555186

SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-152

Analysis Plan for Evaluating Constraints on Colloid Parameters in the WIPP Repository

Task 1.4.2.2

Effective Date: 03/21/11

Authored by:	David Sassani Print Name	Shelly R Nielsen for Signature	3-17-11 Date
Reviewed by:	Gregory Roselle Print Name Technical Reviewer	Signature	3/18/2011 Date
Reviewed by:	Shelly Nielsen Print Name Quality Assurance Reviewer	Shelly R. Nielsen Signature	3-17-11 Date
Approved by:	Christi Leigh Print Name Department Manager	Signature	3-17-11 Date

Table of Contents

1 *Introduction and Objectives*

1.1 Introduction

For the WIPP compliance certification application (CCA – U.S. DOE 1996), the source term contained both dissolved radionuclides constrained by solubility limits of actinide phases and actinides that were associated with a variety of colloids. The parameter constraints used to implement the colloid representations within the performance assessment have changed very little in the compliance recertification applications submitted in 2004 and 2009 (CRA-2004 - U.S. DOE 2004, CRA-2009 - U.S. DOE 2009).

Four types of colloids are included within the source term constraints (U.S. DOE 1996). These are actinide intrinsic colloids that are macromolecules of actinides (i.e., the actinides are a structural part of the colloid atomic makeup) starting in the nanometer range and which may mature/grow into larger particles. When immature the intrinsic colloids are hydrophilic but become hydrophobic as they mature meaning that the stability of their suspension becomes dependent on the electrostatic interactions within the solution. When mature, the intrinsic colloids themselves can be considered as mineral fragment colloids, allowing for other dissolved constituents to attach on their surface. Mineral fragment colloids, also known as pseudo-colloids, are hydrophobic hard sphere particles whose suspensions are stabilized/destabilized by electrostatic forces between their surfaces and the solution. A variety of minerals/substances either crystalline or amorphous may form mineral fragment colloids and they are thermodynamically metastable versions of their larger or more crystalline counterpart minerals. The mineral fragment colloids provide generally either sorptive substrates for transporting actinides or incorporate them via coprecipitation mechanisms. Both of these colloids types (intrinsic and pseudo-colloids) are implemented within the performance assessment using constraints that provide an absolute concentration of the colloid type. This is in contrast to the manner in which the other two colloid types are implemented as described below.

Two types of organic colloids are included within the WIPP performance assessment, humic substances colloids and microbial colloids. Humic substances are hydrophilic, soft-sphere particles which are stabilized by solvation forces within the solution. These particles are large molecules of relatively small size (less than 100,000 atomic mass units) that provide sorptive substrates for actinides. Microbes are relatively large colloidal particles (up to the limit of one micron) and are stabilized by hydrophilic coatings on their surfaces. Microbial colloids provide sorptive substrates for actinides and can have actinides associated via bioaccumulation. For both these types of colloids, the constraints on parameter values used to implement them resulted in concentration factors (with upper limits on capacity) that are multiplied by the dissolved actinide concentration in the performance assessment. Whereas the actinide concentrations associated with intrinsic or mineral fragment (pseudo) colloids are fixed values, the actinide concentrations associated with both humic substance colloids and microbial colloids vary as functions of the concentrations of the dissolved actinides.

During the EPA review of CRA-2009 (U.S. DOE 2009), Xiong et al., (2010) provided a response to Comment 4-C-36 of the EPA's February 22, 2010 letter to the DOE (Kelly, 2010) that stated:

> DOE should address whether significant thorium intrinsic colloids and pseudocolloids could form in the WIPP repository. Unless the formation of such colloids can be ruled out by the available data, DOE should address the possible effects of such colloid formation on repository performance.

In the response, Xiong et al., (2010) stated a number of reasons for which the thorium intrinsic colloids and pseudocolloids (i.e., korshunovskite, $Mg_2Cl(OH)_3{\cdot}4H_2O_{(cr)}$ also referred to as "phase 3") reported by Altmaier et al. (2004) are not relevant to the WIPP and concluded that these colloids will not form in the WIPP and therefore did not attempt to assess their effects on performance assessment results (Xiong et al., 2010). However, the EPA in its Chemistry Technical Support Document (Chemistry TSD - U.S. EPA, 2010) expressed additional interest in both of these types of colloids.

