SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-187
Revision 0

Analysis Plan For the Experimental Investigation of Stability of Mineral Colloids Under WIPP Conditions

Task 4.4.2.2.1

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1  Acronyms and Abbreviations

AP       Analysis Plan
AR       Analysis Report
CBFO     Carlsbad Field Office
CCA      Compliance Certification Application
CRA      Compliance Recertification Application
DOE      Department of Energy
EDL      Electrical Double Layer
EDS      Energy Dispersive Spectroscopy
EPA      Environmental Protection Agency
ERDA-6   Energy Research and Development Administration Well 6 (synthetic Castile Formation brine)
ERS      Electronic Record Management System
GWB      Generic Weep Brine (synthetic Salado Formation brine)
IC       Ion Chromatography
ICP-AES  Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS   Inductively Coupled Plasma Mass Spectroscopy
m        Molal (i.e., moles solute per kilogram solvent)
M        Molar (i.e., moles per liter)
MgO      Magnesium Oxide
mL       Milliliter
mm       Millimeter
nm       Nanometer
NP       Nuclear Waste Management Procedures
PA       Performance Assessment
PC       Particle Concentration
PDI      Potential Determining Ions
pH       Negative logarithm of hydrogen ion activity
QA       Quality Assurance
SEM      Scanning Electron Microscope
SGWB     Simplified Generic Weep Brine
SNL      Sandia National Laboratories
SP       Activity/Project Specific Procedures
TP       Test Plan
µm       Micrometer
UV-vis   Ultraviolet visible spectroscopy
W        Stability ratio
WIPP     Waste Isolation Pilot Plant
XRD      X-ray Diffractometer
[ ]      Concentration
2 Introduction and Objectives

2.1 Introduction

The actinide source term for the WIPP repository consists of the combination of actinides mobilized as colloidal species and as dissolved species. For the 1996 CCA, the potential impact of mobile colloidal actinides was captured through the treatment of four types of colloids. This Analysis Plan focuses on mineral fragment colloids, also known as mineral colloids or pseudo colloids, which have been identified as potential vehicles mobilizing actinides in the WIPP. Dissolved actinide species have the potential to bind to colloidal particles and as such the colloids enhance actinide mobility when they form stable colloidal suspension. After actinide sorption has occurred, the resulting radiocolloids may be referred to as "pseudo-colloids," "carrier colloids," "Fremdkolloide," or "type II colloids" (DOE, 1996, Appendix SOTERM, SOTERM.6). Colloidal particles of interest in this AP are defined as 1 nm to 1 µm in size. Within this size range, particles remain suspended by thermal energy or Brownian motion. Above sizes of about 1 µm, which may be a factor of ten larger depending on geometric aspect ratio or density, particles settle rapidly by gravitational forces. At dimensions smaller than about 1 nm, particles are hydrolyzed (i.e., dissolved). Mineral fragment colloids can be generated by three general mechanisms: natural phenomena, in situ processes in the repository, and anthropogenic activities. The term “mineral” is used here to include naturally occurring, inorganic, crystalline solids in the strict sense, but is also used to include similar colloids regardless of their genesis. This includes iron corrosion products; anthropogenic materials, such as MgO backfill; drilling aids, such as bentonite; and precipitates. Mineral colloids can form due to weathering and be present in groundwater as well as the surrounding geology of the WIPP. Metal corrosion and nucleation and precipitation reactions within the repository can lead to the formation of inorganic colloidal particles. Mechanical disturbance of rock surfaces in the area and drilling operations can also produce mineral colloids (Papenguth and Behl, 1996; Massarotto et al., 2014). Actinides can attach to and become incorporated with mineral fragment colloids primarily by sorption or surface co-precipitation (Mariner and Sassani, 2014).

Mineral colloids are kinetically stabilized and destabilized by electrostatic or steric forces (Einarson and Berg, 1993; Napper, 1970). The particle charge depends on the concentration and identity of PDI, pH, temperature, and pressure of the system. In a kinetically stable colloidal dispersion, colloidal particles repel each other, and therefore stay suspended in the solution. As the ionic strength of the matrix increases, the thickness of the particle’s EDL decreases due to the chemical shielding effect thus the charged particle repelling forces decrease. The weaker repulsion increases the colloid agglomeration and gravimetric settling.

