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Sandia National Laboratories
Waste Isolation Pilot Plant

Calculation of Actinide Solubilities for the WIPP Performance-Assessment Baseline Calculations, Analysis Plan AP-120, Rev. 0

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1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1 defines the abbreviations, acronyms, and initialisms used in this analysis plan (AP).

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym or Initialism	Definition
Am	Americium
am	Amorphous
anhydrite	CaSO ₄
An(III)	actinide element(s) in the +III oxidation state
An(IV)	actinide(s) in the +IV oxidation state
An(V)	actinide(s) in the +V oxidation state
An(VI)	actinide(s) in the +VI oxidation state
AP	analysis plan
aq	Aqueous
ASTP	(WIPP) Actinide Source Term Program
B(OH) _x ³⁻	boric acid/borate
Br, Br ⁻	bromine, bromide (ion)
Brine A	a synthetic brine representative of intergranular Salado brines
brucite	Mg(OH) ₂
C	Carbon
Ca, Ca ²⁺	calcium, calcium ion
calcite	CaCO ₃
CCA	(WIPP) Compliance Certification Application, submitted to the EPA in October 1996
Cl, Cl ⁻	chlorine, chloride ion
CMS	(SNL/WIPP software) Configuration Management System
CO ₂	carbon dioxide
CO ₃ ²⁻	carbonate ion
CPG	(SNL) Carlsbad Programs Group
CRA-2004	(WIPP) Compliance Recertification Application, submitted to the EPA in March 2004
DOE	(U.S.) Department of Energy
EDTA	Ethylenediaminetetraacetate
EPA	(U.S.) Environmental Protection Agency
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)

Table 1. Abbreviations, Acronyms, and Initialisms (cont.).

Abbreviation, Acronym or Initialism	Definition
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
f_{CO_2}	fugacity (similar to the partial pressure) of CO_2
Fe	Iron
Fm.	Formation or formation, depending on usage
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
g	Gaseous
glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
H_2O	water (aq or g)
halite	NaCl
HCO_3^-	bicarbonate ion
hydromagnesite	$\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
K, K^+	potassium, potassium ion
L	liter(s)
LANL	Los Alamos National Laboratory
M	Molar
m	Molal
magnesite	MgCO_3
Mg, Mg^{2+}	magnesium, magnesium ion
mg	milligram(s)
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various impurities
mM	Millimolar
Na, Na^+	sodium, sodium ion
nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$
NP	Nuclear Waste Management Procedure
Np	Neptunium
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
OH ⁻	hydroxide ion
PA	performance assessment
PAVT	(WIPP) Performance Assessment Verification Test

Table 1. Abbreviations, Acronyms, and Initialisms (cont.).

Abbreviation, Acronym or Initialism	Definition
pH	the negative, common logarithm of the activity of H ⁺
Pu	Plutonium
Rev.	Revision
SNL	Sandia National Laboratories
SO ₄ ²⁻	sulfate ion
SPC	Salado Primary Constituents, a synthetic brine similar to Brine A
TDS	total dissolved solids
Th	Thorium
TRU	transuranic waste
U	Uranium
VMS	virtual memory system
WIPP	(U.S. DOE) Waste Isolation Pilot Plant

2 REVISION HISTORY

This is the original version of this AP. The objectives and content of any revisions of this AP will be described in this section of subsequent versions. Changes to this AP, other than those defined as editorial changes by Sandia National Laboratories' (SNL's) Nuclear Waste Management Procedure (NP) 9-1 (see Section 9), shall be reviewed and approved by the same organization(s) that carried out the original review and approval.

3 INTRODUCTION

This AP describes how we will calculate actinide (An) solubilities for use in the An source term for the U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) Performance Assessment Baseline Calculation (PABC). This AP also describes a new An solubility estimate and a change in the colloidal actinide source term required for the PABC.

The WIPP Actinide Source Term Program (ASTP) was a DOE program to establish actinide solubilities and colloidal actinide concentrations for the CCA PA calculations (see U.S. DOE, 1996, Appendix SOTERM). After the CCA PA, additional An solubility studies were carried out (U.S. DOE, 2004, Appendix PA, Attachment SOTERM).

Brush and Xiong (2003a) provided a detailed review of the An solubility calculations for the 1996 CCA PA, the 1997 WIPP Performance Assessment Verification Test (PAVT), and the PA calculations for the first WIPP Compliance Recertification Application (CRA-2004 PA). Therefore, this AP does not discuss these previous calculations in detail.

Thermodynamic speciation and solubility models featuring the Pitzer activity-coefficient model are used to predict the solubilities of actinides in the +III, +IV, and +V oxidation states (An(III), An(IV), and An(V)) under the conditions expected in WIPP disposal rooms. The development of these models by the WIPP ASTP is described in U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM). These models are implemented in the speciation and solubility code Fracture Matrix Transport (FMT) (Babb and Novak, 1997 and addenda; Wang, 1998). Prior to the An(III), An(IV), and An(V) speciation and solubility calculations, the conditions expected in the WIPP have been defined by the EQ3/6 geochemical software package (Daveler and Wolery, 1992; Wolery, 1992a; 1992b; Wolery and Daveler, 1992) and/or FMT.

The ASTP did not develop a thermodynamic speciation and solubility model for the solubility of actinides in the +VI oxidation state (An(VI)). Instead, Hobart (1996) and Hobart and Moore (1996a, 1996b) estimated the solubility of U(VI) for the CCA PA. This estimate was also used for the PAVT and the CRA-2004 PA. This estimate is also described in U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM).

The ASTP carried out laboratory studies to quantify the colloidal source term for the CCA PA (U.S. DOE, 1996, Appendix SOTERM). No additional studies of An colloids have been conducted since the CCA PA, and only a minor change was made in the colloidal source term for the CRA-2004 PA (Brush and Xiong, 2003a; U.S. DOE, 2004, Appendix PA, Attachment SOTERM).

