WPO 39856

9.5 Hobart, D. E. and R. C. Moore 1996. ***Analysis of Uranium (VI) Solubility Data for WIPP Performance Assessment*** **WBS 1.1.10.1.1**

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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

ANALYSIS OF URANIUM(VI) SOLUBILITY DATA FOR WIPP PERFORMANCE ASSESSMENT

WBS 1.1.10.1.1

REVISION 0

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D. E. Hobart and R. Moore

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1.0 Analysis of Uranium(VI) Solubility for WIPP Performance Assessment

1.1 Scope and Purpose of the Analysis

The purpose of this document is to provide an analysis of the available data on the solubility of uranium(VI) expected in a brine-inundated WIPP waste repository room. The concentrations of uranium and other radionuclides (Th, Np, Pu, Am, and Cm) is important in assessing the performance of the WIPP. Upper limit concentrations (solubility limits) provide the "source term" for potential releases of radionuclides to the accessible environment in future human intrusion scenarios. The present analysis is based on results from both extant published literature data and WIPP-directed experimental programs. This analysis was a result of critical assessment by an *ad hoc* Analysis Committee (see Appendix B).

1.2 Summary of the Analysis

The development of thermodynamic models for predicting the solubilities of actinide elements in an inundated WIPP repository have been completed by the WIPP Source Term Project (managed by Sandia National Laboratories and performed at Florida State University and Argonne, Lawrence Livermore, Lawrence Berkeley, Los Alamos, and Pacific Northwest National Laboratories). The models for the trivalent (III), tetravalent (IV), and pentavalent (V) oxidation states have been successfully completed, however, the actinide hexavalent (VI) model is insufficient at this time. Development of the VI model has been difficult for a number of historically significant reasons. For example, the hydrolysis (complexation by hydroxide ligands) behavior is extremely complicated and the carbonate complexation behavior is controversial and is just now being elucidated.

Since uranium is the only actinide element expected to be in the hexavalent state (Weiner *et al.*, 1996) this document addresses only uranium(VI) solubility behavior. The net result of this analysis is a prediction of the concentration of uranium(VI) for use in Performance Assessment calculations. A review of the published literature and WIPP directed research is expected to provide solubility limits for uranium(VI) under conditions expected in a brine inundation scenario. With the recent development of including chemical controls (engineered backfill materials) in the repository design (magnesium oxide), the intruding brine conditions are anticipated to be near pH 9 to 10. In addition, the backfill is expected to effectively absorb microbially-generated CO_2 gas from the repository room, effectively eliminating the potential for the formation of highly soluble actinide carbonate complexes. The literature and experimental solubility data used in the analysis are included in Table 1.

Table 1.
Summary of Selected Solubility Data for Uranium(VI)

Conc. (m)	pH	pCO_2	molality	Solid	Reference
Published Literature Data					
3×10^{-6}	6.4	1 atm	3.8	UO_3-$2H_2O$	Yamazaki *et al.* (1992)
2×10^{-3}	8.4	1 atm	3.8	U_3O_8	Yamazaki *et al.* (1992)
2×10^{-7}	10.4	low	3.6	$K_2U_2O_7$	Yamazaki *et al.* (1992)
10^{-3} to 10^{-6}	4-5	0.03 %	0.1	UO_2CO_3	Pashalidas *et al.* (1993)
Project Experimental Data					
2.3×10^{-6}	7.0	absent	5.1	unknown	Reed *et al.* (1996)
2.6×10^{-7}	8.0	present	4.8	unknown	Reed *et al.* (1996)
$8.8 \times 10^{-5*}$	10.0	absent	4.8	unknown	Reed *et al.* (1996)
$9.2 \times 10^{-5*}$	10.0	present	4.8	unknown	Reed *et al.* (1996)
8.3×10^{-4}	4.9	absent	5.2	UO_2OH_2(?)	Palmer *et al.* (1996)
2.8×10^{-6}	9.8	absent	5.2	UO_2OH_2(?)	Palmer *et al.* (1996)
$9.0 \times 10^{-6*}$	9.7	unknown	unknown	unknown	Villareal *et al.* (1996)

* Not at steady state conditions.