In the Chemistry TSD, the EPA evaluated the potential effects on performance assessment results by including intrinsic thorium colloids based on the values reported in Altmaier et al. (2004). The EPA used Table SOTERM-25 (U.S. DOE 2009, Appendix SOTERM-2009) that provided values of dissolved and colloidal actinide concentrations based on the median parameter values for the CCA performance assessment (U.S. DOE 1996) and the PABC04 (U.S. DOE 2004) summarizing those values in Table 8.1 (U.S. EPA, 2010). The EPA sensitivity study results (which also included changes for dissolved actinide concentrations) are summarized in Table 8.2 (U.S. EPA, 2010) and show about a factor of 2 higher total Th mobilized. The EPA (U.S. EPA, 2010) concluded that the effects on the PA results were only relatively small because of the minor inventory of Th in the WIPP waste forms (as compared to Am and Pu). In their evaluation, the EPA indicated that further evaluation was needed to rule out intrinsic thorium colloids as relevant to the WIPP repository and that the Mg-based mineral-fragment colloids should be further evaluated for WIPP repository conditions.

Because it is expected that phase 5 ($Mg_3Cl(OH)_5{\cdot}4H_2O$) will precipitate rather than korshunovskite under WIPP repository conditions (Xiong et al., 2010), WIPP testing at SNL is assessing the potential colloid formation and stability of phase 5. This specific mineral was not included as part of the constraints for mineral-fragment (pseudo) colloid parameter values in the original WIPP compliance certification application (CCA – U.S. DOE 1996; see appendix SOTERM). However, there are a number of conservatisms in the underlying bases of the parameter values for mineral-fragment (pseudo) colloids that may bound the effects of additional phases such as (a) two-fold factor on the pseudo-colloid actinide concentration to account for potential contributions of mineral fragments in the Culebra and (b) no competition among the actinides (or with other cations) for the sites on the colloid surface (i.e., each species uses the full capacity of the colloid surface). WIPP testing at LANL on intrinsic Th colloids is ongoing to assess their stability over longer periods than reported in the literature.

In its Chemistry TSD (Table 8-1 and discussion; U.S. EPA, 2010), the EPA also noted that the colloid actinide source term as implemented contributes substantially to the calculated total mobilized actinide concentrations and that, based on the actinide solubilities used for CCA PA, the humic substances colloids and microbial colloids were the largest contributors to mobile actinides in the source term. In addition to including some of the same conservatisms as listed above (e.g., no competition for surface sites), there is some indication that humic substance colloids may not be stable within the expected WIPP repository environment as indicated by

Wall and Mathews (2005). In that study, Wall and Mathews (2005) showed that the WIPP brines themselves caused reduction in concentration of humic acids and that reaction with MgO led to complete removal relatively quickly. Constraints on the parameters for microbial colloids were based on a number of studies that also do not take account of potential competition among dissolved elements for surface sites (CCA – U.S. DOE 1996; see appendix SOTERM), and ongoing WIPP testing at LANL is assessing in more detail the association of actinides with microbes.

Based on a review and synthesis of concepts, analytical models, and data in the literature, colloid conceptual models and their requisite parametric constraints have been developed for a variety of colloids for evaluating performance of a repository system at Yucca Mountain (Buck and Sassani, 2007). The Yucca Mountain colloid models are dependent directly on chemical conditions (e.g., pH and ionic strength) and account for competitive sorption among radionuclides (and Ni) for surface sites for iron oxide/hydroxide corrosion product colloids. Much work is available in the literature for more detailed assessment of the conditional formation and stability of colloids and quantification of their ability to transport actinides than existed for the WIPP colloid parameter constraints developed for the CCA (U.S. DOE 1996). Together with the current expected conditions for the WIPP repository system and the additional WIPP testing data being collected in an ongoing fashion, synthesis of the literature studies regarding actinide intrinsic colloids, mineral-fragment (pseudo) colloids, humic substance colloids, and microbial colloids facilitates evaluating the uncertainty and quantifying the level of conservatism within the colloids models and their parameter values, as well as the fundamental applicability to expected WIPP conditions. Such synthesis would also provide a current context within which to evaluate/define updates to parameter values for the WIPP colloid models, either for use in sensitivity analyses to delineate and quantify degrees of conservatism, or for use directly in updated performance assessments. This analysis is a Programmatic Decision analysis per NP 9-1. Any updated or new parameter values that would be used within performance assessment for Recertification decisions would be revised/generated under NP 9-2 in the manner appropriate to support those decisions.

