $pC_{H^+} \sim 8.7$ in carbonate-free ERDA-6 brine. This is in agreement with the experimental value obtained in Subtask 1 for the same system.

When carbonate was initially present in ERDA-6 at $pC_{H^+} \sim 8.7$, the concentration of uranium in solution was still changing with time, even though the pC_{H^+} values remained about the same. Despite the formation of a yellow precipitate in solution after the second uranyl-spike addition, it appeared that uranium steady-state concentrations were not yet achieved even after 1073 days of experiments. There is, however, a significant effect of carbonate on the concentration of uranium (Figure 4-11). Observed uranium concentrations for an initial concentration of 2×10^{-3} M carbonate, were approximately 2×10^{-5} M at day 1073. Only shortly after the third uranyl-spike addition (1.2×10^{-3} M at day 675), the uranium concentration measured in solution became saturated leading to precipitation. At that time, the maximum concentration of uranium measured in solution was about 2×10^{-4} M at days 679 and 724. The uranium concentrations showed a slow, but steady decrease with time after the third spike addition.

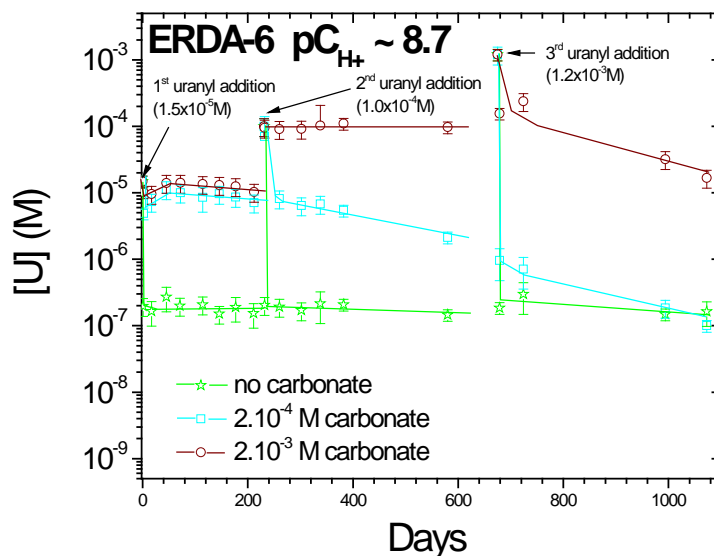


Figure 4-11: Uranium concentration in ERDA-6 as a function of time, at $pC_{H^+} \sim 8.7$, in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments. These data correspond to 18 samplings performed over 1073 days.

The data presented for ERDA-6 at $pC_{H^+} \sim 12$ (Figure 4-12) were obtained in a chemically heterogeneous system, since ERDA-6 brine exhibits precipitation beyond $pC_{H^+} \sim 10.5$ (see section 4.2.2). A white precipitate was observed in all the solutions a few days after the beginning of the experiments. The formation of a yellow precipitate at the bottom of the bottle was noticed after the second uranyl-spike addition in the carbonate-free and low

carbonate content solutions. This precipitate was only visible in the high carbonate content experiments after the third uranyl-spike addition.

Steady-state concentrations of uranium in the ERDA-6 solutions at $pC_{H^+} \sim 12$ were still not achieved by the last day of sampling (day 1073), despite the presence of a yellow precipitate (characteristic of a uranyl precipitate) in all the solutions. At that time (day 1073), the uranium concentrations measured in solutions, in the presence or the absence of carbonate, were between 10^{-8} M and 10^{-7} M. They were in this range of values prior the third uranyl-spike addition, and after a two-unit pH adjustment was performed at days 382 and 580 of the experiments. Prior pH adjustment, the uranium concentrations measured in the solutions containing initially carbonate were consistently about 10^{-7} M, even after the second uranyl-spike addition. This level of concentration was reached in less than 20 days in the low carbonate content solution, but it took more than 120 days in the high carbonate content solution for uranium concentration to stabilize at this level.

Concerning the carbonate-free system, the results obtained in this Subtask is in good agreement with the results obtained in Subtask 1 (see section 4.3.1.2): a uranium concentration of about 10^{-7} M was measured in carbonate-free ERDA-6 at $pC_{H^+} \sim 12$ in both experiments.

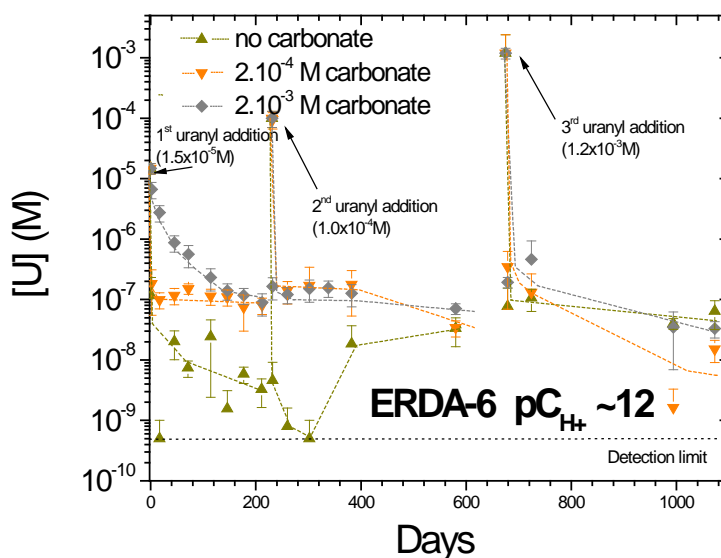


Figure 4-12: Uranium concentration in ERDA-6 as a function of time, at $pC_{H^+} \sim 12$, in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments. These data correspond to 18 samplings performed over 1073 days.

4.3.3 Subtask 4: U(VI) solubility in diluted WIPP brine

To support the interpretation of the higher ionic-strength brine experiments, some lower ionic strength experiments were performed in diluted GWB and ERDA-6 brines to establish the effect of ionic strength on the solubility of uranium (VI).

In Subtask 4, we investigated the uranium (VI) solubility in three diluted GWB brine (section 4.3.3.1): 50% GWB with ionic strengths of 3.4M, 15% GWB with ionic strengths of 1M and 1.5% GWB with ionic strengths of 0.1M at $pC_{H^+} \sim 7.3$ (Figure 4-13) and at $pC_{H^+} \sim 8.3$ (Figure 4-14). The uranium (VI) solubility was also studied in three diluted ERDA-6 brines (section 4.3.3.2): 50% ERDA-6 with ionic strengths of 3M, 17% ERDA-6 with ionic strengths of 1M and 1.7% ERDA-6 with ionic strengths of 0.1M at $pC_{H^+} \sim 8$ (Figure 4-15) and at $pC_{H^+} \sim 11$ (Figure 4-16).

The experiments were initiated when uranyl ion, at a concentration of 1.48×10^{-5} M, was added to all the solutions. A second uranyl-spike addition (9.9×10^{-5} M) was performed at day 251. The solutions were kept in a nitrogen controlled atmosphere since the beginning of the experiment. Fifteen samples were taken to analyze the uranium concentration over a 874 day period.

Some brine solutions, especially the most diluted of them, needed a pH re-adjustment over time. Because of the low ionic strength of some solutions, it was extremely difficult, and in some cases, impossible, to adjust the pH to the initial values. This explains the small differences in the pC_{H^+} values between the experimental matrix (Table 4-3) and what could be achieved in the experiments. It is important to mention that the pC_{H^+} values in diluted brine systems were determined using the correction factors obtained from the interpolation of the linear fitting curve between the pH shift and the ionic strength (Figure 4-1).

4.3.3.1 Evolution of U(VI) concentration with time in diluted GWB brine

Uranium (VI) solubility was investigated in three diluted carbonate-free GWB solutions: 50% GWB with ionic strengths of 3.4M, 15% GWB with ionic strengths of 1M and 1.5% GWB with ionic strengths of 0.1M, and at two difference pC_{H^+} values: ~ 7.3 (Figure 4-13) and ~ 8.3 (Figure 4-14). All the data presented in these two figures correspond to 15 samplings performed throughout 874 days of experiments. Attempts to adjust pH to a value as close as possible to the initial value were made after the second addition of uranyl, and a period of more than 400 days was given for those solutions to equilibrate.

At $pC_{H^+} \sim 7.3$ (Figure 4-13), steady state concentration of uranium were certainly achieved in the 15% GWB and 1.5% GWB solutions. Not only a yellow precipitate was generated in those solutions after the second uranyl-spike addition, but the uranium concentrations measured in solutions, at least from the last two samplings (days 683 and 874), were somewhat reproducible at about 10^{-7} M. Between day 361 and day 683 of the

experiments, the pH of the 15% GWB and 1.5% GWB solutions was adjusted from 4-5 to 7.4 and 8.2 respectively.

In the 50% GWB solution, no precipitate was observed in solution at $pC_{H^+} \sim 7.3$. Therefore, steady state concentration of uranium was not reached in this case. The uranium concentration measured in that solution was higher (4×10^{-6} M) than in the more diluted GWB solutions, but the pC_{H^+} value of the 50% GWB solution was smaller (6.6) than for the 15% GWB and 1.5% GWB solutions.

At $pC_{H^+} \sim 8.3$ (Figure 4-14), the pC_{H^+} values for the 50% GWB and 15% GWB solutions were relatively stable between the first and second addition of uranyl. Consequently, the uranium concentrations measured in each solution were reproducible. In addition to this, a yellow precipitate was generated in these solutions after the second uranyl-spike addition. We can then state that steady-state concentrations of uranium were achieved in these two solutions. The uranium solubility measured in carbonate-free GWB was 2×10^{-7} M in the 50% GWB solution ($pC_{H^+} = 8.5$) and about 4×10^{-8} M in the 15% GWB solution ($pC_{H^+} \sim 7.8$).

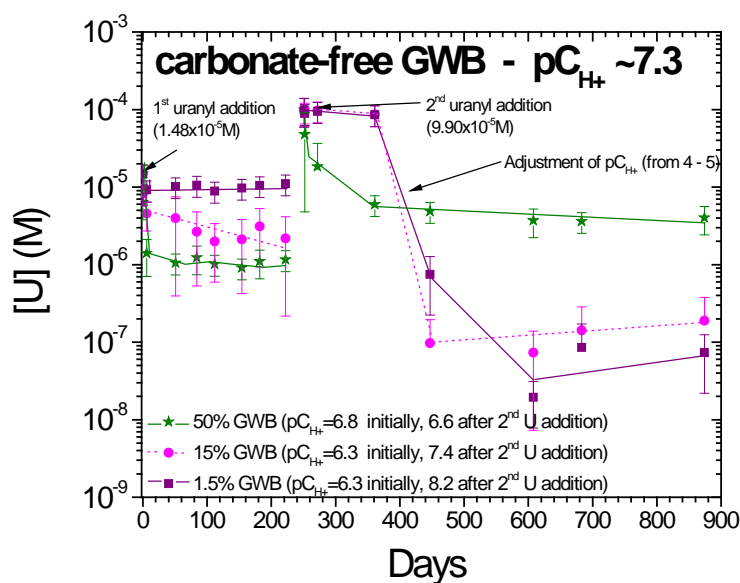


Figure 4-13. Uranium concentration in three diluted GWB solutions (50% GWB, 15% GWB and 1.5% GWB) as a function of time, at $pC_{H^+} \sim 7.3$, in a nitrogen controlled atmosphere, and in the absence of carbonate. Note that the abrupt slope on the curve for the 15% GWB and 1.5% GWB solutions is the consequence of the pH adjustment from $pC_{H^+} \sim 4-5$ to $\sim 7-8$. All these data correspond to 15 samplings performed over 874 days.

At the lowest ionic strength investigated (0.1M – i.e. 1.5% GWB), at $pC_{H^+} \sim 9.1$ (Figure 4-14), the uranium concentration obtained in GWB solution dropped to about 10^{-8} M,

after the second uranyl-spike addition, when the pH of the solution was adjusted (day 361 of the experiment). At the same time, a yellow precipitate started to form. Since that moment (day 361), the uranium concentrations measured in solution were not constant, so steady state was not reached yet. The last data point recorded at day 874 gave a value of 4×10^{-7} M, about three times smaller than the value of 1.2×10^{-6} M measured at day 361 when the precipitate started to form. Considering these results, the uranium solubility in carbonate-free diluted GWB (0.1M ionic strength – i.e. 1.5% GWB) at $pC_{H^+} \sim 9.1$ could be in the range 10^{-7} - 10^{-6} M.

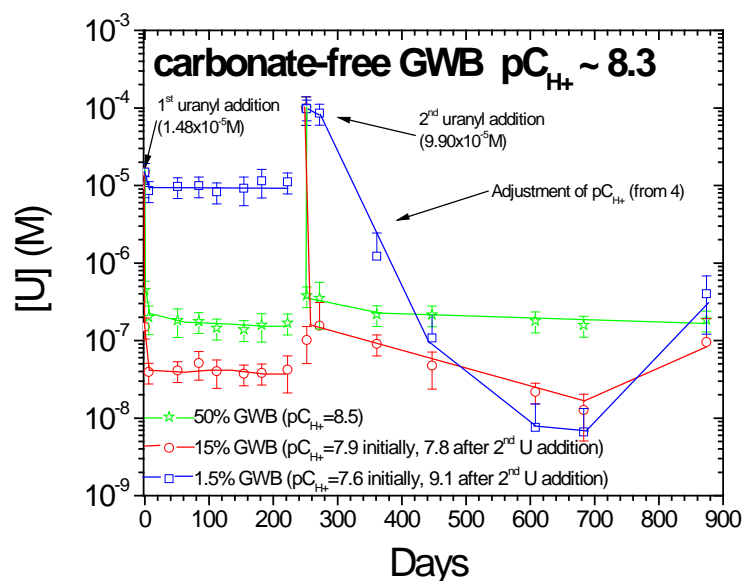


Figure 4-14. Uranium concentration in three diluted GWB solutions (50% GWB, 15% GWB and 1.5% GWB) as a function of time, at $pC_{H^+} \sim 8.3$, in a nitrogen controlled atmosphere, and in the absence of carbonate. Note that the abrupt slope on the curve for the 1.5% GWB solution is the consequence of the pH adjustment from $pC_{H^+} \sim 4$. All these data correspond to 15 samplings performed over 874 days.