4 OBJECTIVES

The primary objective of this analysis is to calculate An(III), An(IV), and An(V) speciation and solubilities for the PABC An source term.

This AP also includes a new U(VI) solubility estimate and a change in the colloidal An source term for the PABC.

5 APPROACH

This section describes the approaches we will use to calculate An(III), An(IV), and An(V) solubilities under conditions expected in WIPP disposal rooms for the PABC source term (see Subsection 5.1).

This section also includes a new estimate of the solubility of An(VI) (Subsection 5.2) and a change in the colloidal source term (Subsection 5.3).

5.1 Chemical Conditions

Definition of the chemical conditions for the PABC An source term will feature: (1) use of Generic Weep Brine (GWB) and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) to simulate Salado and Castile brines, respectively; (2) the assumption that instantaneous, reversible equilibria among GWB or ERDA-6, major Salado minerals such as halite (NaCl) and anhydrite (CaSO₄), and the MgO hydration and carbonation products brucite (Mg(OH)₂) and hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) will control chemical conditions, such as f_{CO₂}, pH, and brine composition; (3) elimination of separate, slightly different chemical conditions characteristic of the absence of microbial activity from the calculations; and (4) use of FMT to calculate these chemical conditions.

The rest of Subsection 5.1 explains these features in detail (see Subsections 5.1.1 through 5.1.4 below).

5.1.1 Use of GWB and ERDA-6 to Simulate WIPP Brines

We will continue to use GWB and ERDA-6 for the An speciation and solubility calculations for the PABC source term.

The ASTP used three synthetic solutions to simulate brines that could be present in the WIPP after filling and sealing: (1) Brine A, representative of intergranular (grain-boundary) brines from the Salado Formation (Fm.) at or near the stratigraphic horizon of the repository (Molecke, 1983); (2) Salado Primary Constituents (SPC) brine, a modified formulation of Brine A (Novak and Moore (1996), Novak et al. (1996), and Novak (1997); and (3) ERDA-6, typical of fluids in brine reservoirs in the underlying Castile Fm. (Popielak et al., 1983). Novak et al. (1996) and Novak (1997) used SPC and ERDA-6 for the An solubility calculations for the CCA PA source term (U.S. DOE, 1996, Appendix SOTERM) and the PAVT, respectively.

After the CCA PA, J. L. Krumhansl of SNL defined GWB as a representative, intergranular Salado brine for use in laboratory studies of MgO in Albuquerque in the mid-to-late 1990s. During the 2000s, investigators at SNL in Carlsbad have used GWB to simulate Salado brines in their laboratory and modeling studies of MgO.

Brush and Xiong (2003a) used GWB (Snider, 2003) and ERDA-6 for the An solubility calculations for the CRA-2004 PA. Snider (2003) documented the formulation of GWB for use in the CRA-2004 PA; Brush and Xiong (2003a) provided additional justification for the use of GWB. In brief, they used GWB "because this brine resembles the average composition of intergranular Salado brines at or near the stratigraphic horizon of the WIPP more closely than Brine A." Table 1 provides the compositions of Brine A, GWB, and ERDA-6.

Table 1. Compositions of Brine A, GWB, and ERDA-6 Prior to Reaction.

Element or Property	Brine A ^A	GWB ^B	ERDA-6 ^C
$B(OH)_x^{3-x}$	20 mM	158 mM	63 mM
Na^+	1.83 M	3.53 M	4.87 M
Mg^{2+}	1.44 M	1.02 M	19 mM
K^+	770 mM	467 mM	97 mM
Ca^{2+}	20 mM	14 mM	12 mM
SO_4^{2-}	40 mM	177 mM	170 mM
Cl^-	5.35 M	5.86 M	4.8 M
Br^-	10 mM	26.6 mM	11 mM
Total inorganic C (as HCO_3^-)	10 mM	-	16 mM
pH	6.5	-	6.17
Specific gravity	1.2	1.2	1.216
TDS	306,000 mg/L	-	330,000 mg/L

A. From Molecke (1983).

B. From Popielak et al. (1993).

C. From Snider (2003).

Brush and Xiong (2003a) carried out solubility calculations with both GWB and Brine A to compare the results of these Salado brines; the results obtained with these brines were very similar (Brush and Xiong, 2003c; Downes, 2003a, 2003b). Because GWB is more representative

of intergranular Salado brine than Brine A and because the solubilities obtained with these brines are so similar, only the results obtained with GWB were used for the CRA-2004 PA (U.S. DOE, 2004, Appendix PA, Attachment SOTERM).

5.1.2 Use of Brine-Solid Equilibria to Control Chemical Conditions

We will continue to assume that instantaneous, reversible equilibria among WIPP brines, major Salado minerals, and MgO hydration and carbonation products will control (buffer) chemical conditions such as f_{CO_2} , pH, and brine composition for the An speciation and solubility calculations for the PABC source term. This assumption is an important feature of the conceptual model of the geochemical behavior of WIPP disposal rooms.

The f_{CO_2} , pH, and brine composition calculated with geochemical speciation and solubility codes such as EQ3NR (Wolery, 1992b) or FMT (Babb and Novak, 1997 and addenda; Wang, 1998), or with geochemical reaction-path codes such as EQ6 (Wolery and Daveler, 1992), are then used - along with other input parameters - in FMT to calculate An(III), An(IV), and An(V) solubilities. Brush and Xiong (2003a) described the history of assumptions as to which brines, evaporite minerals, and MgO hydration and carbonation products will control chemical conditions in the WIPP.