The WIPP intrinsic colloid model, which informs the actinide source term implemented in the PA, dates back to the Compliance Certification Application (DOE, 1996; Papenguth and Behl, 1996). Conservative colloid concentration values as well as conservative assumptions about actinide sorption and association with colloids were used to ensure the colloidal contribution to actinide mobility was not underestimated (Mariner and Sassani, 2014). The concentration of each actinide (thorium, uranium, neptunium, plutonium, and americium) associated with mobile mineral fragment colloids is included in the PA model parameter CONCMIN, which has units of moles colloidal actinide per liter of solution. CONCMIN has been a constant value $2.6 \times 10^{-8}$ M.
2.2 Objective

AP-187 describes the assessment of data reported in Kirkes, 2020. Specifically, this AP outlines proposed methods to analyze currently available experimental results, including exploring differential sedimentation of particles, which has previously not been assessed. Data in the milestone report will be utilized to: assess the experimental approach and provide guidance for subsequent mineral fragment colloids work as well as apply a more complete range of methodologies to help design future experiments. Broader objectives of the AP include: advancing and exploring ideas for a more comprehensive conceptual model and quantification of the colloidal actinide source term; considering ideas to refine the approach used in PA and update PA parameters to reduce conservatism, better reflect realities in the repository post-closure and in the event of a release scenario. Additionally, an aim of the AP will be to address EPA questions and concerns, specifically EPA Issue #4 (Peake, 2018), in which the EPA outlined the expectation that we, “…strengthen current approach by evaluating formation of mineral fragment colloids from MgO”, referring to the use of the maximum value $2.6 \times 10^{-8} \text{ M}$ from the CCA in all realizations.

Experimental studies on mineral fragment colloids would benefit the evaluation of actinide mobility in WIPP by: 1) reaffirming current performance assessment model parameters are sufficiently conservative, or 2) contributing to the revision of bounded concentrations of actinides associated with mineral fragment colloids. The output of this AP may be used for compliance decision analysis per NP 9-1.

3 Approach

Data analysis will involve a combination of analysis of collected experimental and measurement data (total ion concentration, particle size distribution, zeta potential, pH, etc.), calculations, and modeling techniques.

3.1 Physical Data

Experimental data are generated using a combination of techniques to ascertain presence of mineral colloids and characterize the colloidal particles. Analysis of experimental samples might include: particle size analysis and distribution using laser diffraction (Malvern Mastersizer 3000), metal or cation quantification (ICP-AES or ICP-MS), anion quantification (IC), and materials characterization (XRD, SEM with EDS, and Raman spectroscopy).

The first set of data assessed with AP-187 was collected from colloid stability tests and colloid concentrations at various time intervals were determined. Collection procedures and analysis techniques are described in the TP (Kirkes et al., 2018) and in Kirkes, 2020. The TP involves generation of experimental data for determining the stability of mineral fragment or pseudo colloid suspensions in WIPP-relevant conditions, including high ionic strength brines at circumneutral to alkaline pH values. Investigations were proposed for different mineral classes such as: phyllosilicates, tectosilicates, sulfates, and carbonates, though experiments will be refined after reviewing preliminary results.

Data from a couple scoping experiments for strontianite (SrCO$_3$) and calcite (CaCO$_3$) were presented in Kirkes, 2020. Results generated thus far include the elemental concentration of aqueous samples (digested particle dispersions plus dissolved species) over time, nominal ionic
strengths of pre-equilibrated brines, and pH measurements of post-equilibrated brines prior to settling experiments. Particle size distributions were also collected in some instances after grinding of the mineral and months after termination of settling experiments. Conclusions will be reported in the AR.

3.2 Analysis of Stability Experiments

A review of relevant peer-reviewed and programmatic publications related to colloid stability as well as a synthesis of available WIPP experimental results will be completed for the preparation of an AR. General concepts and proposed methods for analyzing the current experimental data are discussed below. The results of preliminary stability experiments will be used to screen out minerals from the same class and refine the overall experimental approach.