4.3.3.2 Evolution of U(VI) concentration with time in diluted ERDA-6 brine

Uranium (VI) solubility was investigated in three diluted carbonate-free ERDA-6 solutions: 50% ERDA-6 with ionic strengths of 3M, 17% ERDA-6 with ionic strengths of 1M and 1.7% ERDA-6 with ionic strengths of 0.1M, and at two different pC_{H^+} values: ~ 8 (Figure 4-15) and ~ 11 (Figure 4-16).

At $pC_{H^+} \sim 8$ (Figure 4-15), the uranium concentration reached a steady state for the two highest ionic strength solutions investigated (3M and 1M, i.e. 50% ERDA-6 and 17% ERDA-6). In these solutions, a yellow precipitate was generated after the second uranyl-spike addition, and the concentrations of uranium measured in solution were relatively constant. In consequence, the uranium solubility in carbonate-free 50% ERDA-6 and 17% ERDA-6 solutions at $pC_{H^+} \sim 8$ was determined to be about 5×10^{-8} M.

Concerning the 1.7% ERDA-6 at $pC_{H^+} \sim 8$, the abrupt slope on the curve (Figure 4-15) was caused by the pH adjustment from $pC_{H^+} \sim 4$ to ~ 8 at day 361 of the experiment. The pH of this low ionic strength brine dropped because of the second uranyl addition. After 874 day of experiment, the uranium concentration didn't achieve a steady-state yet, even though the generation of a yellow precipitate was already ongoing since the second uranyl-spike addition. The last uranium concentration measured in solution was 1.1×10^{-8} M. Considering the shape of the curve in Figure 4-15 for this solution, it is expected that uranium concentration would reach a steady-state at about 10^{-8} M.

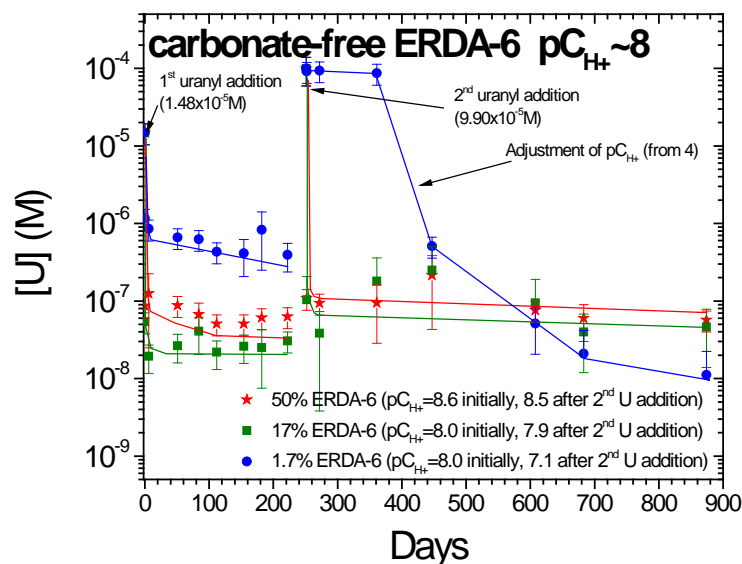


Figure 4-15. Uranium concentration in three diluted ERDA-6 solutions (50% ERDA-6, 17% ERDA-6 and 1.7% ERDA-6) as a function of time, at $pC_{H^+} \sim 8$, in a nitrogen controlled atmosphere, and in the absence of carbonate. Note that the abrupt slope on the curve for the 1.7% ERDA-6 solution is the consequence of the pH adjustment from $pC_{H^+} \sim 4$ to ~ 7 . All these data correspond to 15 samplings performed over 874 days.

At $pC_{H^+} \sim 11$ (Figure 4-16) in carbonate-free ERDA-6, the uranium concentrations were not constant over time for any of the three investigated ionic strengths. Because that pC_{H^+} value corresponded to the extreme end of the chemical stability domain of the brine

(see section 4.2.2, Figure 4-3), a white precipitate was present in the 50% ERDA-6 and 17% ERDA-6 solutions after 10 days of the experiments. It took more than 150 days for a white precipitate to form in the 1.7% ERDA-6 solution. A yellow precipitate was observed after the second uranyl-spike addition in all the three solutions investigated, and the uranium concentrations measured in these solutions didn't equilibrate over a 623-day period. At the last sampling (day 874), the uranium concentrations measured in the carbonate-free ERDA-6 solutions at the three ionic strengths investigated (50% ERDA-6, 17% ERDA-6 and 1.7% ERDA-6) and at $pC_{H^+} \sim 11$ were around 10^{-8} M.

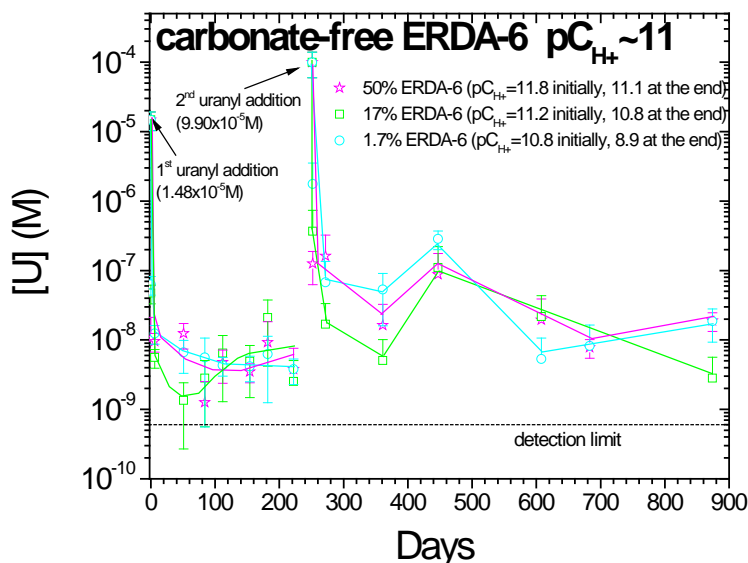


Figure 4-16. Uranium concentration in three diluted ERDA-6 solutions (50% ERDA-6, 17% ERDA-6 and 1.7% ERDA-6) as a function of time, at $pC_{H^+} \sim 11$, in nitrogen controlled atmosphere, and in the absence of carbonate. All these data correspond to 15 samplings performed over 874 days.

4.3.4 Subtask 8: U(VI) solubility in brine from under saturation

In Subtask 8, uranium (VI) solubility experiments were conducted in carbonate-free ERDA-6 and GWB brines using the under-saturation approach. The experimental matrix is given in Table 4-4. Four different uranium solid phases were used: uranium peroxide (UO_4), uranium trioxide (UO_3), uranium hydroxide ($UO_2(OH)_2$), and uranium precipitates obtained in ERDA-6 brine using the over-saturation approach and in similar experimental conditions (same brine, about the same pH value, etc.). The preparation of these uranium solids is described in section 4.2.1.

The experimental data obtained in this Subtask 8 are presented herein. The evolution of uranium concentration with time in GWB brine and ERDA-6 brine is shown in section 4.3.4.1 and 4.3.4.2 respectively.

4.3.4.1 Evolution of U(VI) concentration with time in carbonate-free GWB brine in the under-saturation experiments

A pre-determined amount of each of these four different uranium solid phases was added to carbonate-free GWB solutions, at four different pC_{H^+} values: 6.3, 7.4, 8.2 and 9.3. The amount of uranium released into solution was monitored over time, using ICP-MS. For the four different kinds of the uranium solid phases investigated, the time profile of the uranium concentration measured in solutions was plotted as a function of the four different pC_{H^+} values investigated.

Figure 4-17, Figure 4-18, Figure 4-19 and Figure 4-20 show uranium concentration data obtained at the four different pC_{H^+} values investigated, from the experiments with respectively uranium peroxide (Figure 4-17), uranium trioxide (Figure 4-18), uranium hydroxide (Figure 4-19), and uranium precipitates obtained in over-saturation experiments (Figure 4-20). All these data correspond to 9 samplings performed throughout 1037 days (almost three years) of experiments.

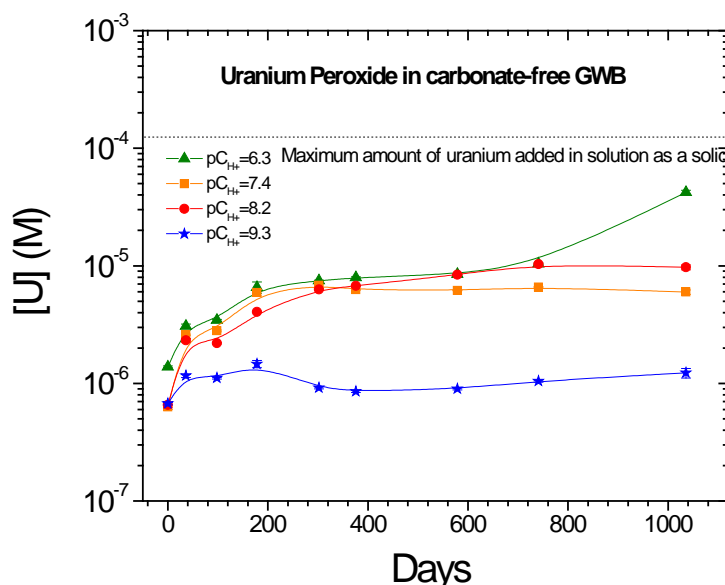


Figure 4-17: Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium peroxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (...) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

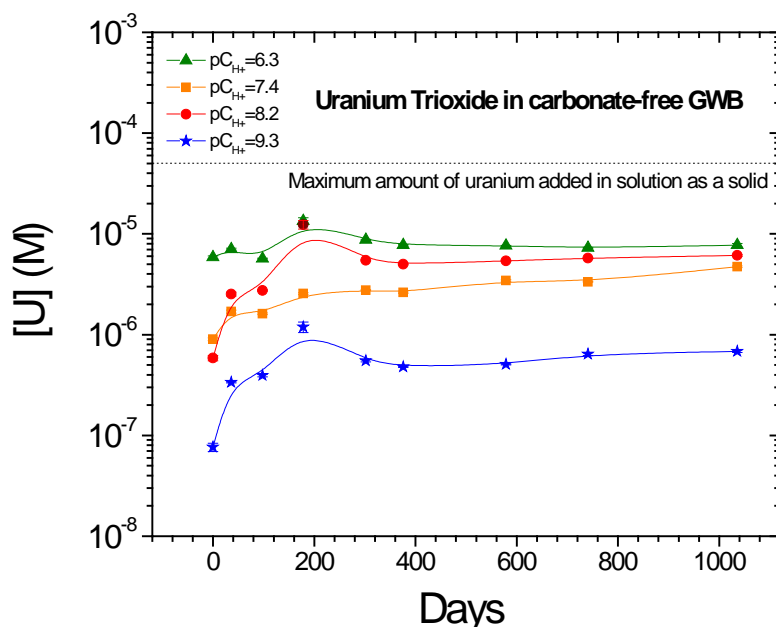


Figure 4-18: Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium trioxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (...) represents the maximum uranium concentration if the entire solid added goes into solution. These data correspond to 9 samplings performed over 1037 days.

A few observations could be made from these data:

- a) Steady-state conditions were reached in most of the experiments.

Steady-state uranium concentrations were achieved after ~ 400 days of the experiments in all solutions except one. The uranium concentrations measured after that time were almost unchanged for each case scenario of pC_{H^+} value and uranium phase investigated, except one. The only exception would be for the data related to the uranium peroxide experiment at $pC_{H^+} = 6.3$ (Figure 4-17): the last data point at day 1037 is higher than the previous data points and a steady increase in concentration was noted.

In addition to the stable concentrations of uranium measured in solutions after ~ 400 days of the experiments, all the uranium solids initially placed in solutions were still visible throughout the 1037 days of experiments. On each graph, a horizontal line shows the maximum amount of uranium (converted to mole/L unit) that was initially placed into solution as a solid phase. In all experimental conditions, this line was not approached by any uranium concentration data measured in solutions. The uranium concentrations measured in solutions were well below the maximum concentration of uranium to be possibly released in solutions (i.e. if the entire solid would be dissolved) after 1037 days of the experiments.

b) Concentrations of uranium released in solution were lower at $pC_{H^+} = 9.3$.

The uranium concentrations measured in solutions were consistently higher at $pC_{H^+} < 9.3$, whatever uranium solid was used. In these conditions of pC_{H^+} , they were in the range $5 \times 10^{-6} - 10^{-5}$ M in the experiments with the synthetic uranium solid phases (peroxide, trioxide, hydroxide), and in the range $10^{-6} - 7 \times 10^{-5}$ M in the experiments performed with the uranium precipitates. At $pC_{H^+} = 9.3$, the uranium concentrations measured in solutions were about or below 10^{-6} M. These lower uranium concentrations were accompanied by a white precipitate which occurred very early in the experiments (after 30 days). As a reminder, at $pC_{H^+} = 9.3$, GWB brine is chemically unstable, and a white precipitate (more likely magnesium hydroxide) is present in solution (see Table 4-3).

c) Data in these under-saturation experiments were in good agreement with the data obtained in the over-saturation experiments.