For the PABC, it will be assumed that equilibria among GWB or ERDA-6; minerals such as halite (NaCl), anhydrite (CaSO₄), and glauberite (Na₂Ca(SO₄)₂); and the MgO hydration and carbonation products brucite (Mg(OH)₂), Mg₂Cl(OH)₃·4H₂O, and hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) will control chemical f_{CO_2} , pH, and brine composition. In particular, the reaction

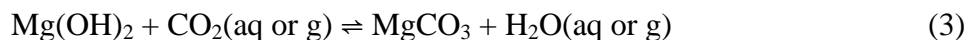


will buffer f_{CO_2} ; and the reaction



will buffer pH (Brush and Xiong, 2003a).

Actually, magnesite (MgCO₃) is the thermodynamically stable, Mg-carbonate mineral under the conditions expected in the WIPP. Furthermore, magnesite is present in the Salado at the stratigraphic horizon of the repository. Therefore, the reaction



would be expected to buffer f_{CO_2} in the WIPP *if* the kinetics of magnesite formation were fast enough for this phase to replace hydromagnesite or other metastable, hydrous Mg carbonates during the 10,000-year period of performance of the repository. However, the EPA specified that the brucite-hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) carbonation reaction (see Reaction 1

above) be used to calculate f_{CO_2} for the An solubility calculations for the PAVT and subsequent PA calculations. Use of the brucite hydromagnesite buffer *does not* preclude the possibility that magnesite will replace brucite to a significant extent - or entirely - in 10,000 years. Based on its review of the CCA (U.S. DOE, 1996), the EPA concluded that hydromagnesite will dehydrate to magnesite in hundreds to thousands of years (U.S. EPA, 1998):

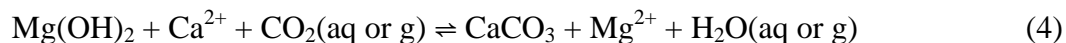
"The available rate data indicate that some portion, perhaps all, of the hydromagnesite will be converted to magnesite over the 10,000-year period for repository performance. The exact time required for complete conversion has not been established for all chemical conditions. However, the available laboratory and field data clearly indicate that magnesite formation takes from a few hundred to, perhaps, a few thousand years. Thus, the early repository conditions can be best represented by the equilibrium between brucite and hydromagnesite. These conditions will eventually evolve to equilibrium between brucite and magnesite."

Nevertheless, the brucite-hydromagnesite carbonation reaction (Reaction 1) has been used to calculate f_{CO_2} for the An solubility calculations for the PAVT and the CRA-2004 PA, and will be used for the PABC.

5.1.3 Elimination of Conditions Characteristic of the Absence of Microbial Activity

We will eliminate separate, slightly-different, chemical conditions characteristic of the absence of microbial activity from the An speciation and solubility calculations for the PABC source term.

Brush and Xiong (2003a) defined separate, slightly-different, chemical conditions characteristic of the absence of microbial activity for the An solubility calculations for the CRA-2004 PA. They concluded that - in the absence of microbial activity - the reaction



would buffer f_{CO_2} , and specified that this f_{CO_2} buffer be used for nonmicrobial vectors.

For the CCA PA, the PAVT, and the CRA-2004 PA, the conceptual model for microbial activity in WIPP disposal rooms featured a probability of 0.5 for significant microbial activity. In the event of significant microbial activity, microbes consumed 100% of the cellulosic materials in the repository. Furthermore, there was a conditional probability of 0.5 that microbes would consume all of the plastic and rubber materials after consuming all cellulosic materials. Thus, there was no microbial activity in about 50% of the PA vectors; microbial consumption of all cellulosic materials, but no plastic or rubber materials, in about 25% of the PA vectors; and microbial consumption of all of the cellulosic, plastic, and rubber materials in the remaining 25% of the vectors. Brush and Xiong (2003a) provided a detailed, geochemical explanation of why use of the brucite-calcite (CaCO_3) carbonation reaction to buffer f_{CO_2} , is appropriate in

the absence of microbial activity. Therefore, values of f_{CO_2} obtained from Reaction 4 were used to calculate An solubilities for the nonmicrobial CRA-2004 PA vectors.

However, the EPA has specified that the microbial conceptual model be changed for the PABC such that there will be a probability of 1 for significant microbial activity in the WIPP (Cotsworth, 2005, Enclosure 1). Therefore, nonmicrobial vectors will be eliminated from the PABC, and the brucite-calcite carbonation reaction will not be used to buffer f_{CO_2} for any of the An solubility calculations.

5.1.4 Use of FMT to Calculate Chemical Conditions

We will continue to use the speciation and solubility code FMT (Babb and Novak, 1997 and addenda; Wang, 1998) to calculate chemical conditions such as f_{CO_2} , pH, and brine composition in WIPP disposal rooms, consistent with the assumptions and specifications described throughout Subsections 5.1 and 5.2.

EQ3NR (Wolery, 1992b) and EQ6 (Wolery and Daveler, 1992) have been used for other purposes (e.g., to show that lime (CaO) or portlandite (Ca(OH)₂) would not overwhelm the capacity of the Mg(OH)₂ pH buffer). However, FMT was used to calculate the chemical conditions used for the actinide speciation and solubility calculations for the CCA PA, the PAVT, and the CRA-2004 PA (Brush and Xiong, 2003a; 2003c; Downes, 2003a, 2003b).

5.2 Actinide Solubilities

The An(III), An(IV), and An(V) speciation and solubility calculations for the PABC source term will feature: (1) use of thermodynamic speciation and solubility models based on the Pitzer activity-coefficient model to calculate Th(IV), Np(V), and Am(III) solubilities; (2) use of instantaneous, reversible equilibria among GWB or ERDA-6 and An-bearing solids such as amorphous ThO₂, KNpO₂CO₃, and Am(OH)₃ to control An solubilities; (3) inclusion of the effects of organic ligands on An solubilities; (4) use of FMT to calculate Th(IV), Np(V), and Am(III) solubilities; (5) use of a new version of the FMT thermodynamic database to calculate An solubilities; (6) speciation of Th, U, Np, Pu, and Am entirely as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III); (7) use of the oxidation-state analogy to apply the solubilities calculated for Th(IV) to U(IV), Np(IV), and Pu(IV); and to apply the solubilities calculated for Am(III) to Pu(III) (the model developed for Np(V) will be used only for Np(V)); and (8) use of the new uncertainty ranges and probability distributions established by Xiong et al. (2004) for the solubilities calculated for An(III) and An(V) solubilities, and establishment of a revised new range and distributions for An(IV) solubilities.

