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Sandia National Laboratories
Waste Isolation Pilot Plant (WIPP)

Test Plan TP 14-03

Experimental Determination of the Existence of a Mobile Colloidal Fraction of Fe(II) Minerals in Two WIPP-relevant Brines

Task 4.4.2.2.1

Revision 0

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APPROVALS

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1. DEFINITION OF ABREVIATIONS, ACRONYMS AND INITIALISMS

ERDA-6	Energy Research and Development Administration well 6 (Synthetic Castile Formation brine)
GWB	Generic Weep Brine (Synthetic Salado Formation brine)
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
ICP-MS	Inductively-Coupled Plasma Mass Spectrometer
M&TE	Measuring and test equipment
NIST	National Institute of Standards and Technology
NP	Nuclear Waste Management Procedure
SEM	Scanning Electron Microscope
WIPP	Waste Isolation Pilot Plant
WIPP PA	Waste Isolation Pilot Plant Performance Assessment

2. REVISION HISTORY

This is Revision 0 of this Test Plan.

3. PURPOSE AND SCOPE

The purpose of this test plan is to experimentally determine the potential existence of a mobile colloidal fraction of various Fe(II) minerals in two synthetic WIPP-relevant brines, GWB (Na-Mg-Cl type) and ERDA-6 (Na-Cl type) (Xiong, 2008). Fe(II) minerals to be tested include, but are not limited to, $Fe(OH)_2(s)$, $Fe_2(OH)_3Cl(s)$, FeS(s), and $FeCO_3(s)$. Several selected additives, such as phosphate, nitrate, and Nd, will be added to GWB and ERDA-6 to test their ability to increase the mobile colloidal fraction of the Fe(II) minerals. The activity of hydrogen ion will be buffered by adding an excess amount of $Mg(OH)_2(s)$. The formation of Fe(II) minerals would mainly involve anoxic corrosion of steel followed by supersaturation of Fe(II) with respect to the minerals mentioned. To mimic this process, some experiments will be initiated by creating supersaturation of Fe(II). A systematic experimental approach for Fe(II) colloid model parameterization will be performed if we observe the mobile colloidal fraction of Fe(II) minerals in GWB or ERDA-6 brines.

4. EXPERIMENTAL PROCESS DESCRIPTION

4.1 Overall Strategy and Process

The existence of a mobile Fe(II) colloidal fraction will be determined by the concentration of Fe(II) in the filtrates that have passed through sequential filtration, including ultrafiltration. If any mobile colloidal fraction of Fe(II) mineral is present, the concentration of Fe(II) in the sequential filtration will decrease as the filter pore size (or its equivalent) decreases. Mg(II) concentration in the filtrates will be monitored since $Mg(OH)_2(s)$ will be used to buffer H^+ activity, which is a possible source of Mg colloids. Cation concentrations will be measured with ICP-AES or ICP-MS, and the H^+ activity will be measured with pH electrode and meters. Fe(II)-containing experiments will be performed in anoxic gloveboxes to minimize the air oxidation of Fe(II).

Four tasks have been identified below:

Task 1. Existence of mobile $Fe(OH)_2(s)$ colloidal fraction in GWB and ERDA-6.
Task 2. Existence of mobile $Fe_2(OH)_3Cl(s)$ colloidal fraction in GWB and ERDA-6.
Task 3. Existence of mobile FeS(s) colloidal fraction in GWB and ERDA-6.
Task 4. Existence of mobile $FeCO_3(s)$ colloidal fraction in GWB and ERDA-6.

Note that, for all four tasks above, the effect of phosphate, nitrate, and Nd will be explored. Phosphate and nitrate were selected due to their ability to modify surface charge of colloidal particles. Nd was selected as an analogue of actinide to investigate whether Nd can increase the mobile Fe(II) colloidal fraction.

Because the filters are made of porous materials of high surface area, they can retain dissolved cations via sorption as well as colloidal entities. Thus, any decrease of Fe(II) concentration in the filtrates cannot be solely attributed to the removal of colloidal fraction without elucidating how much dissolved Fe(II) was removed by the filtration methods used. Mobile mineral colloidal fractions typically show low concentration, therefore, retention of dissolved cations by filtration devices, if any, could be overwhelming at such low concentrations.