The data obtained with uranium precipitates (see Figure 4-20) in these under-saturation experiments were about 10^{-6} M at $6.3 \leq pC_{H^+} \leq 9.3$. Similar conclusion was drawn in the over-saturation experiments in carbonate-free GWB (see section 4.3.1.1).

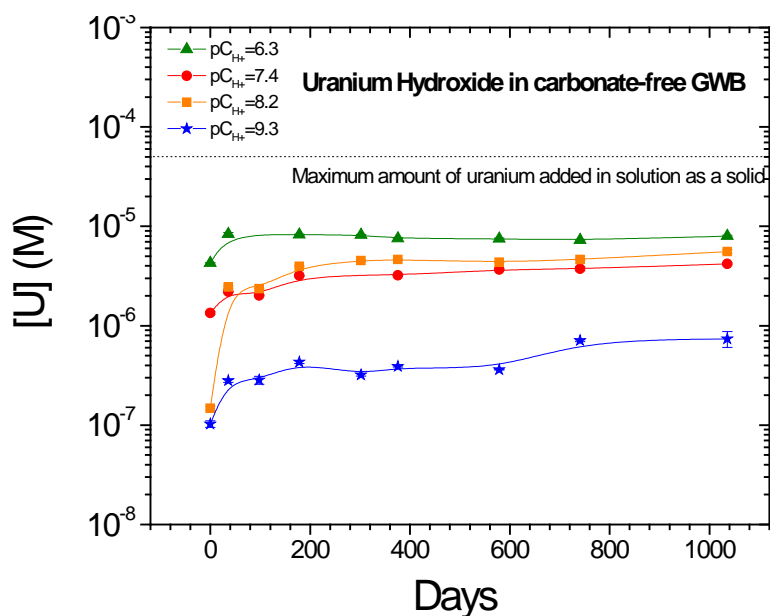


Figure 4-19 Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium hydroxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (...) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

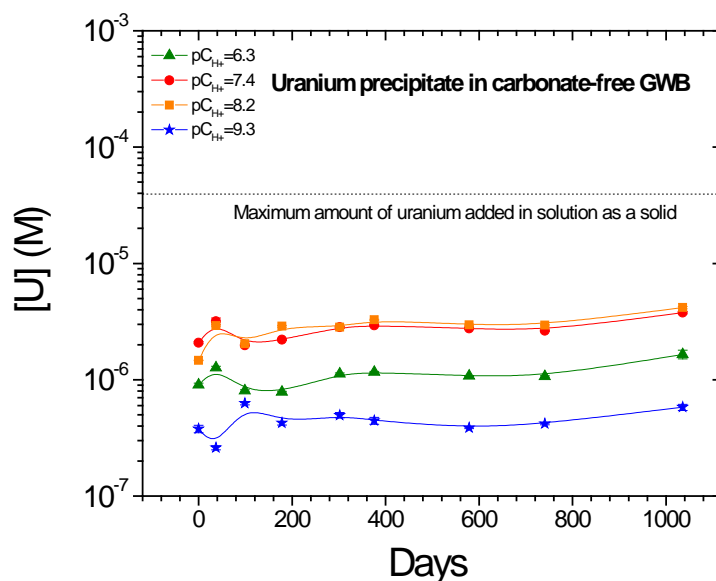


Figure 4-20: Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium precipitate obtained in over-saturation experiments, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (...) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

4.3.4.2 Evolution of U(VI) concentration with time in carbonate-free ERDA-6 brine in the under-saturation experiments

A pre-determined amount of each of four different uranium solid phases was added to carbonate-free ERDA-6 solutions, at four different pC_{H^+} values: 7.0, 8.2, 9.6, 10.5 and 12.5. The amount of uranium released into solution was monitored over time, using ICP-MS. For the four different kinds of the uranium solid phases investigated, the time profile of the uranium concentration measured in solutions was plotted as a function of the five different pC_{H^+} values investigated.

Figure 4-21, Figure 4-22, Figure 4-23 and Figure 4-24 show uranium concentration data obtained at the five different pC_{H^+} values investigated, from the experiments with respectively uranium peroxide (Figure 4-21), uranium trioxide (Figure 4-22), uranium hydroxide (Figure 4-23), and uranium precipitates obtained in over-saturation experiments (Figure 4-24). All these data correspond to 9 samplings performed throughout 1037 days (almost three years) of the experiments.

A few observations could be made from these data:

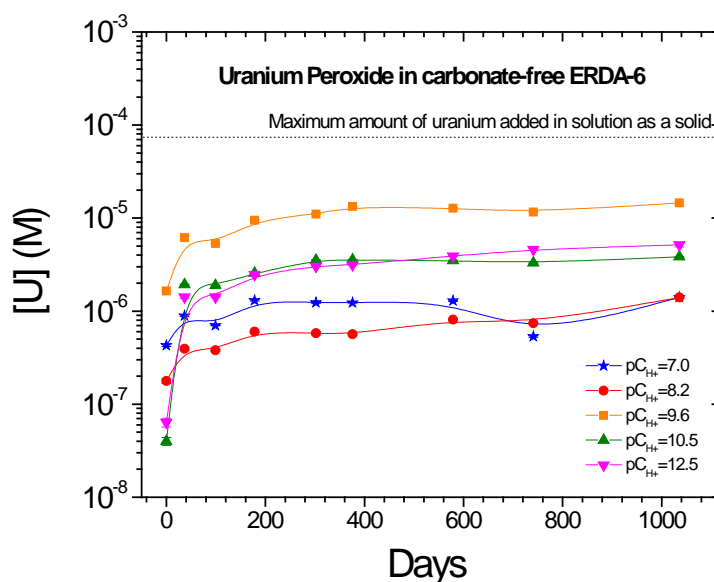


Figure 4-21: Evolution of uranium concentration in carbonate-free ERDA-6 solutions in the presence of solid uranium peroxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

a) Steady-state conditions were apparent in most of the experiments.

According to three observations, steady-state uranium concentrations in solutions could be considered as achieved in all the experiments.

First, in all the experiments, the uranium concentrations measured in solutions after 1037 days of the experiments were well below the concentrations expected if the entire uranium solid would dissolve.

Second, for each experiment, the uranium concentrations measured were almost unchanged over time after ~ 400 days (or earlier in some cases).

Third, the uranium oxides (peroxide, trioxide, and hydroxide) initially introduced as a solid in solutions were still visually observed in all solutions. On each graph, a horizontal line shows the maximum amount of uranium (converted to mole/L unit) that was initially placed into solution as a solid phase. In all experimental conditions, this line was not approached by any uranium concentration data measured in solutions. The uranium concentrations measured in solutions were well below the maximum concentration of uranium to be possibly released in solutions (i.e. if the entire solid would be dissolved) after 1037 days of the experiments. An exception to that was with the uranium precipitates, which could not be seen anymore in ERDA-6 solutions at $pC_{H^+} < 11$. However, in this case, since

the uranium measured in solution was also below what was expected if the entire uranium solid would dissolve, we suspect the uranium to be present in solutions in the colloidal forms, with a bigger size than the filter size used (30 kDa nominal molecular weight limit).

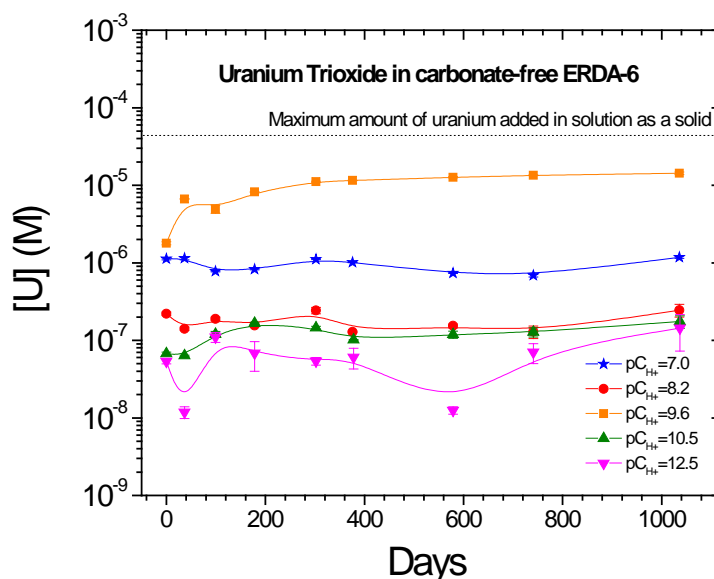


Figure 4-22: Evolution of uranium concentration in carbonate-free ERDA-6 solutions in the presence of solid uranium trioxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

- b) Concentrations of uranium released in solution were approximately 10^{-5} M or lower.

The uranium concentrations measured in solutions were approximately 10^{-5} M or lower at any pC_{H^+} conditions investigated (8.2-12.5), whatever uranium solid was used. They were in the range $10^{-7} - 10^{-5}$ M in the experiments with the uranium peroxide and trioxide, and in the range $3 \times 10^{-8} - 3 \times 10^{-6}$ M in the experiments performed with the uranium precipitates and hydroxide. At the two highest pC_{H^+} investigated (10.5 and 12.5), the uranium concentrations measured in solutions were about or below 10^{-7} M, with the exception of the experiments performed with uranium peroxide ($10^{-7} - 10^{-5}$ M). These lower uranium concentrations obtained at the two highest pC_{H^+} values investigated were accompanied by a white precipitate which occurred very early in the experiments (after 30 days). As a reminder, the chemical stability of ERDA-6 brine is in the range $(7.0 \pm 0.5) \leq pC_{H^+} \leq (10.8 \pm 0.5)$ (see Table 4-3). The two highest pC_{H^+} investigated (10.5 and 12.5) in

these Subtask 8 experiments were beyond this range, and therefore, it was expected to observe a white precipitate (most likely magnesium hydroxide) present in solution.

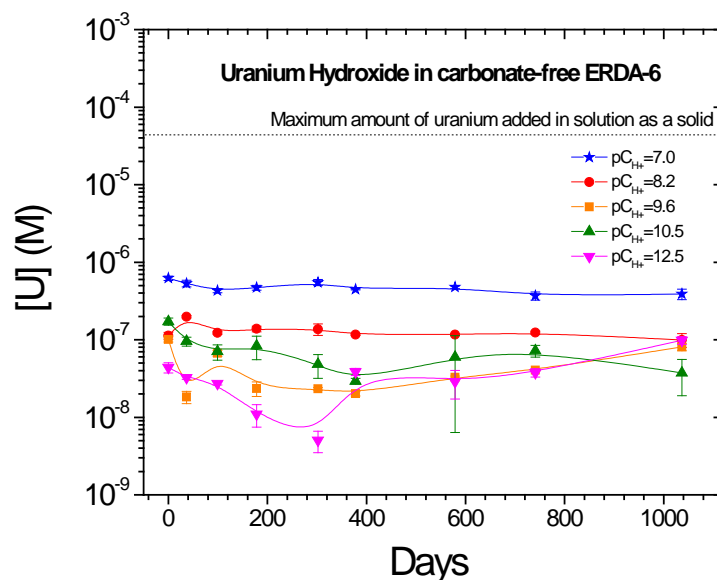


Figure 4-23: Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium hydroxide, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

- c) Data in these under-saturation experiments were in good agreement with the data obtained in the over-saturation experiments.

The data obtained with uranium precipitates (see Figure 4-24) in these under-saturation experiments were about 10^{-7} M at all investigated pC_{H^+} conditions (7.0-12.5). Similar conclusion was drawn in the over-saturation experiments at pC_{H^+} higher than 8 (see section 4.3.1.2).

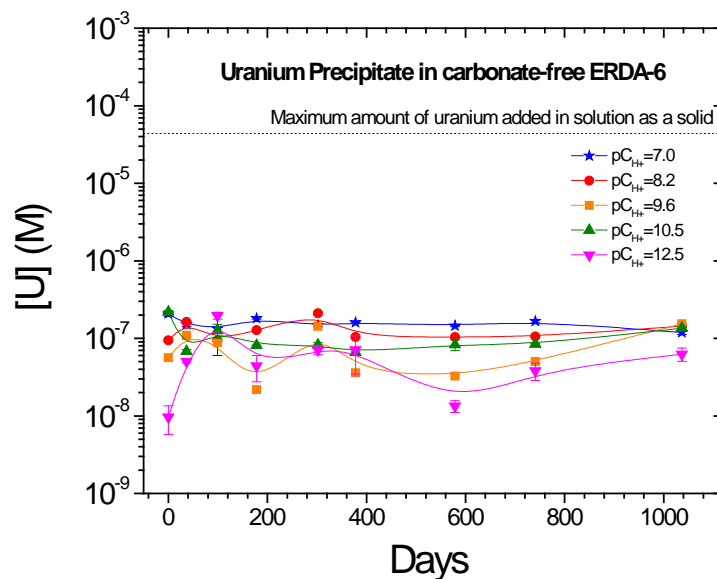


Figure 4-24: Evolution of uranium concentration in carbonate-free GWB solutions in the presence of solid uranium precipitate obtained in over-saturation experiments, with time at different pC_{H^+} values, in nitrogen controlled atmosphere. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution. All these data correspond to 9 samplings performed over 1037 days.

4.4 Solubility of U(VI) in the Absence of Carbonate

The evolution of uranium (VI) concentration with time in carbonate-free brines were presented in section 4.3.1 for the over-saturation approach, and in section 4.3.4 for the under-saturation approach.