We will also use a new U(VI) solubility estimate for the PABC source term.

The rest of Subsection 5.1 explains these features in detail (see Subsections 5.2.1 through 5.2.9 below).

5.2.1 Use of Models to Calculate Th(IV), Np(V), and Am(III) Solubilities

We will use the thermodynamic speciation and solubility models developed by the ASTP for Th(IV), Np(V), and Am(III) to calculate solubilities for the PABC source term. These models feature the Pitzer model to predict activity coefficients for dissolved species in high-ionic-strength solutions such as WIPP brines. U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM) provided a detailed description of the development of these models.

Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2002f, 2003) revised and updated the Th(IV), Np(V), and Am(III) thermodynamic models for the CRA-2004 PA. Her changes featured: (1) improved implementation of previously obtained laboratory data; (2) results of WIPP-funded laboratory studies carried out at Florida State University and the Pacific Northwest National Laboratory from the time of the PAVT through 1999; (3) results of recent laboratory studies carried out for applications other than the WIPP, especially the German radioactive waste-management program.

Subsection 5.2.5 (see below) describes corrections of the models made since the CRA-2004 PA.

5.2.2 Use of Brine-Solid Equilibria to Control Th(IV), Np(V), and Am(III) Solubilities

We will continue to use instantaneous, reversible stable (or, in the case of Th) metastable equilibria among GWB or ERDA-6 and actinide-bearing solids such as amorphous, hydrated $\text{ThO}_2 \cdot n\text{H}_2\text{O}$; KNpO_2CO_3 ; and $\text{Am}(\text{OH})_3$ to control An(III), An(IV), and An(V) solubilities for the PABC source term. This assumption is another important feature of the conceptual model of the geochemical behavior of WIPP disposal rooms.

The actinide-bearing solids that actually control the solubilities of Th(IV), Np(V), and Am(III) will be the phases that have the lowest free energies of formation (relative to other possible Th(IV)-, Np(V)-, or Am(III)-bearing solids) for the conditions under which these solubilities are calculated (e.g., f_{CO_2} , pH, and brine composition). Nevertheless, we have no reason to expect that these solids will be phases other than $\text{ThO}_2 \cdot n\text{H}_2\text{O}$, KNpO_2CO_3 , and $\text{Am}(\text{OH})_3$, because these solids were present in the solubility calculations for the CRA-2004 PA, and because the conditions used for the PABC solubility calculations will be very similar to those used for the CRA-2004 PA.

Note that, as in the past, sorption is not included in the processes that control dissolved actinide concentrations in WIPP disposal rooms. Omission of sorption may add conservatism to the An source term.

5.2.3 Inclusion of Organic Ligands in Th(IV), Np(V), and Am(III) Solubilities

We will continue to include the effects of acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate in the An speciation and solubility calculations for the PABC source term.

Brush and Xiong (2003a, 2003b, 2003c) and Downes (2003a, 2003b) included the effects of these organic ligands in the An solubility calculations for the CRA-2004 PA. This was the first time that organic ligands were included in compliance-related solubility calculations since the completion by Choppin (2001) of the experimental program carried out to obtain data to calculate the complexation of dissolved An(III), An(IV), and An(V) species by acetate, citrate, EDTA, lactate, and oxalate. This program also included experiments to obtain data on the complexation of Mg^{2+} by these ligands and – hence – the extent to which Mg^{2+} and dissolved An species will compete for the binding sites on these ligands, thereby reducing the complexation of these An species by organic ligands.

Brush and Xiong (2003b) calculated the dissolved concentrations of acetate, citrate, EDTA, and oxalate used in the An solubility calculations for the CRA-2004 PA by assuming that all of these ligands present in the waste (Crawford, 2003) will dissolve in 29,841 m³ of brine, “the smallest quantity of brine required to be in the repository [for] transport away from the repository” (Larson, 1996; U.S. DOE, 1996). After the An solubility calculations, Crawford and Leigh (2003) and Leigh (2003) corrected Crawford’s (2003) estimates of the total masses of organic ligands to be emplaced in the WIPP. These corrections decreased slightly the masses of organic ligands in the WIPP inventory. Therefore, the An solubilities calculated by Brush and Xiong (2003d) were somewhat higher than they would have been if they had been recalculated using the corrected organic-ligand concentrations. The An solubilities from Brush and Xiong (2003d) were thus used in the CRA PA calculations.

The parameters for some of the organic ligands in the thermodynamic models used by Brush and Xiong (2003a, 2003b, 2003c) and Downes (2003a, 2003b) for the An solubility calculations for the CRA-2004 PA have been corrected (see Subsection 5.2.5.1 below).

We will calculate the concentrations of acetate, citrate, EDTA, and oxalate in the same manner as Brush and Xiong, (2003b, 2003d) for the PABC, except that we will use the latest estimates from Los Alamos National Laboratory - Carlsbad Operations of the masses of these organic ligands in the WIPP inventory. Furthermore, we will allow solid Ca oxalate (see Subsection 5.2.5.1) to precipitate from the WIPP brines GWB and ERDA-6 if - as expected - the oxalate concentration calculated by assuming that the total mass of oxalate in the waste dissolves in 29,841 m³ of brine results in supersaturation with respect to Ca oxalate (see Subsections 5.1.2 above).