1.2 Objectives

The objectives of this Analysis are to:

1. Provide an updated understanding of the colloidal component of the WIPP repository source term that evaluates and synthesizes more recent literature data on colloid formation and stability in the context of the WIPP repository conditions. This will provide a methodology for assessing emerging studies in colloid science in terms of applicability to the WIPP repository system.
2. Develop a strategy to quantify the degree of uncertainty and/or conservatism in the current parameter values implementing the colloid models in performance assessment. This strategy will include updating the colloid parameter values as warranted by the additional information and data available.

Table 1. Abbreviations, Acronyms, Chemical Elements and Compounds, Initialisms, and Minerals.

Abbreviation, etc.	Definition
Am, Am(III)	americium, americium in the +III oxidation state
An, An(III), An(IV), An(V), An(VI)	actinide element(s), actinide(s) in the +III, +IV, +V, or +VI oxidation state
AP	analysis plan
aq	aqueous
Ca, Ca(II)	calcium, calcium in the +II oxidation state
CCA	(WIPP) Compliance Certification Application, submitted to the EPA in October 1996
Cl, Cl^-	chlorine, chlorine in the −I oxidation state, chloride ion
CRA-2004	first WIPP Compliance Recertification Application, submitted to the EPA in March 2004
CRA-2009	second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
CRA-2014	third WIPP Compliance Recertification Application, (to be) submitted to the EPA in March 2014
DOE	(U.S.) Department of Energy
EPA	(U.S.) Environmental Protection Agency
eq.	Equation or equilibration
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
Florida State University	FSU
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
g	gaseous
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
H or H_2	Hydrogen atom, or molecular (elemental) hydrogen
halite	NaCl
H_2O	water (aq, g, or contained in solid phases)
I	ionic strength
kg	kilogram(s)
LANL — CO	Los Alamos National Laboratory - Carlsbad Operations
LLNL	Lawrence Livermore National Laboratory

Table 1 continued on next page

Table 1. Abbreviations, Acronyms, Chemical Elements and Compounds, Initialisms, and Minerals (continued).

Abbreviation, etc.	Definition
M	molar (moles/liter)
m	meter(s) or molal (moles/kilogram)
Mg, Mg(II)	magnesium, magnesium in the +II oxidation state
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(I)	sodium, sodium in the +I oxidation state
NP	(SNL WIPP) Nuclear Waste Management Procedure
Np, Np(V)	neptunium, neptunium in the +V oxidation state
OH, OH−	hydroxide or hydroxide ion
ρ	density
PA	performance assessment
PABC	Performance Assessment Baseline Calculations
PAVT	1997 WIPP Performance Assessment Verification Test
pH	the negative, common logarithm of the activity of H+
phase 3 (korshunovskite)	$Mg_2Cl(OH)_3{\cdot}4H_2O$
phase 5	$Mg_3Cl(OH)_5{\cdot}4H_2O$
Pu, Pu(III), Pu(IV)	plutonium, plutonium in the +III or +IV oxidation state
QA	quality assurance
Rev.	revision
RH	relative humidity
SOTERM	Source Term appendix to CCA and CRA
SNL	Sandia National Laboratories
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C
TRU	transuranic waste
TSD	Technical Support Document of the U.S. EPA
U, U(IV), U(VI)	uranium, uranium in the +IV or +VI oxidation state
WIPP	(U.S. DOE) Waste Isolation Pilot Plant

2 Approach

2.1 Project Resources

This work will involve review and synthesis of literature studies and data collected (including from ongoing testing at WIPP) since the original parameterization of the various colloid types was completed for the original WIPP Certification (U.S. DOE 1996). The synthesis will be used to develop a more detailed understanding of the constraints on actinide colloids within the WIPP source term. For each of the colloid types, the constraints for the original parameter values will be evaluated in the context of the expanded information to assess further the likely stability, the quantitative assessment of their concentrations and the amount of their associated actinides.