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 herein, respectively in section 4.4.1 and 4.4.2.

4.4.1 Solubility of U(VI) in GWB brine in the absence of carbonate

The overall uranium (VI) solubility measured in GWB in the absence of carbonate and in a nitrogen controlled atmosphere is plotted in Figure 4-25 as a function of pC_{H^+} . This plot is based on the time-dependent experimental data given in sections 4.3.1.1 and 4.3.4.1 (Figure 4-20).

At $7 \leq \text{pC}_{\text{H}^+} \leq 9.2$, 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 possibly reflects a small effect of borate complexation (see section 4.8.1).

We noticed that, when carbonate was rigorously excluded from our brine systems, the uranium solubilities were 10-100 times lower than any reported in the literature for similar systems [Yamazaki 1992; Diaz-Arocas 1998]. Comparison with literature data is discussed in section 4.8.1.

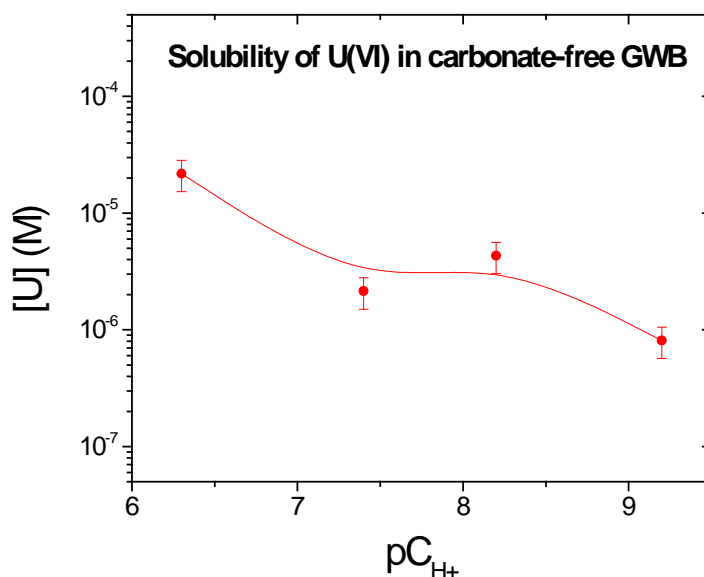


Figure 4-25: Uranium (VI) solubility in carbonate-free GWB brine solutions versus pC_{H^+} . The curve compiles data obtained from the over-saturation experiments (see section 4.3.1.1) and the under-saturation experiments (see section 4.3.4.1).

4.4.2 Solubility of U(VI) in ERDA-6 brine in the absence of carbonate

Figure 4-26 is a compilation of the U(VI) solubility values obtained experimentally in initially carbonate-free ERDA-6 brine solutions in a nitrogen controlled atmosphere from the over-saturation experiments (see section 4.3.1.2) and the under-saturation experiments (see section 4.3.4.2).

In the over-saturation experiments, the uranium concentration reached a steady state over time and precipitation occurred in the solutions at $\text{pC}_{\text{H}^+} \geq 8$ (see section 4.3.1.2). In the under-saturation experiments, at $\text{pC}_{\text{H}^+} < 11$, the uranium precipitates could not be seen

anymore in solution, but the uranium concentration measured in ERDA-6 solutions was below what was expected if the entire uranium solid would dissolve (see section 4.3.4.2). Therefore, the solubility limit from under-saturation could be considered to be reached. Only the data obtained at $pC_{H^+} \geq 8$ in Figure 4-26 correspond to the true U(VI) solubility in the investigated systems.

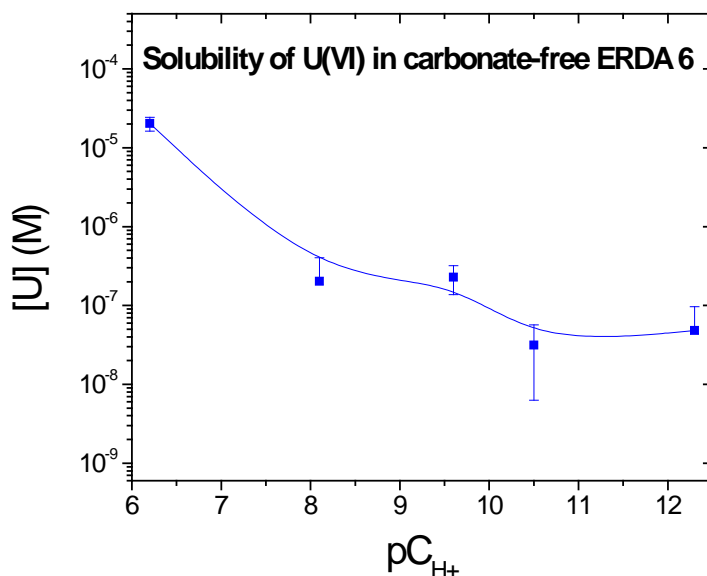


Figure 4-26: Uranium (VI) solubility estimates in carbonate-free ERDA-6 brine solutions versus pC_{H^+} . The curve compiles data obtained from the over-saturation experiments (see section 4.3.1.2) and the under-saturation experiments (see section 4.3.4.2).

Because the over-saturation conditions were not completely fulfilled (no precipitation) in the solutions at $pC_{H^+} < 8$ (see section 4.3.1.2), the corresponding data in Figure 4-26 are preliminary and not yet complete, even though the under-saturation conditions were fulfilled (see section 4.3.4.2). The uranium solubility estimate at $pC_{H^+} = 6.2$ was more than two orders of magnitude higher than the uranium solubility values obtained at $pC_{H^+} \geq 8$.

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 $pC_{H^+} \sim 8$ to $pC_{H^+} \sim 11$.

At $pC_{H^+} \sim 12.3$, which is beyond the chemical stability of ERDA-6, the solubility of uranium (VI) in carbonate-free solution was $\sim 4.8 \times 10^{-8}$ M. This solubility was within the range of the data measured at $pC_{H^+} \geq 8$. Overall uranium (VI) solubility found in ERDA-6 brine when carbonate was carefully excluded were 10-100 times lower than any reported in the literature for similar systems [Yamazaki 1992; Diaz-Arocas 1998]. Comparison with literature data is discussed in section 4.8.1.

4.5 Solubility of U(VI) as a Function of Ionic Strength

Herein, we discuss the data obtained on the solubility of uranium (VI) for different ionic strengths under anoxic atmosphere and using the over-saturation approach. Section 4.5.1 summarizes the data collected in GWB brine, and the following section (section 4.5.2) deals with the data collected in ERDA-6 brine. The objective is to evaluate the effect of the ionic strength of the two brines on uranium (VI) solubility at different pC_{H^+} values.

4.5.1 Solubility of U(VI) in carbonate-free GWB brine as a function of ionic strength

The solubility of uranium (VI) in carbonate-free GWB brine at four different ionic strengths is given in Figure 4-27 as a function of pC_{H^+} . The data presented in the graph were obtained in the over-saturation experiments described in section 4.3.1.1 (GWB) and in section 4.3.3.1 (50% GWB, 15% GWB and 1.5% GWB).

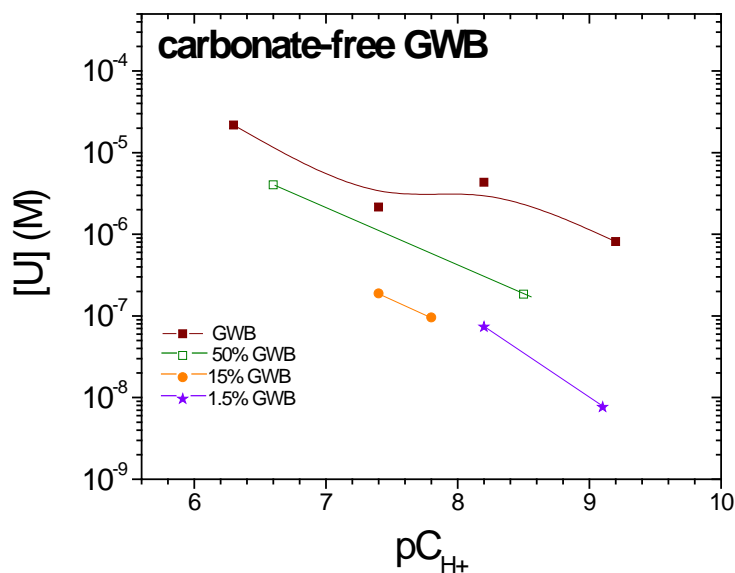


Figure 4-27. Uranium concentration in four different carbonate-free GWB solutions: GWB, 50% GWB, 15% GWB and 1.5% GWB, as a function of pC_{H^+} , in a nitrogen controlled atmosphere, and in the absence of carbonate.

The uranium (VI) solubility data obtained in GWB at $pC_{H^+} \geq 7$ in the over-saturation experiments (see section 4.3.1.1) were confirmed by the data obtained using the under-saturation approach (see section 4.3.4). The data obtained in the diluted GWB brines (see section 4.3.3.1), however, cannot be completely considered as U(VI) solubility data, 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, these data can be considered as reliable U(VI) solubility estimates, since the uranium concentration reached a steady state over time and precipitation occurred in solution for all the solutions, with the exception of the 3.4M ionic strength solution at $pC_{H^+} \sim 7.3$.

We noticed that for a same ionic strength, the concentration of uranium (VI) measured in solutions decreased when pC_{H^+} increased (Figure 4-27). This was systematically true with the results obtained in the diluted brines (50% GWB and lower ionic strengths). In the 15% GWB experiments, the solubility of uranium was about 1.9×10^{-7} M at $pC_{H^+} \sim 7.4$ and 9.6×10^{-8} M at $pC_{H^+} \sim 7.8$. Similarly, in the 1.5% GWB experiments, the solubility of uranium was about 7.3×10^{-8} M at $pC_{H^+} \sim 8.2$ and 7.6×10^{-9} M at $pC_{H^+} \sim 9.1$. This trend suggests that hydrolysis is the main complexation mechanism for uranium (VI), at least in carbonate-free diluted GWB brines at $pC_{H^+} \geq 7$.

In non-diluted GWB, i.e. at 6.8M ionic strength, the concentration of uranium (VI) measured did not decrease when pC_{H^+} increased, at least in the pC_{H^+} region of interest [7.3 – 9] (Figure 4-27 and section 4.4.1). For that ionic strength, the solubility of uranium was about 2.1×10^{-6} M at $pC_{H^+} \sim 7.4$ and 4.3×10^{-6} M at $pC_{H^+} \sim 8.2$. This slight increase of uranium solubility at the pC_{H^+} region of interest [7.4 – 8.5] was observed in non-diluted GWB, and to a lesser extent in diluted GWB brines. It is possible that one (or more) component of the GWB brine was competing with the hydroxide ion for the complexation of the uranyl ion at this defined pC_{H^+} region. Beyond that pC_{H^+} region ($pC_{H^+} \geq 8.5$), it seems that the solubility of uranium decreased again when pC_{H^+} increased in non-diluted GWB brine.

By analogy with the neodymium- brine systems [Borkowski 2009], we believe there is evidence that borate complexation is influencing the uranium solubility in pC_{H^+} region of 7.4 to 9.2 (see section 4.8.1). At $pC_{H^+} \sim 7.4$, the uranium solubility in GWB was about 2.1×10^{-6} M, which was about 11 times more than in 50% GWB. Also, at $pC_{H^+} \sim 8.2$, the uranium solubility in GWB was about 4.3×10^{-6} M, which was about 60 times more than in 1.5% GWB. In these two cases, the factor between the uranium concentrations taken at the same pC_{H^+} values was very close to the ratio between the concentration of brine components: 6.8 in the first case at $pC_{H^+} \sim 7.4$, 68 in the second case at $pC_{H^+} \sim 8.2$. In these two cases, the uranium solubility was proportional to the concentration of borate in the brine.

4.5.2 Solubility of U(VI) in carbonate-free ERDA-6 brine as a function of ionic strength

The solubility of uranium (VI) was also investigated in carbonate-free ERDA-6 brine at four different ionic strengths. The data presented in Figure 4-28 as a function of pC_{H^+} were

obtained in the over-saturation experiments described in section 4.3.1.2 (ionic strength: 6M) and in section 4.3.3.2 (ionic strengths: 3M, 1M, and 0.1M).

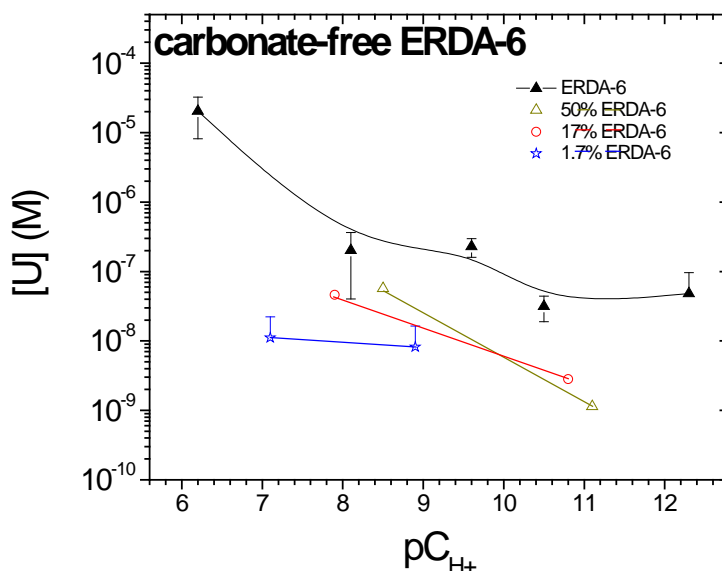


Figure 4-28. Uranium concentration in four carbonate-free ERDA-6 solutions: ERDA-6, 50% ERDA-6, 17% ERDA-6 and 1.7% ERDA-6 as a function of pC_{H^+} , in a nitrogen controlled atmosphere, and in the absence of carbonate.