5.2.4 Use of FMT to Calculate Th(IV), Np(V), and Am(III) Solubilities

We will continue to use the speciation and solubility code FMT (Babb and Novak, 1997 and addenda; Wang, 1998) to implement the high-ionic-strength, thermodynamic speciation and solubility models developed for Th(IV), Np(V), and Am(III) (U.S. DOE, 1996, Appendix SOTERM; U.S. DOE, 2004, Appendix PA, Attachment SOTERM). FMT was also used for the An solubility calculations for the CCA PA, the PAVT, and the CRA-2004 PA source terms. The current (and previous) versions of this code are archived in the SNL/WIPP (software) Configuration Management System (CMS).

5.2.5 Use of a New Version of the FMT Thermodynamic Database

We will use a new version of the FMT thermodynamic database for the An speciation and solubility calculations for the PABC source term. This database will be archived in the CMS.

5.2.5.1 CHANGES IN THE DATABASE MADE SINCE THE CRA-2004 PA

Brush and Xiong (2003a, 2003c) and Downes (2003a, 2003b) used the database FMT_021120.CHEMDAT for the An solubility calculations for the CRA-2004 PA source term. Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2002f, 2003) established FMT_021120.CHEMDAT by revising and updating FMT_970407.CHEMDAT, the version used by Novak (1997) at the time of the PAVT.

Since the CRA-2004 PA, four changes have been made in FMT_021120.CHEMDAT and three new versions of the database have been released. Xiong (2004a): (1) corrected the molecular weight of oxalate ($C_2O_4^{2-}$) from 28.84000 to 88.0196 g, and (2) added a value of -326.0981 for the dimensionless standard chemical potential (μ^0/RT) for the stable solid Ca oxalate whewellite ($CaC_2O_4 \cdot H_2O$) to the database; and Xiong (2004b) released FMT_040628.CHEMDAT. Later, Xiong (2004c) changed the value of μ^0/RT for the dissolved Np(V)-acetate complex $NpO_2Ac(aq)$ from -519.615 to -526.061, and Xiong (2004d) released FMT_041116.CHEMDAT. Finally, Xiong (2004e) changed μ^0/RT for $NpO_2Ac(aq)$ from -526.061 back to -519.615, and Xiong (2004f) released FMT_041210.CHEMDAT. Xiong (2004a, 2004c, 2004e) provided detailed explanations of the reasons for these changes.

Addition of the solid Ca oxalate whewellite to the FMT database is a significant change from the standpoint of the solubility of Np(V). Prior to the addition of whewellite, FMT_021120.CHEMDAT contained three oxalate-bearing solids: $H_2C_2O_4 \cdot H_2O$, $NaHC_2O_4 \cdot H_2O$, and $Na_2C_2O_4$. These three solids are very soluble relative to whewellite. Therefore, the dissolved oxalate concentration calculated for the CRA-2004 PA and its corrected concentration (see Subsection 5.2.3 above) - 2.16×10^{-2} and 1.53×10^{-2} M, respectively - were not high enough to precipitate any of these solids. However, these concentrations are high enough to precipitate whewellite, which will actually control the solubility of oxalate in the WIPP. Whewellite will control the solubility of oxalate because: (1) this solid has the lowest free energy of the Ca-oxalate solids for which thermodynamic data are available (see Xiong, 2004a), and (2) whewellite precipitates rapidly from solutions supersaturated with respect to this phase (see Nancollas and Gardner, 1974).

Brush and Xiong (2004) calculated that inclusion of whewellite in the FMT database and the resulting precipitation of this solid decreased the oxalate concentration from 1.63×10^{-2} to 1.17×10^{-3} M (Runs FMT_CRA1V_ORGS_006 and FMT_CRA1V_ORGS_010, respectively), and from 2.14×10^{-2} to 2.46×10^{-4} M (Runs FMT_CRA1V_ORGS_008 and Run FMT_CRA1V_ORGS_012). These results pertain to GWB with f_{CO_2} buffered by the brucite-hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) carbonation reaction, which will buffer

f_{CO_2} in the event of microbial activity; and to ERDA-6 and the brucite-hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) buffer, respectively. Because oxalate complexes NpO_2^+ strongly, precipitation of whewellite decreased the solubility of Np(V) from 7.89×10^{-7} to 2.99×10^{-7} M (Runs FMT_CRA1V_ORGS_006 and FMT_CRA1V_ORGS_010, respectively), and from 5.06×10^{-6} to 6.68×10^{-7} M (Runs FMT_CRA1V_ORGS_008 and FMT_CRA1V_ORGS_012).

However, addition of whewellite to the database will have essentially no impact on the long-term performance of the WIPP because: (1) Np is the only An element expected to speciate in the +V oxidation state (see Subsection 5.2.6 below), (2) the probability that Np will speciate as Np(V) is 0.5, and (3) from the standpoint of its potential effects on long-term performance, Np is much less important than Pu, Am, U, or Th (see Brush and Garner, 2005).

5.2.5.2 CHANGES IN THE DATABASE STILL REQUIRED FOR THE PABC

We will correct the FMT thermodynamic database for the An speciation and solubility calculations for the PABC. Recently, Xiong et al. (2004) re-established the uncertainty ranges and probability distributions associated with the An(III), An(IV), and An(V) solubilities calculated with FMT. Xiong et al. (2005) concluded that: (1) the An(III) thermodynamic speciation and solubility model implemented in the speciation and solubility code FMT overpredicted the measured An(III) solubilities slightly, (2) the An(IV) model in FMT underpredicted the measured An(IV) solubilities, (3) the An(V) model in FMT overpredicted the measured An(V) solubilities slightly, and (4) overall, the An(III), An(IV), and An(V) models in FMT underpredicted the measured An(III), An(IV), and An(V) solubilities.