3.2.1 Aggregation Kinetics

3.2.1.1 Concepts

Aggregation kinetics can be estimated by fitting a model to the results of stability experiments, namely colloid suspension concentration as a function of time. A second-order rate law (as shown in equation 1) describes the rate of formation of two-particle clusters in monodisperse suspensions due to collisions by Brownian motion or diffusion (Czigany et al., 2005; Stumm and Morgan, 1981).

\[
\frac{dn}{dt} = -kn^2
\]  

where \(k\) is the bimolecular aggregation rate constant and \(n\) is the number of colloid particles per a unit volume (i.e., particle concentration). Equation 1 describes a situation wherein similarly sized particles are assumed to be colliding with each other at equal rates (Elimelech et al., 1998).

For polydisperse suspensions (also referred to as heterodisperse suspensions), the particle size and distribution of particle sizes affect agglomeration kinetics; heterogeneous particle sizes can lead to significant increases in agglomeration rates due to the increased collision rates of larger particles (Stumm and Morgan, 1981).

Collisions can also occur between two particles that settle at different gravitational settling velocities (Stumm and Morgan, 1981). A larger particle with a higher settling velocity can approach a smaller particle with a relatively slower settling velocity, collide with the other particle, and capture it as they both settle (Benjamin and Lawler, 2013). This agglomeration process is referred to as differential sedimentation. The kinetics of agglomeration by differential sedimentation can be described by equation 2 (Stumm and Morgan, 1981):

\[
k_S = \frac{\pi g (\rho - 1)}{72 \nu} (d_1 + d_2)^3 (d_1 - d_2)
\]  

where \(k_S\) is the bimolecular rate constant, \(d_1\) and \(d_2\) are the diameters of two different sized particles, \(g\) is gravitational acceleration, \(\rho\) is the specific gravity of the solids and 1 is the specific gravity of water, and \(\nu\) is the kinematic viscosity.
3.2.1.2 Proposed Approach

The solutions in our stability experiments are polydisperse as there was no size fractionation performed to ensure removal of larger particles prior to starting the experiments. In groundwater and other natural systems, it can be expected that suspensions will have particles of different sizes and display broad, essentially continuous particle size distributions with particles between some lower and upper size limit (Benjamin and Lawler, 2013). Particle collision in the batch systems could be governed by both Brownian motion for sufficiently small particles and differential sedimentation, amongst other possible particle transport mechanisms. Therefore, data fitting will be performed using different trendlines to find the most appropriate model fit based on metrics like the coefficient of determination (R²) for linear regressions or the standard error of regression for nonlinear regressions such as non-linear least squares. Commercial off-the-shelf software such as Minitab, MATLAB, Origin, or R will be utilized to perform the fitting and statistical calculations as well as generate graphics. Statistics packages available with the respective software programs will be employed and Sandia statisticians will be consulted as needed.

Assuming that the particle concentrations in our system are equivalent to the change in concentration of metal elements quantified (e.g., $\Delta [Me] = [Particles]$), we can generically represent the kinetics in equations 3 and 4, where $k_p$ is defined as the settling rate of the particles:

$$\frac{\Delta [Me]}{\Delta t} = k_p$$

(3)

$$\Delta [Me] = k_p \Delta t$$

(4)

Respective aggregation rates for the different electrolyte solutions will be derived from the fitted model(s), if possible. Characteristic settling time, also called coagulation time or the half-life of aggregation, for each suspension could be estimated from the rate constant. This parameter can be thought of as the average time a particle in the original suspension spends before colliding with another particle and provides an overall sense of the lifetime of a stable suspension (i.e., a higher characteristic time indicates slower settling behavior for destabilized particles) (Elimelech et al., 1998; Xie et al., 2012).