The data points obtained in the pC_{H^+} range [8-9] and for $I > 0.1$ M plotted in Figure 4-28 correspond to the true U(VI) solubility value in carbonate-free ERDA-6 brine. There is good agreement between the data obtained using the over and under-saturation approach (see section 4.3.4). Concerning the data obtained in the diluted ERDA-6 brines, they cannot be completely considered as U(VI) solubility data, 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 in 50% ERDA-6 and 17% ERDA-6 can be considered as reliable U(VI) solubility estimates in the pC_{H^+} range [7.5-9], since the uranium concentration reached a steady state over time and precipitation occurred in solution for all the solutions in those conditions of pC_{H^+} (see section 4.3.3.2). All the other data shown in Figure 4-28 are uranium concentrations measured experimentally at the time we reported them (day 874 of the experiments), but they may not represent a definitive estimate of the uranium solubility. They were plotted in the graph as an example to show the current status.

The uranium solubility values determined by the experiments in ERDA-6 at $pC_{H^+} \sim 8.1$ were 2.0×10^{-7} M, which is about 4.3 times the value of 4.6×10^{-8} M determined in 17% ERDA-6 at $pC_{H^+} \sim 7.9$. Similarly to what was observed in GWB (see section 4.5.1), we may see a match between the factor between these two uranium solubility values and the ratio

between the borate concentrations. Overall, the data plotted in Figure 4-28 show that hydrolysis fixed the uranium concentrations in solutions in the 10^{-9} - 10^{-8} M range for the diluted brine experiments over a broad range of pC_{H^+} , but in the non-diluted ERDA-6 brine, the uranium concentrations could be about an order of magnitude higher.

4.6 Solubility of Uranium (VI) Solids in Carbonate-free Brines

The uranium (VI) solubility experiments conducted in carbonate-free ERDA-6 and GWB brines using the under-saturation approach (see section 4.3.4) were performed to achieve two goals: to confirm the data obtained in Subtask 1 on the uranium (VI) solubility in carbonate-free brines at different pC_{H^+} values, and to investigate the solubility of various uranium solid phases in those experimental conditions. The first part of these goals was developed in section 4.4.

In this section, we are discussing the second aspect of these goals. The solubility of four different uranium (VI) solids is presented in carbonate-free GWB (see section 4.6.1) and ERDA-6 (see section 4.6.2). The four different uranium solid phases that were used are the following: uranium peroxide (UO_4), uranium trioxide (UO_3), uranium hydroxide ($UO_2(OH)_2$), and uranium precipitates obtained in GWB or ERDA-6 brine using the over-saturation approach. The preparation of these uranium solids was described in section 4.2.1. The first three uranium solids were synthetic uranium (VI) phases that could be formed in high radiation media (UO_4), or in potentially high oxidation media (UO_3), or in highly basic conditions ($UO_2(OH)_2$). The uranium precipitates were generated in the same experimental conditions described in the over-saturation experiments in carbonate-free brine reported in section 4.3.1 and more extensively in the LCO-ACP-10 report [Lucchini 2010a].

The uranium precipitates generated in all the over-saturation experiments described in this report have not been fully characterized yet, so their structure and composition is unknown at this time. Some attempts of solid characterization have been made by XANES and SEM/EDS, and are reported in section 4.3.1.2.

4.6.1 Solubility of uranium (VI) solids in carbonate-free GWB brine

Figure 4-29 shows the solubility of the four investigated uranium solids in carbonate-free GWB brine as a function of pC_{H^+} .

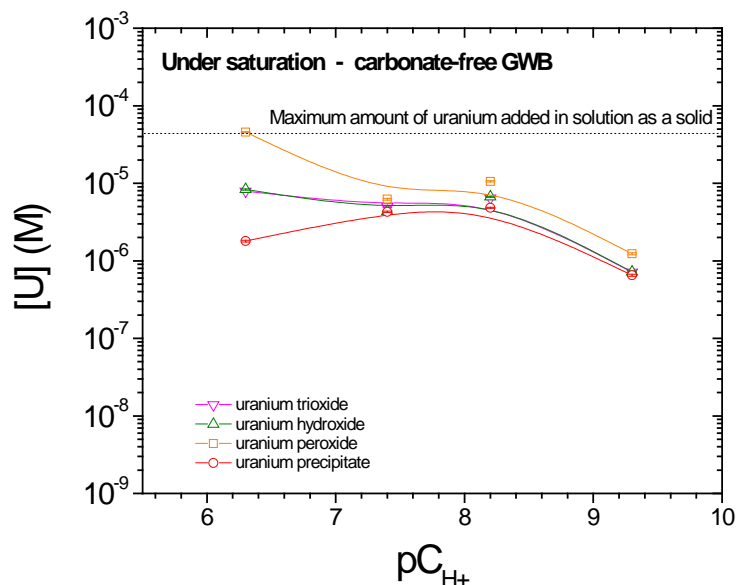


Figure 4-29: Solubility of four uranium solids in carbonate-free GWB solutions in nitrogen controlled atmosphere and at different pC_{H^+} values. From the top to the bottom of the legend, the uranium solids are respectively the uranium trioxide, the uranium hydroxide, the uranium peroxide, and a uranium precipitate obtained in over-saturation experiments. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution.

Two distinct pC_{H^+} regions could be noted in Figure 4-29. At $pC_{H^+} \leq 7.4$, the solubility of the four investigated uranium (VI) solids in carbonate-free GWB was different: the uranium peroxide was more soluble, and the uranium precipitates were the least soluble. At $pC_{H^+} = 6.3$, the uranium solubility was about 4.5×10^{-5} M for the uranium peroxide, and it was about 1.8×10^{-6} M for the uranium precipitates. The other two uranium solids (trioxide and hydroxide) had a solubility of about 8.0×10^{-6} M at $pC_{H^+} = 6.3$.

At $pC_{H^+} \geq 7.4$, however, the investigated uranium solids had similar solubility in carbonate-free GWB. At $pC_{H^+} = 8.2$, the uranium solubility for uranium trioxide, hydroxide and precipitates was from 5×10^{-6} M to 7×10^{-6} M, and slightly higher for the uranium peroxide (10^{-5} M). At $pC_{H^+} = 9.3$, the uranium solubility for uranium trioxide, hydroxide and precipitates was about 7×10^{-7} M, and again slightly higher for the uranium peroxide (1.2×10^{-6} M). At $pC_{H^+} \geq 7.4$, the uranium precipitates generated in the over-saturation experiments were as soluble as the other uranium solid phases.

Also, as it was developed in section 4.3.4.1, the concentrations of uranium released in carbonate-free GWB brine were lower at $pC_{H^+} = 9.3$ than at any other pC_{H^+} values, whatever uranium solid phase was in solution. These uranium concentrations measured in solutions were about or below 10^{-6} M. This result could be due to the increasing hydrolysis occurring at high pC_{H^+} . Also, since at $pC_{H^+} = 9.3$, GWB brine was chemically unstable, the presence of

the white brine precipitate (most likely magnesium hydroxide) may influence the accessibility of the uranium solids to dissolve in solution.

4.6.2 Solubility of uranium (VI) solids in carbonate-free ERDA-6 brine

In Figure 4-30, the solubility of the four investigated uranium solids in carbonate-free ERDA-6 brine is plotted as a function of pC_{H^+} .

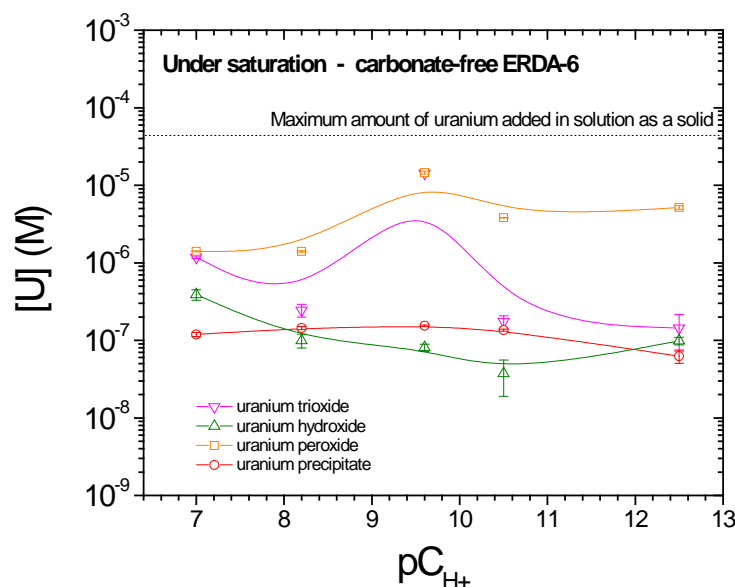


Figure 4-30: Solubility of four uranium solids in carbonate-free ERDA-6 solutions in nitrogen controlled atmosphere and at different pC_{H^+} values. From the top to the bottom of the legend, the uranium solids are respectively the uranium trioxide, the uranium hydroxide, the uranium peroxide, and a uranium precipitate obtained in over-saturation experiments. The horizontal line (.....) represents the maximum uranium concentration if the entire solid added goes into solution.

Unlike the results obtained in GWB brine (see section 4.6.1), the uranium solubilities obtained in carbonate-free ERDA-6 brine and plotted in Figure 4-30 were very different between the four uranium (VI) solid phases investigated.

Over the broad range of pC_{H^+} of this study (from 7 to 12.5), uranium peroxide released the most uranium in ERDA-6 solution. The maximum concentration measured in solution from the dissolution of uranium peroxide was 1.5×10^{-5} M at $pC_{H^+} = 9.6$. The uranium release from uranium peroxide was lower at pC_{H^+} values other than 9.6 (1.4×10^{-6} M at $pC_{H^+} < 9.6$, 3.8×10^{-6} M at $pC_{H^+} = 10.5$, 5.2×10^{-6} M at $pC_{H^+} = 12.5$). The solubility of uranium trioxide was also significant, with a maximum of release at $pC_{H^+} = 9.6$ similar to the uranium peroxide (1.5×10^{-5} M). But it went slowly down with increasing pC_{H^+} . The

concentration of uranium measured in solution from the dissolution of uranium trioxide was 1.2×10^{-6} M at $pC_{H^+} = 7$, 2.5×10^{-7} M at $pC_{H^+} = 8.2$ and 1.8×10^{-7} M at $pC_{H^+} = 10.5$.

The profile of the solubility of uranium hydroxide versus pC_{H^+} matched the profile of the solubility of uranium precipitates at $pC_{H^+} > 8$. At $pC_{H^+} = 8.2$, the uranium solubility for uranium hydroxide was about 10^{-7} M, and the solubility of the uranium precipitates was 1.4×10^{-7} M. At $pC_{H^+} = 12.5$, the uranium solubility for uranium hydroxide was 9.8×10^{-8} M, and the solubility of the uranium precipitates was 6.2×10^{-8} M, which was close to the solubility of uranium trioxide at this pC_{H^+} value (7.1×10^{-8} M). Between those two pC_{H^+} values (8.2 and 12.5), the solubility of the uranium precipitates was a little higher than the solubility of the uranium hydroxide. For example, at $pC_{H^+} = 9.6$, the uranium solubility for uranium hydroxide was 8.1×10^{-8} M, and the solubility of the uranium precipitates was 1.5×10^{-7} M.

At a given pC_{H^+} value, the uranium steady-state concentration in the brine solution was lower for the uranium hydroxide and the uranium precipitates previously generated in over-saturation experiments at the same experimental conditions, than in the presence of the peroxide and trioxide uranium phases. At pC_{H^+} values between 8.2 and 10.5 particularly, the peroxide and trioxide solids used were out of equilibrium with the brine and led to higher apparent solubility.

4.7 Solubility of U(VI) in the Presence of Carbonate

The experimental data obtained in the experiments performed in Subtask 3 (see section 4.3.2) are presented in the following two sections as a function of pC_{H^+} . Figure 4-31 and Figure 4-32 show the uranium concentration measured respectively in GWB (Figure 4-31) and in ERDA-6 (Figure 4-32) over a broad range of pC_{H^+} values and in the absence or presence of carbonate. The potential impact of carbonate on the solubility of U(VI) is then discussed.

4.7.1 Solubility of U(VI) in GWB brine in the presence of carbonate

Figure 4-34 shows the uranium concentrations measured in GWB brine in the absence of carbonate and in the presence of initial carbonate concentrations of 2×10^{-4} M and 2×10^{-3} M. These data were presented as a function of time in section 4.3.2.1. Here in Figure 4-31, they are plotted as a function of pC_{H^+} .

These data in Figure 4-31 were obtained in solubility experiments using the over-saturation approach, and they may need to be confirmed by experiments using the under-saturation approach. At $pC_{H^+} \geq 7$, steady-state U(VI) concentrations and precipitation were always noted.