We are attempting to identify and correct the cause for the underpredictions of An(IV) solubilities. However, we currently believe that the cause of these underpredictions is that the value of μ^0/RT for the dissolved Th(IV) hydroxide complex $\text{Th}(\text{OH})_4(\text{aq})$ incorporated by Giambalvo (2002c) in FMT_021120.CHEMDAT for use in the An(IV) solubility calculations for the CRA-2004 PA, -622.4700, is too high. (This value of μ^0/RT for $\text{Th}(\text{OH})_4(\text{aq})$ is still in FMT_041210.CHEMDAT, the current version of the FMT database.) Furthermore, we believe that adjustment of this parameter to the value recommended by Neck et al. (2002), -626.8467, would result in excellent agreement between measured solubilities and FMT predictions over the pH range of about 5 to 10, the range within which $\text{Th}(\text{OH})_4(\text{aq})$ is the dominant dissolved Th species. (According to Brush and Xiong, 2003c, the pH expected in WIPP disposal rooms is about 9.)

We will confirm our hypothesis that this change would correct the underpredictions of An(IV) solubilities observed by Xiong et al. (2004) by recomparing the measured An(IV) solubilities and predictions made with FMT using the corrected values of μ^0/RT (and any other necessary corrections). If, as we expect, these corrections significantly reduce the underprediction of An(IV) solubilities observed by Xiong et al. (2004), we will then: (1) use this comparison to revise the new An(IV) uncertainty range and probability distribution from Xiong et al. (2004), and (2) submit the revised range and distribution to the SNL/WIPP Records Center and to PA personnel for use in the PABC.

5.2.6 Redox Speciation of Th, U, Np, Pu, and Am

We will continue to use the following oxidation-state distribution for dissolved Th, U, Np, Pu, and Am in the PABC source term. Under the strongly reducing conditions expected in WIPP disposal rooms: (1) Th will have a probability of 1 of speciating essentially entirely as Th(IV); (2) U will have a probability of 0.5 of speciating entirely as U(IV), and a probability of 0.5 of speciating entirely as U(VI); (3) Np will have a probability of 0.5 of speciating entirely as Np(IV) and a probability of 0.5 of speciating entirely as Np(V); (4) Pu will have a probability of 0.5 of speciating entirely as Pu(III) and a probability of 0.5 of speciating entirely as Pu(IV); (5) Am will have a probability of 1 of speciating entirely as Am(III).

This redox speciation is based on the results of experimental studies summarized in the CCA and the CRA-2004 PA (U.S. DOE, 1996, Appendix SOTERM; U.S. DOE, 2004, Appendix PA, Attachment SOTERM). Strongly reducing conditions will be established by reactions among WIPP brines, metallic iron (Fe) and other metals in steel waste containers and/or the waste, and Fe(II)-bearing solids and/or dissolved species produced by anoxic corrosion of these metals. Microbial activity, to which the EPA has recently assigned a probability of 1, will also create reducing conditions. It is recognized that Pu(V) and Pu(VI) could occur in isolated microenvironments in the repository. However, Pu(V) and Pu(VI) would not persist in significant quantities because diffusive and - especially in the event of human intrusion - advective transport would expose any oxidized Pu to the reductants that will be present in the repository. Note that equilibria between or among the possible oxidation states of these actinide elements *is not* featured in the conceptual model for the geochemical behavior of the repository.

5.2.7 Use of the Oxidation-State Analogy

We will continue to use the oxidation-state analogy to apply the solubilities calculated for Th(IV) to U(IV), Np(IV), and Pu(IV), and to apply the solubilities calculated for Am(III) to Pu(III). We will use the model developed for Np(V) only for Np(V). Finally, we will use the revised estimate of the solubility of U(VI) (see Subsection 5.2.9 below) only for U(VI). All four of these applications of the oxidation-state analogy are consistent with the expected redox speciation of Th, U, Np, Pu, and Am described in Subsection 5.2.6 (above).

This application of the oxidation-state analogy is identical to that used since the An solubility calculations for the CCA PA source term (U.S. DOE, 1996, Appendix SOTERM).

Justification for the use of the oxidation-state analogy to predict the solubilities (or other chemical properties) of An elements was provided by U.S. DOE (1996, Appendix SOTERM), Choppin (1999), and U.S. DOE (2004, Appendix PA, Attachment SOTERM).

5.2.8 Use of New Uncertainty Ranges and Probability Distributions

PA personnel will use the new uncertainty ranges and probability distributions for calculated An(III) and An(V) solubilities established by Xiong et al. (2004, Tables 2 and 4) in the PABC source term. Brush et al. (2005) provided additional information about how these ranges and distributions are implemented in PA.

The new An(IV) range and distribution developed by Xiong et al. (2004) will be re-established after correction of the value of μ^0/RT for Th(OH)₄(aq) in FMT_041210.CHEMDAT, the current version of the FMT database (see Subsection 5.2.5.2).

5.2.9 Use of New Solubility Estimate for U(VI)

The EPA has specified that a revised estimate of 1×10^{-3} M for the solubility of U(VI) in WIPP brines be used for the PABC source term. The EPA specified this value during a DOE-EPA teleconference on March 2, 2005.

The EPA estimate of 1×10^{-3} M is higher by a factor of about 100 than that of Hobart (1996) and Hobart and Moore (1996a; 1996b), who estimated a solubility of 1×10^{-5} m in both Salado and Castile brines. The 1996 estimate, also described in U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM), was also used for the PAVT and the CRA-2004 PA.

During the same teleconference, the EPA has also specified that a fixed value be used for their revised estimate. In the CCA PA, the PAVT, and the CRA-2004 PA, the uncertainty range of +1.4 and -2.0 orders of magnitude was applied to the U(VI) solubility estimate of Hobart (1996) and Hobart and Moore (1996a; 1996b).

5.3 Colloidal Concentrations

We will eliminate separate, somewhat different colloidal An concentrations characteristic of the absence of microbial activity from the PABC An source term.