To clarify the filtration issue described above, the following solutions of known cation concentration will be filtered and the cation concentrations will be measured before and after the filtration: 10^{-1}, 10^{-3}, 10^{-5}, 10^{-7}, and 10^{-9} M $FeCl_2$ and $MgCl_2$ solutions.

Laboratory activities will be recorded in scientific notebooks, and they will be maintained as QA records. Due to intensive use of centrifuge, cumulative rotor-time log notebook will be maintained as a record for safety.

4.2 Sample Control

The sample control for the work under this Test Plan will follow WIPP Procedure NP 13-1. Each sample will be appropriately labeled. Sample preparation, utilization, and final disposition will be documented in scientific notebooks. When samples are not in the possession of individuals designated as responsible for their custody, they shall be stored in a secure area with associated documentation (e.g., SNL WIPP Activity/Project Specific Procedure (SP) Form SP 13-1-1, "Chain of Custody").

4.3 Data Quality Control

4.3.1 Measuring and Test Equipment (M&TE)

A calibration program will be implemented for the work described in this Test Plan in accordance with NP 12-1, "Control of Measuring and Test Equipment". This M&TE calibration program will meet the requirements in procedure NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of standards to nationally recognized standards such as those from the National Institute of Standards and Technology; and (4) maintaining calibration records. In addition, NP 13-1 and SNL Activity/Project Specific Procedure (SP) 13-1, "Chain of Custody", identify requirements and appropriate forms for documenting and tracking samples possession. Computer-based data handling will follow NP 9-1, "Analyses".

4.3.2 Data Acquisition System

Data collection procedures are specific to individual instruments. For details of the data acquisition for a particular instrument, see the Specific Procedures (SP) or User's Manual for that instrument. Any data acquired by a data acquisition system (DAS) will be attached directly to the Scientific Notebook or compiled in separate loose leaf binders with identifying labels to allow cross reference to the appropriate Scientific Notebook. If the instrument allows data to be recorded electronically, copies of the data disks will be submitted to the Records Center

according to procedure NP 17-1 "Records." If possible, data files may be transferred to ZIP disks or CD ROM for submittal to the records center. For instruments that do not have direct data printout, the instrument readings will be recorded directly into the scientific notebook. Current versions of the DAS software will be included in the SNL WIPP Baseline Software List, as appropriate.

Quality control of the Scientific Notebooks will be established by procedures described in procedure NP 20-2 "Scientific Notebooks." Methods for justification, evaluation, approval, and documentation of deviation from test standards and establishment of special prepared test procedures will be documented in the Scientific Notebooks. Procedures including use of replicates, spikes, split samples, control charts, blanks, and reagent controls will be determined during the development of experimental techniques.

4.4 Data Identification and Use

All calculations performed as part of the activities of TP 14-03 will be documented in a scientific notebook. The notebook will be technically and QA reviewed periodically to ensure that the requirements of procedure NP 20-2, "Scientific Notebooks", are addressed. If a discrepancy is found, that discrepancy and its resolution will be documented during the review on a Document Review and Comment (DRC) Form NP 6-1-1.

4.5 Equipment

A variety of measuring and analytical equipment will be used for the work described in this test plan. A complete equipment list, including serial numbers, will be maintained in the scientific notebook. Scientific notebooks will be used to record all laboratory work activities.

4.5.1 Weighing Equipment

Several balances are present in the facility and may be used for this project. Balance calibration checks will be performed daily or prior to usage, using NBS-traceable weight sets, which, in turn, are calibrated by the SNL Calibration Laboratory. Calibration checks will be recorded in Balance Calibration Records.

4.5.2 Liquid Measuring Equipment

Standard Laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times. In addition, several adjustable Eppendorf pipettes are available for use in the laboratory. The calibration of pipettes will be checked routinely against a calibrated balance, and will be recorded in the scientific notebook. The accuracy of pipettes will be within ± 1%.