2.0 Analysis of Uranium(VI) Solubility Data

2.1 Background

Development of reliable thermodynamic models based on Pitzer formalism for prediction of actinide element solubilities has been successfully accomplished for the actinide III, IV, and V oxidation states (Novak *et al.*, 1996). The actinide(VI) model, however, has not yet been sufficiently developed for reliable use in predicting concentration of An(VI) in WIPP brines under various solution conditions. Uranium(VI) solubility modeling has proven difficult even after fifty years of research. The hydrolysis behavior of U(VI) is an important component of the model and is quite complex and not well known. Even given a great deal more funding and effort, it is unlikely that a model could be constructed for Actinide(VI) solubility in the near future. The hexavalent states of neptunium and plutonium are not expected to be present in the repository rooms and are thus not included in WIPP PA calculations by virtue of their ready reduction in the presence of excessive amounts of elemental iron(0) and soluble iron(II). (Weiner *et al.*, 1996) Uranium(VI) can also be reduced to uranium(IV) in the presence of iron(0) and iron(II), however, a number of oxidants are readily available for "re-oxidizing" uranium back to the (VI) state. These oxidants include, Fe(III), Np(IV), and Pu(IV), to name a few. Consequently, uranium is the only actinide element expected to exist in WIPP brines in the hexavalent state. Published literature data and experimental data collected under contract to the WIPP project have been analyzed for MgO backfill-specific pH regions in the absence of CO_2.

2.2 Literature Data

Published literature values for uranium(VI) solubilities under various conditions used for this analysis are provided in Table 1 and include reasonably high values of 2×10^{-3} molal at pH 8.4 in the presence of carbon dioxide, which promotes the formation of quite soluble uranium(VI) carbonate complexes (Yamazaki *et al.* ,1992). Note, however, that in this same publication, that at a slightly higher pH value of 10.4 and in the absence of carbonate ions in solution, the U(VI) solubility dropped to 1.5×10^{-7} molal! Pashalidis *et al.* (1993) report a values ranging from 10^{-3} to 10^{-5} even with 0.03% carbon dioxide present.

2.3 WIPP Specific Experimental Data

Laboratory experiments presently in progress in WIPP brines by Reed *et al.*(1996) provide U(VI) solubility values of 8.8×10^{-5} molal with carbonate absent at pH 10. These results should be regarded as preliminary since some of the vessels are still approaching steady state conditions. In previous experiments, Palmer *et al.*, (1996) reported values of 8.3×10^{-4} m at pH 4.9 and down to 2.8×10^{-6} at pH 9.8 in the absence of carbonate. Further, empirical results are reported by Villareal *et al.*,.(1996) on Source Term Test Program (STTP) experiments with simulated wastes at Los Alamos National Laboratory. Preliminary data of uranium(VI) solubilities of 9×10^{-9} m at pH 9.7 for some containers. Although STTP results are reported herein, these should be considered as highly provisional because the containers are by no means at steady state conditions nor under highly defined parameters. These data are being used in this analysis only to acknowledge data showing solubility values well below the value provided by this present analysis.

2.4 Assessment

Based on analysis of literature data and WIPP Project experimental data (primarily from experiments that have reached or are approaching steady state conditions), it was determined that all of the values fall within an order of magnitude or thereabouts to a concentration value of approximately 1 x 10^{-5} molal. Therefore, based on the best information available, ***a value of 1.0 x 10^{-5} molal is provided*** for the uranium(VI) concentration input parameter for performance assessment calculations for WIPP. This value is consistent with recommendations set forth by the Expert Panel Elicitation for Source Term conducted in 1990. With little relevant experimental data available at the time, this panel suggested a value of 3.0 x 10^{-5} M for the 25th fractile value. (Hobart *et al.*, 1996).

3.0 References

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Yamazaki, H., Lagerman, B., Symeopoulos, V., and Choppin, G., (1992) "Solubility of Uranyl in Brine," *Proceedings of the Third International High Level Radioactive Waste Management Conference*, Las Vegas, NV, April 12-16, 1992, Am.Nucl. Society, La Grange Park and Am. Soc. of Engineers, New York.

Appendix A

Information required by QAP 9-1

The authors are qualified to analyze solubility data from a variety of sources. They are experts at one or more of the following areas: actinide chemistry, geochemistry, environmental chemistry, computer modeling of environmental systems, and data analysis. Furthermore the Analysis Committee consisted of a number of qualified scientists with expertise in a wide variety of relevant subjects.

Appendix B

Concurrence of the Analysis Committee

R. V. Bynum		5/28/96
R. Vand Bynum, SAIC	Signature	Date
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David E. Hobart		5/28/96
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