Based on the results of this synthesis, a strategy will be developed for additional quantitative constraints on the parameter values of each colloid type, as appropriate. This strategy could range from simply confirming the existing set of parameter values, to developing expanded quantified uncertainties for the existing parameter values, to developing a set of new parameter values to be used to evaluate quantitatively the degree of conservatism in the current implementation, to updating the existing set of parameter values to a revised current set for use in the next performance assessment for WIPP.

2.2 Project Tasks and Milestones

The list of tasks for this analysis is given in Section 4 below. For this work, a number of milestones have been defined as listed below:

Milestone:	Date:
Colloids Analysis report	June 01, 2012
Updated humic colloid parameters with supporting documentation	December 31, 2012
Updated intrinsic colloid parameters with supporting documentation	December 31, 2012
Updated microbial colloid parameters with supporting documentation	December 31, 2012
Updated mineral fragment colloid parameters with supporting documentation	December 31, 2012

As discussed above, the updated parameters for each colloid type will be based on the results documented within the Colloids Analysis Report, and as such, the update may vary for each type of colloid as dependent on the available information.

3 Software List

During review and assessment of data reported in the literature or obtained from additional testing, the geochemical code package EQ3/6 that is qualified for use according to SNL/WIPP software QA requirements (currently version 8.0a, Wolery, 2008) may be used. This set of codes may be used for evaluating: 1) equilibria among minerals, dissolved species, and colloidal species; and 2) the reaction paths either for experimental results or for observations of natural systems in which irreversible reactions occurred. This qualified version of EQ3/6 will be run on personal computer(s) qualified for this version according to SNL/WIPP QA requirements.

4 Tasks

Task 1. Literature Review and Synthesis of information. This task will involve compilation, review, and synthesis of the literature to use, as well as collected WIPP testing data, to perform the following activities and will be performed using NP 9-1. For each colloid type, the original list of sub-parameter constraints that was used to calculate the parameters values used in the CCA, CRA-2004, and CRA-2009 (U.S. DOE 1996,; 2004; 2009 – see Appendices SOTERM) will be first compiled for use as the comparative reference point for all relevant values derived from additional information. The primary analyst for Task 1 is David Sassani. This task will result in completion of the Colloids Analysis report by its due date given above.

A. *Evaluate Conditions of Colloid Formation/stability*
   i. Intrinsic Colloids
   ii. Mineral (Pseudo) Colloids
   iii. Humic Substance Colloids
   iv. Microbial Colloids

B. *Evaluate Stability of Colloids in expected WIPP Conditions*
   i. Intrinsic Colloids
   ii. Mineral (Pseudo) Colloids
   iii. Humic Substance Colloids
   iv. Microbial Colloids

C. *Compile Additional Quantitative Constraints for sub-parameter values used to quantify Colloidal radionuclides*
   i. Intrinsic Colloids
      a. Provide Sensitivity cases (i.e., define conditionally expected Colloid concentrations)
      b. Assess uncertainties relative to current values
      c. Delineate/Quantify degree of conservatism relative to current values

   ii. Mineral (Pseudo) Colloids
      a. Provide Sensitivity cases (i.e., define conditionally expected Colloid concentrations)
      b. Assess uncertainties relative to current values
      c. Delineate/Quantify degree of conservatism relative to current values

   iii. Humic Substance Colloids
      a. Provide Sensitivity cases (i.e., define conditionally expected Colloid concentrations)
      b. Assess uncertainties relative to current values
      c. Delineate/Quantify degree of conservatism relative to current values

   iv. Microbial Colloids
      a. Provide Sensitivity cases (i.e., define conditionally expected Colloid concentrations)
      b. Assess uncertainties relative to current values
      c. Delineate/Quantify degree of conservatism relative to current values

Task 2. Update Parameter Values. Using NP 9-2 update the colloid parameter values for use in performance assessment as needed, including the supporting documentation and technical bases. The primary analyst for Task 2 is David Sassani. This task will result in completion of the applicable parameter updates with documentation by the due dates given above.