Brush and Xiong (2003a) concluded that inclusion of microbial colloids, one of the four types of colloids described in U.S. DOE (1996, Appendix SOTERM0 and U.S. DOE (2004, Appendix PA, Attachment SOTERM), in nonmicrobial vectors was inconsistent with the probability of 0.5 for significant microbial activity featured in the conceptual model of microbial activity in the WIPP (see Subsection 5.1.3, above).

However, the EPA has specified that the microbial conceptual model be changed for the PABC such that there will be a probability of 1 for significant microbial activity in the WIPP (Cotsworth, 2005). Therefore, nonmicrobial vectors will be eliminated from the PABC and microbial colloids will be included in all of the PABC vectors.

6 SOFTWARE DESCRIPTION

We will use the speciation and solubility code FMT, Version 2.4, supported by the new version of the FMT thermodynamic database described in Subsection 5.1.9 (see above) to calculate revised An(III), An(IV), and An(V) solubilities for the PABC. Wang (1998) validated FMT, Version 2.4, for An(III), An(IV), and An(V) speciation and solubility calculations in WIPP brines. The user's manual for Version 2.3 (Babb and Novak, 1997, and addenda) is still the current FMT user's manual. The addenda to Babb and Novak (1997) describe minor changes made during the upgrade from Version 2.3 to Version 2.4.

We will use FMT to calculate: (1) the mineral assemblages in equilibrium with the WIPP brines GWB, ERDA-6, and - if specified by the EPA - Brine A (see Subsection 5.1.1 above) after reactions among these brines, CO₂, Salado minerals such as halite and anhydrite, and periclase; (2) the speciation and total concentration of nonradioactive constituents of WIPP brines, such as B(OH)_x^{3-x}, Na⁺, Mg²⁺, K⁺, Ca²⁺, SO₄²⁻, Cl⁻, Br⁻, inorganic C, and f_{CO₂} and pH, in equilibrium with these brines and mineral assemblages; (3) the speciation and solubilities of Am(III), Th(IV), and Np(V) in equilibrium with the solubility-controlling solids under these conditions. Section 7 (below) provides a detailed description of the FMT runs.

SNL/WIPP PA personnel will execute all of these FMT runs under the WIPP PA run-control system. We will provide PA personnel with the input files for these runs; they will run them using FMT, Version 2.4, and the new version of the FMT database (Subsection 5.1.9); and provide us the output files. Therefore, the FMT executable file, the database, and all of the I/O files used to calculate actinide solubilities for the PABC will be archived in the Sandia/WIPP CMS for future inspection by the EPA during its review of the PABC. The implementation of this analysis under the WIPP PA run control system and the archiving of all relevant files in the CMS will also ensure that SNL can provide DOE with any and all files requested by any review panels that might replace the Environmental Evaluation Group.

SNL/WIPP PA personnel will run FMT on a Compaq Computer Corp. (now a part of the Hewlett-Packard Co.) ES40 computer with the Open VMS 7.3-1 operating system, or on a Compaq ES45 computer with Open VMS 7.3-1. They could also run FMT on other machines in the Open VMS cluster, if other machines are qualified for such use.

7 TASKS

The three tasks required to calculate An(III), An(IV), and An(V) solubilities for the PABC source term are to: (1) recalculate the concentrations of acetate, citrate, EDTA, and oxalate in WIPP brines; (2) establish a new FMT thermodynamic database; (3) establish a new uncertainty range and probability distribution for calculated An(IV) solubilities; and (4) carry out FMT speciation and solubility calculations. PA personnel will change the U(VI) solubility estimate and the colloidal actinide source term (see Subsections 5.29 and 5.3 above and Subsection 7.5 below). The first, second, and third tasks must be completed before starting the fourth task to ensure that up-to-date organic-ligand concentrations and thermodynamic data are used in the solubility calculations.

The rest of this section describes these tasks in detail (see Subsections 7.1, 7.2, 7.3, 7.4, and 7.5 below).

7.1 Recalculation of Organic-Ligand Concentrations

Los Alamos National Laboratory - Carlsbad Operations (LANL - CO) is currently updating the WIPP transuranic (TRU) waste inventory for the PABC calculations. This update could change the estimated masses of acetate, citrate, EDTA, and oxalate in the WIPP inventory, and could result in the addition of lactate to the inventory. If the masses of these organic ligands change, we will recalculate them in a manner identical to that used at the time of the CRA-2004 PA (see Subsection 5.2.3). If not, we will use the most recent, corrected masses of these organic ligands from Crawford and Leigh (2003) and Leigh (2003).

Furthermore, we are currently re-evaluating the assumption all of these organic ligands will dissolve in 29,841 m³ of brine, “the smallest quantity of brine required to be in the repository [for] transport away from the repository” (Larson, 1996; U.S. DOE, 1996). If it is inappropriate to continue to use a volume of 29,841 m³ of brine, we will change this assumption by preparing a memorandum that recommends a new value, describes the source(s) of this value, and explains our reason(s) for making this change. After the technical, QA, and management reviews required by SNL NP 9-1, we will distribute it to the appropriate recipients and submit it to the SNL/WIPP Records Center.

7.2 Establishment of a New FMT Database

We will correct FMT_041210.CHEMDAT, the current version of the FMT thermodynamic database and release a new version for the An speciation and solubility calculations for the PABC source term. This database will be archived in the CMS.

Xiong (2004a, 2004b, 2004c, 2004d, 2004e, 2004f) made four changes in the FMT database and released three new versions since the An solubility calculations for

the CRA-2004 PA (see Subsection 5.2.5.1 above). Subsequently, however, Xiong et al. (2004) showed that the An(IV) model in FMT underpredicted measured An(IV) solubilities.

We believe that the cause of this problem is that the value of μ^0/RT for Th(OH)₄(aq) recommended by Giambalvo (2002c) for use in the CRA-2004 PA, -622.4700, is too high; and that adjustment of this parameter to the value recommended by Neck et al. (2002), -626.8467, would result in excellent agreement between measured and predicted Th solubilities.