4.5.3 Other Analytical Equipment

Ovens and Furnace–Six Precision Telco Lab ovens are being used to hold samples at elevated temperatures, if needed. Temperature is monitored, maintained, and recorded on a daily schedule.

Centrifuge–Beckman Centrifuge (floor model). The user should weigh opposing buckets on a balance to ensure that the weight between buckets is distributed correctly. Cumulative rotor spinning time should be recorded in log book to determine adequate decommission time.

pH Meters and Autotitrators – Solution pH may be measured using pH meters and/or autotitrators. A Mettler Model MA235 pH/Ion Analyzer (and its equivalent hand-held models) and a Mettler Model DL25 Autotitrator will be used for this purpose. The range for all pH meters is 0.00 to 14.00. Electrodes will be calibrated before each use or daily (whichever is less frequent) with a minimum of two pH buffers manufactured by chemical companies with unique lot numbers and expiration dates; traceable to the National Institute of Standards and Technology (NIST). Calibration checks will be recorded in the scientific notebook.

Equipment for Chemical Analysis – Five instruments may be used for chemical analyses. The first is a Perkin Elmer NexIon 300D Inductively-Coupled Plasma Mass Spectrometer (ICP-MS). The second is a Perkin Elmer Optima 3300 DV Inductively-Coupled Plasma Atomic Emission Spectrometer (ICP-AES); the third is a Cary 300 UV-Visible Spectrophotometer; and the fourth is a UIC, Inc. Carbon Analyzer, consisting of an acidification module, a furnace module, and a CO2 coulometer, and the fifth is a DIONEX Ion Chromatograph (IC) 3000. These instruments will be user-calibrated per instrument requirement. The ICP-MS and ICP-AES are two primary instruments that will be used.

Equipment for Mineralogical, and Textural Characterization – The mineralogy and texture may be characterized using either an Olympus BX60 Polarizing Microscope or a JEOL JSM 5900LV scanning electron microscope (SEM). Bulk sample mineralogy will be determined using a Bruker AXS D-8 Advance X-Ray Diffractometer (XRD). A mineral standard will be run periodically to verify diffraction line positions.

The usage of these instruments will follow Activity/Project Specific Procedures (SPs).

5. TRAINING

All personnel involved in the experiments described in this Test Plan 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) and Activity/Project Specific Procedures (SPs) are applicable:

- SOP CPG-CHEM-TWD-2011-001 – "ES&H Standard Operating Procedure (ES&H SOP) for Activities in the Sandia National Laboratories/Carlsbad Program Group Laboratory, Building NPHB (U)."
- TWD 001 – "Safety Management of Bruker Analytical X-ray Systems D8 Advance X-ray Diffractometer"
- Standard Operating Procedure (SOP) for Oxygen Deficiency Hazard Alarm Response for Carlsbad (Building NPHB)
- SP 13-1 – "Chain of Custody"
- NP 6-1 – "Document Review Process"
- NP 13-1 – "Sample Control"

- NP 12-1 – "Control Of Measuring And Test Equipment"
- NP 20-2 – "Scientific Notebooks"
- NP 2-1 – "Qualification and Training"
- NP 17-1 – "Records"

6. HEALTH AND SAFETY

All of the health and safety requirements relevant to the work described in this Test Plan and the procedures that will be used to satisfy these requirements are described in ES&H standard operating procedures (SOP). ES&H SOP describes the non-radiological hazards associated with these experiments and describes the procedures to deal with those hazards, including all the training requirements for personnel involved in conducting the experiments. Additional SOPs may be mandated by SNL ES&H requirements and their issuance will not require revision of this Test Plan.

7. PERMITTING/LICENSING

There are no special license or permit requirements for the activities described in this Test Plan.

8. REFERENCES

Xiong, Y.-L., 2008. Specific Procedure SP 20-4, Preparing Synthetic Brines for Geochemical Experiments, Revision 2. Sandia National Laboratories, Carlsbad, NM.

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