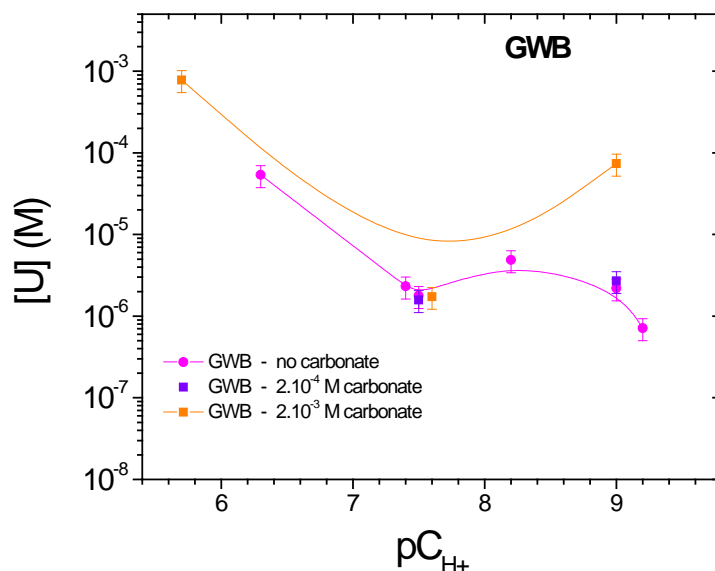


Figure 4-31. Uranium concentrations versus pC_{H^+} , obtained in GWB in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M at the beginning of the experiments). These data correspond to 17 samplings performed over 994 days. The pink curve shows the uranium concentration in the absence of carbonate, or in the presence of very low carbonate. The orange curve shows the uranium concentration in the presence of significant amount of carbonate (2×10^{-3} M at the beginning of the experiments).

At pC_{H^+} value ranging from 6 to 8, the uranium concentrations measured in GWB solutions were almost identical in all cases, in the presence or absence of carbonate. At $pC_{H^+} \sim 7.5$, the uranium concentrations measured in solution were 1.8×10^{-6} M in the absence of carbonate, 1.6×10^{-6} M in the presence of 2×10^{-4} M carbonate at the beginning of the experiments, and 1.7×10^{-6} M in the presence of 2×10^{-3} M carbonate at the beginning of the experiments. We do not have a definitive explanation for this because we did not analyze for carbonate throughout the experiment. There are likely multiple contributions to this observation including loss of carbonate during sampling, precipitation of uranyl carbonate phases, and the relatively weak complexation of uranyl with bicarbonate that predominates at these lower pC_{H^+} values.

At $pH \sim 9$, there is a much more pronounced effect of carbonate on the steady-state concentrations of uranium in the GWB brine systems investigated. This can be directly attributed to carbonate complexation at the higher initial carbonate concentrations investigated.

4.7.2 Solubility of U(VI) in ERDA-6 brine in the presence of carbonate

The uranium concentrations measured in ERDA-6 brine in the absence of carbonate and in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments are plotted versus pC_{H^+} in Figure 4-32.

By analogy with the GWB results (see section 4.7.1), these data in Figure 4-32 were obtained in solubility experiments using the over-saturation approach, but they need to be confirmed by experiments using the under-saturation approach. Since steady-state concentrations were not yet achieved, the over-saturation experiments have not been completed at this time, and therefore, the data presented in this section should be used qualitatively.

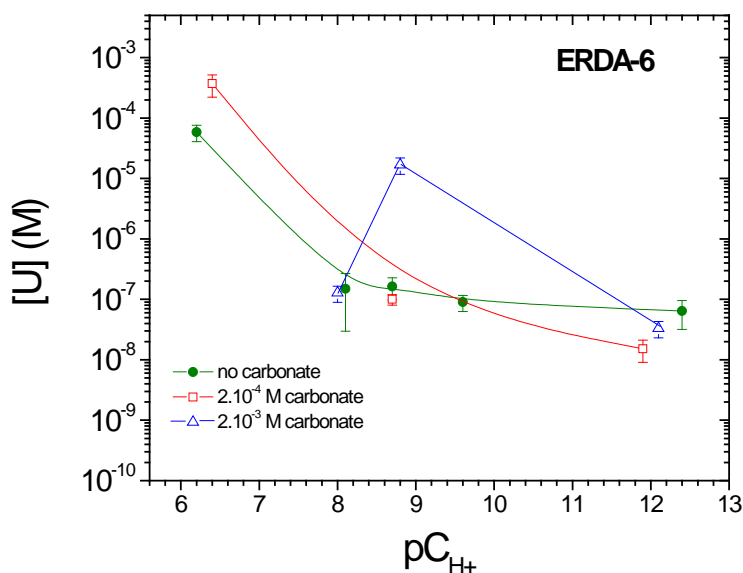


Figure 4-32. Uranium concentrations versus pC_{H^+} , obtained in ERDA-6, in nitrogen controlled atmosphere, in the absence of carbonate and in the presence of 2×10^{-4} M and 2×10^{-3} M carbonate (initial concentrations). These data correspond to 17 samplings performed over 994 days. The green curve shows the uranium concentration in the absence of carbonate. The red curve shows the uranium concentration in the presence of a low amount of carbonate (2×10^{-4} M). The blue curve shows the uranium concentration in the presence of significant amount of carbonate (2×10^{-3} M).

The profiles of uranium concentrations versus pC_{H^+} obtained in ERDA-6 (Figure 4-32) were similar to the profiles obtained in GWB (Figure 4-31). Below $pC_{H^+} \sim 7$, the presence of carbonate slightly enhanced the uranium concentration measured in solution. At $pC_{H^+} \sim 8$, the uranium measured in solution was about 1.3×10^{-7} M, in the absence of carbonate or in the presence of the high amount of carbonate initially added to the solution. At that pC_{H^+} value, the amount of carbonate available in solution after equilibrium with other carbon species (CO_2 , HCO_3^-) and possible reaction with brine components was probably too low to react with the uranium in solution. Therefore, like in GWB in very similar pC_{H^+} conditions, uranium (VI) probably reacted with hydroxide at $pC_{H^+} \sim 8$, in the absence of carbonate and even in the presence of a substantial amount of carbonate at the beginning of the experiments.

At $pC_{H^+} \sim 8.8$, we also observed the same trend in ERDA-6 as in GWB for similar experimental conditions. The uranium concentration measured in ERDA-6 in the initial presence of low amount of carbonate was about 10^{-7} M, which was comparable to the uranium concentration measured in ERDA-6 in the absence of carbonate (1.6×10^{-7} M). But in the presence of the highest amount of carbonate added in solution in our experiments, the uranium concentration was increased by two orders of magnitude to 1.6×10^{-5} M.

At $pC_{H^+} \sim 12$, beyond the chemical stability range of ERDA-6, the impact of carbonate on the uranium concentration measured in solution could not be seen through the experimental results (see Figure 4-32). The uranium concentrations measured in ERDA-6 were 6.4×10^{-8} M at $pC_{H^+} \sim 12.4$ in the absence of carbonate, 1.5×10^{-8} M at $pC_{H^+} \sim 11.9$ in the presence of a low amount of carbonate at the beginning of the experiments, and 3.3×10^{-8} M at $pC_{H^+} \sim 12.1$ in the presence of a high amount of carbonate at the beginning of the experiments. Hydrolysis is certainly the predominant pathway in the mechanism of uranium solubility in ERDA-6 at $pC_{H^+} \sim 12$.

4.8 Summary of Experimental Results and Conclusions

All the data obtained in the experiments described in this report were presented (see section 4.3) and discussed (see sections 4.4 to 4.7) earlier. In this section and sub-sections, the key data developed in this report are summarized, and supported or challenged by published literature.

4.8.1 Solubility of U(VI) in brine in the absence of carbonate: evidence of borate complexation

The uranium (VI) solubility data obtained in carbonate-free WIPP brines using both the over-saturation approach and the under-saturation approach are summarized in Figure 4-33 for both simulated brines.

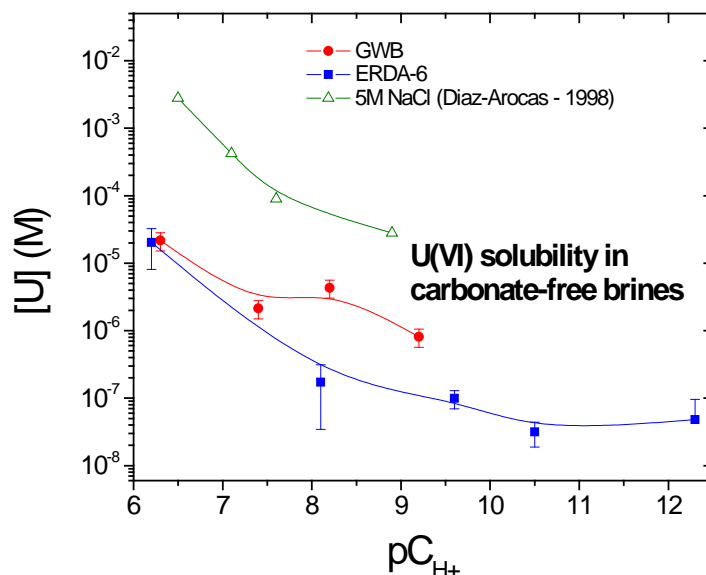


Figure 4-33: Uranium (VI) solubility in carbonate-free brines versus pC_{H^+} . The two curves at the bottom the graph are from data obtained from our solubility experiments in GWB (curve in the middle of the graph) and in ERDA-6 (curve at the bottom of the graph) using the over-saturation approach and the under-saturation approach. The top curve is based on the Diaz-Arocas' data in 5 M NaCl [Diaz-Arocas 1998].

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^+} (~ 9.3), the solubility of uranium was about one order of magnitude higher in GWB than in ERDA-6 (Figure 4-33). This is likely due to the differences in ionic strength and complexant concentration in the two brines (Table 4-5). It is possible that uranium (VI) could undergo some complexation with borate ion near the pC_{H^+} value expected in the WIPP (~ 9.3). The borate complexation effect in the WIPP brine was demonstrated on neodymium (III) by Borkowski [2009]. The effect of borate on the uranyl system was confirmed by saturating three ERDA-6 solutions at an initial pC_{H^+} of 8.1, 9.6 and 10.5 with sodium tetraborate solid, reaching a total concentration of $\sim 5 \times 10^{-2}$ M tetraborate in solution [Lucchini 2011]. The impact of the tetraborate addition is depicted in Figure 4-34. A significant increase of uranium in solution and a shift of pC_{H^+} to values close to the pK_a (9.02) of boric acid at $I = 5.0$ M, were observed after 55 days of experiments. The change in pC_{H^+} can be explained in terms of the strong buffering capacity of the tetraborate salt.

At pC_{H^+} values up to 10.5, the uranium concentration trends observed over time in carbonate-free ERDA-6 brine indicated that uranium (VI) did not exhibit strongly amphoteric behavior under the conditions investigated.

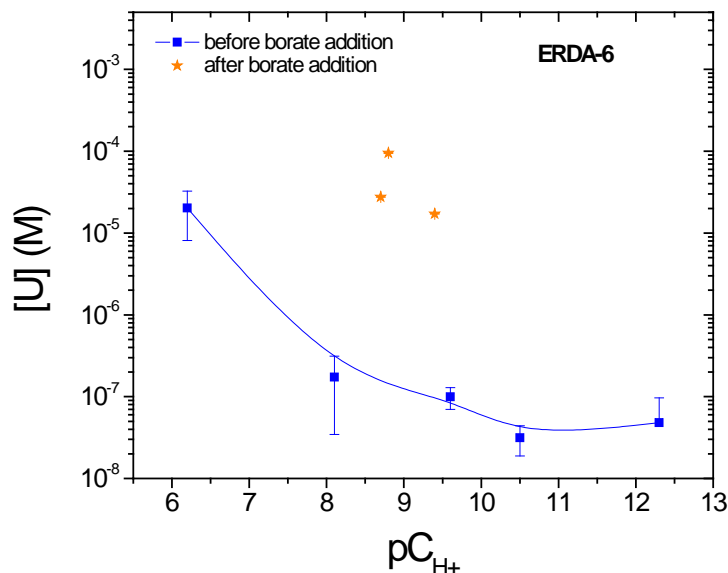


Figure 4-34: Uranium (VI) concentrations versus pC_{H^+} , measured in three carbonate-free ERDA-6 brines 55 days after saturation with sodium tetraborate (orange symbols). The blue curve at the bottom of the graph represents the data obtained in ERDA-6 before the addition of tetraborate [Lucchini 2011].

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 4-7, 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 4.31 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 4-23). The lower uranium concentrations reported in our experiments primarily reflect 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.

Table 4-7 Uranium (VI) solubility in chloride-based brines (1~5 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

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, 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 4-7). It is not clear why there is a large difference between these data and our results.

4.8.2 Solubility of U(VI) in carbonate-free brine as a function of brine dilution and pC_{H+}

The solubility of U(VI) in carbonate-free brine as a function of pC_{H+} at the different ionic strengths investigated is summarized in Figure 4-35. This figure regroups the data obtained in GWB and ERDA-6 and presented in section 4.5.

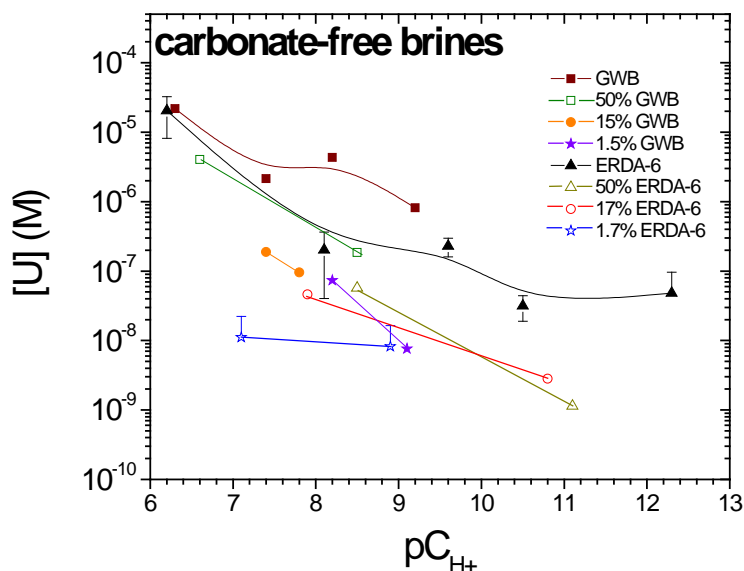


Figure 4-35. Uranium concentration in simulated WIPP brines at six different ionic strengths (6.8M, 6M, 3.4M, 3M, 1M and 0.1M) as a function of pC_{H^+} , in a nitrogen controlled atmosphere, and in the absence of carbonate.