The influence of ionic strength variations and electrolyte composition might be parsed from these rates in order to draw general conclusions on their impacts on aggregation. GWB has substantially more Mg$^{2+}$ and slightly elevated Ca$^{2+}$ concentrations compared to ERDA-6; it might be suspected that these divalent cations could have an enhanced destabilizing effect for mineral suspensions in GWB brines. Suspension stability at the differing ionic strengths of the brine solutions will be compared based on aggregation rates and also by simply comparing the percent difference between initial particle concentrations (analogous to the measured metal element concentration of the mineral), remaining concentrations near the termination of the experiment, and/or baseline concentrations in solution (from prior equilibration of mineral solids i.e. $[Me]_{Matrix}$).

3.2.2 Particle Concentration and Number

Particle concentration (PC) might be determined from the point at which the particle concentration plateaus (see Figure 1) and using equation 5.
where $[\text{Me}]_{\text{Total}}$ = the element contribution from the colloids introduced into the batch reactors + the same species contributed to colloids in the equilibrated brines, and $[\text{Me}]_{\text{Matrix}}$ is the same metal species contributed to colloids generated only from the equilibrated system. Ideally, this concentration minus a presumably dissolved baseline concentration would serve as a surrogate for colloid concentration in the system; however, this may not necessarily be applicable with the data at hand, especially in heterodisperse systems where noncolloidal larger particles are present. Stokes Law calculations might be of value to estimate gravitational settling rates for 1 µm particles to see whether coarse particles were completely settled at the beginning of the experiment and focus on the portion of the experiment where the concentrations described relate to colloids.

Means of translating experimental data to particle number and comparing with natural analogs (Filella and Buffle, 1993) in the future will be explored in the AR.

3.2.2.1 Particle Size Distributions

Available results generated from these analyses will be evaluated to assess data quality and limitations and biases of laser diffraction. Population balance modeling (Degueldre et al., 2009) might also be discussed conceptually in the AR as related to future colloids work.

3.2.3 Summary

While inorganic colloids may be destabilized and rapidly aggregate in a quiescent system inundated with high ionic strength brine solution, literature indicating potentially counterintuitive behavior of colloids or indicating breakthrough of colloids in transport studies conducted at higher ionic strengths or different pH ranges warrant closer evaluations of our current WIPP colloids program (Behrens et al., 2000; Magal et al., 2011; Missana and Adell, 2000). This AP focuses on analyzing data produced from recent batch stability experiments to determine a path forward with the research to better address prior assumptions, conceptual models, and release scenarios with an ultimate goal of validating or revising current PA parameters.
4 Software List

The software that may be used for this analysis include commercial off the shelf software such as: Microsoft Excel, Python 3.8, R and R Studio, Minitab, Origin, and/or MATLAB. All software will meet the requirements of NP 19-1 “Software Requirements”.

5 Task List

<table>
<thead>
<tr>
<th>Task Description/Deliverable</th>
<th>Individual to Perform Task</th>
<th>Expected Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Analysis of Strontianite Colloidal Stability</td>
<td>P. Hora</td>
<td>FY 2021</td>
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<tr>
<td>2. Analysis of Calcite Colloidal Stability</td>
<td>P. Hora</td>
<td>FY 2021</td>
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<tr>
<td>3a. Analysis of MgO Colloidal Stability</td>
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<tr>
<td>3b. Analysis of Magnesite Colloidal Stability</td>
<td>P. Hora</td>
<td>FY 2023</td>
</tr>
<tr>
<td>3c. Analysis of Brucite Colloidal Stability</td>
<td>P. Hora</td>
<td>FY 2024</td>
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</tbody>
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6 Special Considerations

The conclusions drawn from the analysis conducted under this AP will be summarized in memos and/or ARs that will be submitted to the WIPP Records Center. Analyses will be performed and documents in accordance with NP 9-1 “Analyses”.

7 Applicable Procedures

All personnel involved in the tasks described herein will be trained and qualified for their assigned work. This requirement will be implemented through procedure NP 2-1 “Qualification and Training.” Specifically, the following Nuclear Waste Management Procedures (NPs) are applicable:

- NP 2-1 – “Qualification and Training”
- NP 9-2 – “Parameters”
- NP 12-1 – “Control of Measuring and Test Equipment”
- NP 13-1 – “Control of Samples and Standards”
- NP 17-1 – “Records”
- NP 20-2 – “Scientific Notebooks”

8 References


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