A. Update Intrinsic Colloids Parameters

B. Update Mineral (Pseudo) Colloids Parameters

C. Update Humic Substance Colloids Parameters

D. Update Microbial Colloids Parameters

5 Special Considerations

The literature review and evaluation of parameters for intrinsic colloids will also incorporate the data and results from the ongoing LANL testing for intrinsic thorium colloids. It is anticipated that the data will provide additional bases for delineating the stability of intrinsic thorium colloid suspensions and whether or not they would be expected to form under WIPP repository conditions.

The literature review and evaluation of parameters for mineral fragment colloids will also incorporate the data and results from the ongoing SNL testing for mineral fragment (pseudo) colloids. It is anticipated that the data will provide additional bases for (1) delineating the stability of mineral (pseudo) colloid suspensions (e.g., phase5), (2) whether or not they would be expected to form under WIPP repository conditions, and (3) constraints on their parameter values related to the actinide colloid source term.

The literature review and evaluation of parameters for microbial colloids will also incorporate the data and results from the ongoing LANL testing for microbial colloids. It is anticipated that the data will provide additional bases for delineating the stability of microbial colloid suspensions, (2) whether or not they would be expected to form under WIPP repository conditions, and (3) constraints on their parameter values related to the actinide colloid source term.

6 Applicable Procedures

All applicable WIPP QA procedures (NP and SP) will be followed when implementing this analysis plan (AP). The following listing does not identify the specific version of the procedures because in all cases the current versions are to be used and are provided as controlled documents on the SNL/WIPP Online Documents web site (www.nwmp.sandia.gov/onlinedocuments/).

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training*.
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses*.

- All software used will meet the requirements laid out in NP 19-1, *Software Requirements*, and NP 9-1, as applicable.
- The analyses will be reviewed following the requirements in NP 6-1, *Document Review Process*.
- All required records will be submitted to the WIPP Records Center in accordance with the requirements in NP 17-1, *Records*.
- All new and revised parameters will be created/revised according to requirements in NP 9-2, *Parameters*.

7 References

Altmaier, M., V. Neck, and T. Fanghänel. 2004. "Solubility and Colloid Formation of Th(IV) in Concentrated NaCl and $MgCl_2$ Solution," Radiochimica Acta. Vol. 92, 537-543.

Buck, E., and D. Sassani. 2007. "Waste Form and In-Drift Colloids-Associated Radionuclide Concentrations: Abstraction and Summary." MDL-EBS-PA-000004 REV 03. Las Vegas, NV. Sandia National Laboratories, OCRWM Lead Laboratory for Repository Systems. DOC.20071018.0019.

Kelly, T. 2010. Untitled letter with enclosure to D.C. Moody with fourth set of CRA comments and requests for additional information, February 22, 2010. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation. ERMS 553142.

U.S. DOE. 1996. Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Vol. 1 21. DOE/CAO-1994-2184. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office.

U.S. DOE. 2004. Title 40 CFR 191 Parts B and C Compliance Recertification Application for the Waste Isolation Pilot Plant, 10 vols. DOE/WIPP 2004-3231. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

U.S. DOE. 2009. Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application for the Waste Isolation Pilot Plant. DOE/WIPP 09 3424. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

U.S. EPA 2010. "Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification Actinide Source Term, Backfill Efficacy and Culebra Dolomite Distribution Coefficient Values (Revision 1)." Office of Radiation and Indoor Air. Docket No. A-98-49, Item II-B1-25. EDOCKET NO: EPA-HQ-OAR-2009-0330. November 2010.

Wall, N.A. and S.A. Mathews. 2005. "Sustainability of humic acids in the presence of magnesium oxide." Applied Geochemistry 20:1704-1713.

Wolery, T. 2008. "Analysis Plan for EQ3/6 Analytical Studies." AP-140. Rev. 0, May 15, 2008, Carlsbad, NM: Sandia National Laboratories. ERMS 548930.

Xiong, Y.L., L.H. Brush, J.W. Garner, and J.J. Long. 2010. "Responses to Three EPA Comments Pertaining to Comparisons of Measured and Predicted Dissolved and Colloidal Th(IV) and Am(III) Concentrations." Analysis report, May 4, 2010. Carlsbad, NM: Sandia National Laboratories. ERMS 553409.