Generally, for a same ionic strength, the concentration of uranium (VI) measured in solutions decreased as the pC_{H^+} increased. This trend demonstrates that hydrolysis is the main complexation mechanism for uranium (VI), at least in carbonate-free dilute brines. In non-diluted brines however, in some specific pC_{H^+} regions of interest depending on the brine ([7.3 – 9] for GWB, [8-10] for ERDA-6), the concentration of uranium (VI) measured in solutions did not decrease when pC_{H^+} increased. It is possible that one (or more) component of the GWB brine was competing with the hydroxide ion for the complexation of the uranyl ion to keep it in solution at these defined pC_{H^+} regions. Similarly to the neodymium solubility results obtained in GWB brine [Borkowski 2009], we demonstrated that borate could also influence the uranium solubility (see section 4.8.1).

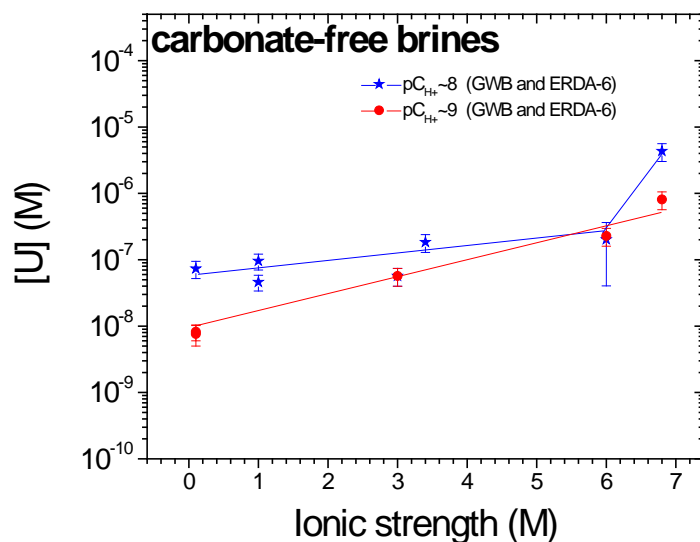


Figure 4-36. Uranium concentration in simulated WIPP brines as a function of ionic strength at three different pC_{H^+} values (blue curve: $pC_{H^+} \sim 8$, red curve: $pC_{H^+} \sim 9$), in a nitrogen controlled atmosphere, and in the absence of carbonate.

Figure 4-36 shows the uranium concentration measured in carbonate-free WIPP brines (GWB and ERDA-6) as a function of ionic strength at three different pC_{H^+} values: ~ 8 , ~ 9 and ~ 11 . The three curves exhibit some linear feature, but with different slopes. An extensive and very accurate study on the characterization of the uranium precipitates obtained in those experimental conditions would support this hypothesis. In this case, since the two other curves are different from that one, the complexation of uranium (VI) at pC_{H^+} values ~ 8 and ~ 9 is more likely to also involve additional ion(s) from the solution. It is also possible that the solid precipitates generated in our experiments could undergo some structural transformation over time. According to the literature [Yamazaki 1992, Diaz-Arocas 1998], sodium uranates were identified in experiments similar to ours. An extensive solid characterization of the solid phases obtained in our experiments is needed to fully address these complexities.

4.8.3 Solubility of U(VI) in WIPP brines in the presence of carbonate

The impact of carbonate concentration on the solubility of uranium (VI) in the two simulated WIPP brines is shown in Figure 4-37 as a function of pC_{H^+} .

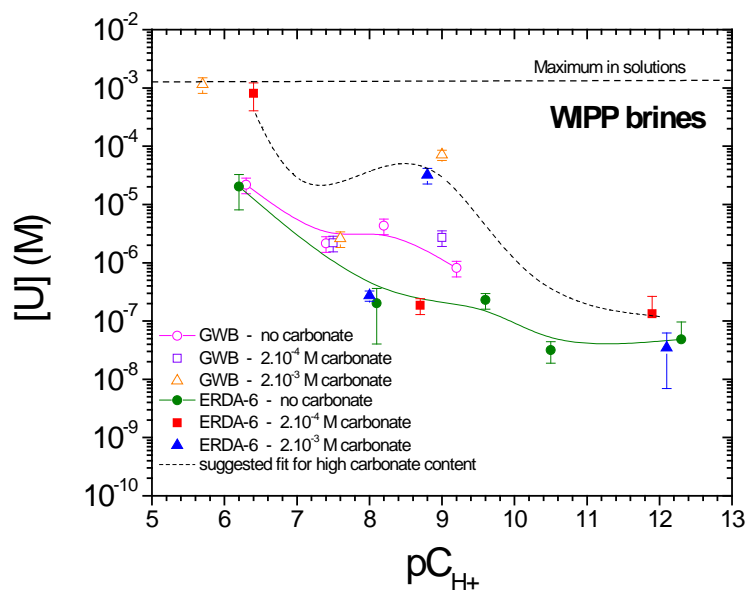


Figure 4-37. Uranium concentrations in ERDA-6 (open symbols) and GWB (filled symbols) versus pC_{H^+} in nitrogen controlled atmosphere, in the absence of carbonate or in the presence of two concentrations of carbonate (2×10^{-4} M and 2×10^{-3} M) at the beginning of the experiments. These data correspond to 17 samplings performed over 994 days.

Four distinctive regions were noted. The first region, when $pC_{H^+} \leq 7$, had the highest uranium concentration in solution, due to the low pC_{H^+} . The measured uranium concentrations were 10^{-5} M or higher. These high concentrations of uranium measured at $pC_{H^+} \leq 7$ were not due to carbonate complexation and this pC_{H^+} region is not relevant to the WIPP based on current assumptions.

The second pC_{H^+} region was $7 \leq pC_{H^+} \leq 8.5$. In this pC_{H^+} region, the uranium concentration was stable in both brines and independent of the carbonate concentration. However, there were differences in the uranium solubility due to differences in the composition of the brine: $\sim 10^{-6}$ M in GWB, and $\sim 10^{-7}$ M in ERDA-6. These data indicated that there was no impact of carbonate in this pC_{H^+} region ($7 \leq pC_{H^+} \leq 8.5$), but there was certainly an effect due to one or more component of the brines that were present in higher amounts in GWB than in ERDA-6. Based on our investigation of neodymium solubility [Borkowski 2009], we postulate that borate may also play a role in defining the uranium (VI) solubility in this pC_{H^+} region, but this possibility needs to be confirmed.

The third pC_{H^+} region of interest, $8.5 \leq pC_{H^+} \leq 9.5$, was directly relevant to the WIPP. In this pC_{H^+} region, not only there was a compositional effect between the two brines studied (higher uranium concentrations in GWB than in ERDA-6 for identical carbonate content), but there was also an impact of carbonate on the observed uranium solubility in each brine. At high carbonate content (2×10^{-3} M in our experiments), the uranium concentrations reached 10^{-4} M, which was two or more orders of magnitude higher than in

the absence of carbonate. The low carbonate content data (2×10^{-4} M) did not reflect a strong influence of carbonate on uranium solubility, since these data were similar to the ones obtained in carbonate-free systems. The concentration of bicarbonate-carbonate species expected in solution at $8.5 \leq \text{pC}_{\text{H}^+} \leq 9.5$ was lower than the amount of uranium introduced in solution, so carbonate complexation could not occur in these conditions.

Lastly, the fourth pC_{H^+} region of interest is at $9.5 \leq \text{pC}_{\text{H}^+}$. In that pC_{H^+} region, the uranium concentrations were stable around 10^{-7} - 10^{-8} M. It is likely that hydrolysis overwhelmed any other possible effects on uranium solubility.

Our experimental results were in good agreement with the understanding of the carbonate effects on uranium (VI) solubility in similar media published in the literature [Clark 1995]. Carbonate can have a significant impact in uranium solubility in a certain range of pC_{H^+} and depending upon the amount of carbonate that was introduced in the solution. This conclusion from our experimental work corroborates what Clark observed [Clark 1995]: carbonate complexation will dominate the speciation of the uranyl ion as long as there is ample carbonate-bicarbonate available (see section 3.3). Also, according to Clark, when the uranyl ion concentration exceeds the carbonate concentration, hydrolysis competes with carbonate complexation and plays an increasingly important role [Clark 1995]. This was also demonstrated with our experiment results for pC_{H^+} beyond 9.5.

The range of pC_{H^+} when uranium and carbonate generated a complex that was stable in the WIPP simulated brines was determined to be between 8.5 and 9.5. We assume that this pC_{H^+} range could be extended in the higher pC_{H^+} values if the concentration of carbonate gets higher. In our WIPP simulated brines, at a pC_{H^+} range (between 8.5 and 9.5), an effect of carbonate on uranium concentrations was detected when the concentration of carbonate introduced initially into the solutions was 2×10^{-3} M. Higher concentration of carbonate should enhanced even more the carbonate complexation of uranium (VI). The initial carbonate concentration of 2×10^{-3} M was about an order of magnitude higher than the concentration of uranium introduced in solution when precipitation occurred in our experiments. This excess of carbonate could have allowed the soluble 2:3 complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$, or other polymeric complexes suggested by Grenthe *et al.* and Clark [Grenthe 1994, Clark 1995] to form in our experimental solutions (see section 3.3). Future spectroscopy work on our experimental samples could help to identify the major uranium carbonate species in solution.

Our experimental results, though, were different from the data collected for carbonate effects on uranium (VI) solubility in similar media, and published in the literature [Grenthe 1984, Kramer-Schnabel 1992, Yamazaki 1992, Reed 1997, Peper 2004]. For example, the experimental curves of the solubility of UO_2CO_3 obtained by Kramer-Schnabel *et al.* and Grenthe *et al.* (Figure 3-3) didn't match our solubility data. According to these published data, the uranium concentration in solution would be at the millimole level or higher when the concentration of carbonate is higher than micromole level. This is not what we observed in our experiments: the uranium concentrations measured in solution at any pC_{H^+} and for carbonate concentrations as high as 2 mM were below the millimole level. However, we must admit that the experimental points from Kramer-Schnabel *et al.* were obtained in the region $3 < \text{pH} < 6$ and for $-11 < \log[\text{CO}_3^{2-}] < -6$ where UO_2CO_3 is the solid phase. These

conditions were far different from our experimental conditions. Therefore, extrapolation of Kramer-Schnabel's data to our system is certainly not accurate.

Yamazaki *et al.* reported millimole concentrations of uranium (Figure 3-2) in his U(VI) solubility experiments performed in a synthetic brine at $pC_{H^+} = 8.4$ and in an air atmosphere [Yamazaki 1992]. Yamazaki's results at that pC_{H^+} value were over-estimating, by an order of magnitude, the results we obtained, even with the highest carbonate concentration introduced in the solutions ($[CO_3^{2-}]_{total} = 2 \times 10^{-3}$ M). The highest uranium concentration we measured in our experiments was in GWB at $pC_{H^+} \sim 9$ in the presence of 2 mM of carbonate: the value was 7.4×10^{-5} M. The difference between Yamazaki's results and ours is not readily explained based on what is published although one speculative explanation is that there was more carbonate present in this system than acknowledged by the author. At $pC_{H^+} = 10.4$, however, in a brine solution with an initial concentration of bicarbonate of 0.11 mM, Yamazaki *et al.* measured uranium concentrations in solution about 3.5×10^{-7} M. These uranium concentrations were approximately the same order of magnitude that we obtained in our experiments at the same pC_{H^+} and CO_3^{2-} conditions (Figure 4-36). At $pC_{H^+} = 10.4$, we expect hydrolysis to predominate over carbonate complexation. These data were a few orders of magnitude lower than the data obtained by Reed [1997]. In Reed's experiments conducted under a hydrogen atmosphere at $25 \pm 5^\circ C$, the uranium (VI) concentration was stable at approximately 1×10^{-4} M when measured as a function of time in ERDA-6 brine at $pH \sim 10$ in the presence of ~up to 10 mM CO_3^{2-} initially placed in solution [Reed 1997]. There is not a good explanation for these differences.

5.0 CONCLUSION

The solubility of uranium (VI) was determined in WIPP-relevant brines as a function of pC_{H^+} and ionic strength, both in the absence and presence of carbonate. Additionally, a literature review on the solubility of uranium (VI) 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 VI 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 or presence 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, and an upper limit of $\sim 10^{-4}$ M uranyl concentration at the reference pC_{H^+} WIPP case in the presence of carbonate
- Confirmed a lack of significant amphotericity in WIPP simulated brines at high pH values.
- Demonstrated a small effect of borate complexation in the pC_{H^+} range [7.5 – 10].

These experimental data on solubility of uranium (VI) in carbonate-free WIPP simulated brines were the first at high pC_{H^+} under WIPP conditions. They established uranium solubility, in the absence of carbonate that was 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 possibly with a less rigorous control of a carbon dioxide free environment than in our experiments. The lower uranium solubilities we reported herein were indicative of a good experimental protocol and point towards a lower overall solubility of uranium in the WIPP. 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 solubility trends observed in carbonate-free pointed towards lower uranium solubilities in WIPP brine, a lack of significant amphotericity, an insignificant effect of borate complexation, and a predominance of hydrolysis at $pC_{H^+} > 10.5$.