We will make this correction by preparing a memorandum that recommends a change in the value of μ^0/RT for Th(OH)₄(aq) in FMT_041210.CHEMDAT from -622.4700 to -626.8467, describes the sources of these data, and explains our reason(s) for making this change. After the technical, QA, and management reviews required by SNL NP 19-1, we will distribute it to the appropriate recipients and submit it to the SNL/WIPP Records Center. Next, we will make this change in FMT_041210.CHEMDAT. Finally, we will prepare an e-mail message authorizing the appropriate PA personnel to release the new version of the database and - after all necessary reviews - distribute it to the appropriate recipients and submitting it to the SNL/WIPP Records Center.

We will not issue a Parameter Problem Report because the problem is FMT_041210.CHEMDAT, not in the Performance Assessment Parameter Database.

7.3 Establishment of a New An(IV) Uncertainty Range and Distribution

We will establish a new uncertainty range and probability distribution for calculated An(IV) solubilities after we correct the current version of the FMT thermodynamic database. We will do so to confirm that the correction described above (see Subsection 7.2) results in better agreement between measured Th(IV) solubilities and FMT predictions using the new value of μ^0/RT for Th(OH)₄(aq), -626.8467.

We will use the same methods used by Xiong et al. (2004). However, the measured solubilities used for the new comparison might not be identical to those used for the previous one. For example, we will eliminate from the new comparison any solubility data used by Neck et al. (2002) to obtain the new value of μ^0/RT for Th(OH)₄(aq). Use of such data would jeopardize the independent nature of the comparison and - hence - undermine the usefulness of the comparison as a test of the model. Furthermore, we might restrict the conditions under which the measured solubilities used in the comparison were obtained if we believe that the model is not valid under certain conditions.

We will document the completion of this task by preparing a revised version of the analysis report of Xiong et al. (2004) that includes the new uncertainty range and distribution for An(IV) solubilities and - after the technical, QA, and management reviews required by SNL NP 19-1 - distributing it to the appropriate recipients and submitting to the SNL/WIPP Records Center.

7.4 FMT Calculations

We will calculate revised An(III), An(IV), and An(V) solubilities for the PABC source term in two WIPP brines: GWB and ERDA-6. Table 1 (see Subsection 5.1.1 above) gives the compositions of these brines. We will not include Li^+ (see Snider, 2003) in our calculations with GWB because there are no data for Li^+ in the FMT thermodynamic database.

For both brines, we will use the brucite-magnesite and the brucite-hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) carbonation reaction to buffer f_{CO_2} . We will calculate An solubilities with both of these buffers to compare the effects of possible replacement of (metastable) hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) by (stable) magnesite during the 10,000-year, WIPP regulatory period on f_{CO_2} and these solubilities. The brucite-calcite carbonation reaction will not be used to buffer f_{CO_2} because the EPA has specified that the microbial conceptual model be changed for the PABC such that there will be a probability of 1 for significant microbial activity in the WIPP (see Subsection 5.1.3 above). We will suppress (prevent the formation of) calcite to force the brucite-magnesite reaction to buffer f_{CO_2} , and we will suppress calcite and magnesite to force the brucite-hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) reaction to buffer f_{CO_2} . The brucite dissolution reaction will buffer pH in these calculations.

For each brine and carbonation reaction, we will conduct one set of calculations with the organic ligands acetate, citrate, EDTA, and oxalate present; and another without organic ligands. For the calculations with organics, the concentrations estimated at the time of the CRA-2004 PA will be updated, if necessary (see Subsection 7.1 above). We will calculate An solubilities with and without organic ligands to quantify the effects of these complexants on these solubilities.

We will document the completion of this task by preparing an analysis report that contains two sets of solubilities calculated under each of the following two sets of conditions for the PABC source term: (1) GWB, with acetate, citrate, EDTA, and oxalate, in equilibrium with halite, anhydrite, $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, brucite, and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$); and (2) ERDA-6, with organic ligands, in equilibrium with halite, anhydrite, brucite, and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). After the technical, QA, and management reviews required by SNL NP 9-1, we will distribute this analysis report to the appropriate recipients and submit it to the SNL/WIPP Records Center.

7.5 Other Changes in the An Source Term

The EPA specified that a revised estimate of 1×10^{-3} M for the solubility of U(VI) in WIPP brines be used for the PABC source term, and that a fixed value be used for their estimate. PA personnel will make this change in the PA parameter database. The EPA specified this fixed value during a DOE-EPA teleconference on March 2, 2005.

The EPA also specified that the microbial conceptual model be changed for the PABC such that there will be a probability of 1 for significant microbial activity in the WIPP

(Cotsworth, 2005). Therefore, PA personnel will eliminate nonmicrobial vectors from the PABC and microbial colloids will be included in all of the PABC vectors.

8 SPECIAL CONSIDERATIONS

LANL - CO must finalize its estimates of the quantities of the acetate, citrate, EDTA, and oxalate to be emplaced in the repository – part of its update of WIPP TRU waste inventory for the PABC – before we can start the fourth task of this analysis (see Section 7 above). If - as we expect - this update results in changes in the quantities of these ligands, we will proceed as described in Subsection 5.1.8 and Subsection 7.1. If not, we will use the concentrations calculated by Brush and Xiong (2003d).

9 APPLICABLE PROCEDURES

The following NPs are applicable to the work described in this AP. This list does not identify the current version of these NPs and SPs; the current versions of these and other procedures are provided on the SNL/WIPP Online Documents web site (www.nwmp.sandia.gov/onlinedocuments/):

- NP 2-1, “Qualification and Training;”
- NP 6-1, “Document Review Process;”
- NP 9-1, “Analyses;”
- NP 9-2, “Parameters;”
- NP 17-1, “Records;”
- NP 19-1, “Software Requirements.”

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