These experimental data were also the first data on the impact of carbonate on uranium solubility in WIPP brines. For WIPP-related conditions ($pC_{H^+} \sim 9$), the highest uranium solubility obtained experimentally was $\sim 10^{-4}$ M, which is an order of magnitude lower than the uranium (VI) solubility currently assumed by WIPP PA and mandated by the EPA. This high uranium solubility was obtained at the highest carbonate concentration (2×10^{-3} M) investigated which is ~ 10 times higher than the carbonate concentration

predicted by WIPP PA. Our experimental data obtained for an initial carbonate content of 2×10^{-4} M showed that the uranium solubility was then below 10^{-5} M, so more than two orders of magnitude lower than the currently used value of 10^{-3} M.

The data we reported in this document showed that the 1 mM value for uranium (VI) solubility used in WIPP PA was conservative, by over a factor of 50, relative to our experimental results. Our data clearly support the current position on An(VI) solubility under WIPP-relevant conditions.

6.0 QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION

The data presented in this report 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 four Test Plan-specific scientific notebooks designated ACP-TIP-002/1, ACP-TIP-002/3, ACP-TIP-002/4 and ACP-TIP-002/5 and in a series of 75 data packages designated U0 to U74. Table 6.0 gives the title of these 75 data packages. Copies of the scientific notebooks and the data packages are kept at the LANL-CO Record Center. Data shown in ACRSP-generated figures in this document are traceable to the scientific notebooks and data packages. Documentation of this linkage is included in data package U74. 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 – Subtask 1 – U0 – U stock
U1	LCO-ACP-02 Task 1 – Subtask 1 – U1 – Sampling #1
U2	LCO-ACP-02 Task 1 – Subtask 1 – U2 – Sampling #2
U3	LCO-ACP-02 Task 1 – Subtask 1 – U3 – Sampling #3
U4	LCO-ACP-02 Task 1 – Subtask 1 – U4 – Sampling #4
U5	LCO-ACP-02 Task 1 – Subtask 1 – U5 – Sampling #5
U6	LCO-ACP-02 Task 1 – Subtask 1 – U6 – Sampling #6
U7	LCO-ACP-02 Task 1 – Subtask 1 – U7 – Sampling #7
U8	LCO-ACP-02 Task 1 – Subtask 1 – U8 – Sampling #8
U9	LCO-ACP-02 Task 1 – Subtask 1 – U9 – Sampling #9
U10	LCO-ACP-02 Task 1 – Subtask 1 – U10 – Sampling #10
U11	LCO-ACP-02 Task 1 – Subtask 1 – U11 – Sampling #11
U12	LCO-ACP-02 Task 1 – Subtask 1 – U12 – Sampling #12
U13	LCO-ACP-02 Task 1 – Subtask 1 – U13 – Sampling #13
U14	LCO-ACP-02 Task 1 – Subtask 1 – U14 – Sampling #14
U15	LCO-ACP-02 Task 1 – Subtask 1 – U15 – Sampling #15
U16	LCO-ACP-02 Task 1 – Subtask 1 – U16 – Sampling #16
U17	LCO-ACP-02 Task 1 – Subtask 1 – U17 – Sampling #17
U18	LCO-ACP-02 Task 1 – Subtask 1 – U18 – Sampling #18
U19	LCO-ACP-02 Task 1 – Subtask 1 – U19 – Sampling #19
U20	LCO-ACP-02 Task 1 – Subtask 3 – U20 – Sampling #1
U21	LCO-ACP-02 Task 1 – Subtask 3 – U21 – Sampling #2
U22	LCO-ACP-02 Task 1 – Subtask 3 – U22 – Sampling #3
U23	LCO-ACP-02 Task 1 – Subtask 3 – U23 – Sampling #4
U24	LCO-ACP-02 Task 1 – Subtask 3 – U24 – Sampling #5

U25	LCO-ACP-02 Task 1 – Subtask 3 – U25 – Sampling #6
U26	LCO-ACP-02 Task 1 – Subtask 3 – U26 – Sampling #7
U27	LCO-ACP-02 Task 1 – Subtask 3 – U27 – Sampling #8
U28	LCO-ACP-02 Task 1 – Subtask 3 – U28 – Sampling #9
U29	LCO-ACP-02 Task 1 – Subtask 3 – U29 – Sampling #10
U30	LCO-ACP-02 Task 1 – Subtask 3 – U30 – Sampling #11
U31	LCO-ACP-02 Task 1 – Subtask 3 – U31 – Sampling #12
U32	LCO-ACP-02 Task 1 – Subtask 3 – U32 – Sampling #13
U33	LCO-ACP-02 Task 1 – Subtask 3 – U33 – Sampling #14
U34	LCO-ACP-02 Task 1 – Subtask 3 – U34 – Sampling #15
U35	LCO-ACP-02 Task 1 – Subtask 3 – U35 – Sampling #16
U36	LCO-ACP-02 Task 1 – Subtask 3 – U36 – Sampling #17
U37	LCO-ACP-02 Task 1 – Subtask 3 – U37 – Sampling #18
U38	LCO-ACP-02 Task 1 – Subtask 4 – U38 – Sampling #1
U39	LCO-ACP-02 Task 1 – Subtask 4 – U39 – Sampling #2
U40	LCO-ACP-02 Task 1 – Subtask 4 – U40 – Sampling #3
U41	LCO-ACP-02 Task 1 – Subtask 4 – U41 – Sampling #4
U42	LCO-ACP-02 Task 1 – Subtask 4 – U42 – Sampling #5
U43	LCO-ACP-02 Task 1 – Subtask 4 – U43 – Sampling #6
U44	LCO-ACP-02 Task 1 – Subtask 4 – U44 – Sampling #7
U45	LCO-ACP-02 Task 1 – Subtask 4 – U45 – Sampling #8
U46	LCO-ACP-02 Task 1 – Subtask 4 – U46 – Sampling #9
U47	LCO-ACP-02 Task 1 – Subtask 4 – U47 – Sampling #10
U48	LCO-ACP-02 Task 1 – Subtask 4 – U48 – Sampling #11
U49	LCO-ACP-02 Task 1 – Subtask 4 – U49 – Sampling #12
U50	LCO-ACP-02 Task 1 – Subtask 4 – U50 – Sampling #13
U51	LCO-ACP-02 Task 1 – Subtask 4 – U51 – Sampling #14
U52	LCO-ACP-02 Task 1 – Subtask 4 – U52 – Sampling #15
U53	LCO-ACP-02 Task 1 – Subtask 5 – U53 – Sampling #1
U54	LCO-ACP-02 Task 1 – Subtask 5 – U54 – Sampling #2

U55	LCO-ACP-02 Task 1 – Subtask 5 – U55 – Sampling #3
U56	LCO-ACP-02 Task 1 – Subtask 5 – U56 – Sampling #4
U57	LCO-ACP-02 Task 1 – Subtask 5 – U57 – Sampling #5
U58	LCO-ACP-02 Task 1 – Subtask 5 – U58 – Sampling #6
U59	LCO-ACP-02 Task 1 – Subtask 5 – U59 – Sampling #7
U60	LCO-ACP-02 Task 1 – Subtask 5 – U60 – Sampling #8
U61	LCO-ACP-02 Task 1 – Subtask 5 – U61 – Sampling #9
U62	LCO-ACP-02 Task 1 – Subtask 5 – U62 – Sampling #10
U63	LCO-ACP-02 Task 1 – Subtask 5 – U63 – Sampling #11
U64	LCO-ACP-02 Task 1 – Subtask 5 – U64 – Sampling #12
U65	LCO-ACP-02 Task 1 – Subtask 8 – U65 – Sampling #1
U66	LCO-ACP-02 Task 1 – Subtask 8 – U66 – Sampling #2
U67	LCO-ACP-02 Task 1 – Subtask 8 – U67 – Sampling #3
U68	LCO-ACP-02 Task 1 – Subtask 8 – U68 – Sampling #4
U69	LCO-ACP-02 Task 1 – Subtask 8 – U69 – Sampling #5
U70	LCO-ACP-02 Task 1 – Subtask 8 – U70 – Sampling #6
U71	LCO-ACP-02 Task 1 – Subtask 8 – U71 – Sampling #7
U72	LCO-ACP-02 Task 1 – Subtask 8 – U72 – Sampling #8
U73	LCO-ACP-02 Task 1 – Subtask 8 – U73 – Sampling #9
U74	Summary Data Package for this document

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
- [Borkowski 2009] Borkowski M., J.F. Lucchini, Reed D.T., M.K. Richmann, Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations, LCO-ACP-08, LANL-CO\ACRSP Report. LA-14360, Los Alamos, NM: Los Alamos National Laboratory (2009)
- [Brady 1948] Brady L.J., C.D. Susano, C.E. Larson, Chemical and Physical Properties of Uranium Peroxide, United States Atomic Energy Commission, Oak Ridge, AECD-2369 Report (1948)
- [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
- [Brush 2009] Brush L.H., Y. Xiong, J.J. Long, Results of the Calculations of Actinide Solubilities for the WIPP CRA-2009 PABC, Sandia National Laboratories Carlsbad Programs Group, Carlsbad, NM, Analysis Report, October 7, 2009. ERMS 552201.
- [Cahill 1990] Cahill, A.E., L.E. Burkhart, Continuous precipitation of uranium with hydrogen peroxide, *Metallurgical Transactions B* **21B** (1990) 819
- [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 191 Compliance Certification Application for the Waste Isolation Pilot Plant, DOE/CAO-1996-2184, October 1996, DOE Carlsbad Field Office, Carlsbad, NM
- [EPA 2005] 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 2006] 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 2010] Evaluation of the Compliance Recertification Actinide Source Term, Backfill Efficacy and Culebra Dolomite Distribution Coefficient Values, Technical Support Document for Section 194.24, November 2010, U.S. Environmental Protection Agency Office of Radiation and Indoor Air
- [Fanghänel 2002] Fanghänel, T.; Neck, V.: Aquatic Chemistry and Solubility Phenomena of Actinide Oxides/Hydroxides. *Pure and Applied Chemistry* **74/10**, 1895-1907 (2002).
- [Grenthe 1984] Grenthe, I., D. Ferri, F. Salvatore, and G. Riccio., Studies on Metal Carbonate Equilibria. Part 10. A Solubility Study of the Complex Formation in the Uranium (VI)-Water-Carbon Dioxide (g) System at 25°. *Journal of Chemical Society, Dalton Trans.* (1984) 2439–43.
- [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 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
- [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
- [Lucchini 2010a] Lucchini J.F., H. Khaing, M. Borkowski, M.K. Richmann, D.T. Reed, Actinide (VI) Solubility in Carbonate-free WIPP Brine: Data Summary and Recommendations, LCO-ACP-10, LANL-CO\ACRSP Report. LA-UR-10-00497. Los Alamos, NM: Los Alamos National Laboratory (2010)
- [Lucchini 2010b] Lucchini J.F., H. Khaing, D.T. Reed, Uranium (VI) Solubility in Carbonate-free ERDA-6 Brine, Scientific Basis for Nuclear Waste Management XXXIV, edited by K.L. Smith, S. Kroeker, B. Uberuaga, K.R. Whittle, Material Research Society Symposium Proceedings, Volume 1265. LA-UR-10-01817 (2010)

- [Lucchini 2011] Lucchini J.F., H. Khaing, M.K. Richmann, D.T. Reed, Uranium (VI) Solubility in Carbonate-free WIPP Brine, submitted to *Radiochimica Acta*. LA-UR-11-10963 (2011)
- [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
- [PAIR-2008] Crawford B., D. Guerin, S. Lott, B. McInroy, J. McTaggart, G. Van Soest, Performance Assessment Inventory Report, LANL-CO\Inventory Report INV-PA-08, Revision 0. LA-UR-09-02260. Los Alamos, NM: Los Alamos National Laboratory (2009)
- [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)
- [Peper 2004] Peper S.M., L.F. Brodnax, S.E. Field, R.A. Zehnder, S.N. Valdez, W.H. Runde, Kinetic Study of the Oxidative Dissolution of UO₂ in Aqueous Carbonate Media, *Ind. Eng. Chem. Res.* **43** (2004) 8188-8193
- [Perrin 1976] Perrin A., Structure Cristalline du Nitrate de Dihydroxo Diuranyle Tetrahydrate, *Acta Crystallographica* **B32** (1976) 1658-1661
- [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 1997] Reed, D.T., D. G. Wygmans, Actinide Stability/Solubility in Simulated WIPP Brine, WPO44625. Argonne, IL: Argonne National Laboratory, Actinide Speciation and Chemistry Group, Chemical Technology Group (1997)
- [Reed 2010] Reed, D.T., Private Communication (2010)
- [Runde 2000] Runde W. The Chemical Interactions of Actinides in the Environment. *Los Alamos Science*, **26** (2000) 330
- [SOTERM 2003] Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2004, Appendix PA, Attachment SOTERM, November 10 (2003) DOE Carlsbad Field Office, Carlsbad, NM

- [SOTERM 2009] Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2009, Appendix PA, Attachment SOTERM, DOE Carlsbad Field Office, Carlsbad, NM
- [TWBIR-2004] U.S. Department of Energy (DOE), Transuranic Waste Baseline Inventory Report – 2004, Revision 0, DOE/TRU-2006-3344, DOE Carlsbad Field Office, Carlsbad, NM (2006)
- [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