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Sandia National Laboratories
Waste Isolation Pilot Plant

Test Plan TP 16-02

Test Plan for the Measurement of the Concentration of Aqueous Complexes of Iron(II) and Organic Ligands in the Solutions of High Ionic Strength

Task 4.4.2.2.1

Revision 0

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APPROVALS

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1 DEFINITIONS OF ABBREVIATIONS, ACRONYMS, INITIALISMS, ETC.

DAS	Data Acquisition System
DB	database
DRC	Document Review and Comment
DOE	Department of Energy
EDTA	ethylenediaminetetraacetate, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$ or $(CH_2CO_2)_2N(CH_2)_2N(CH_2CO_2)^{4-}$
ES&H	Environmental Safety and Health
Fe, Fe(II)	iron, iron in its +2 oxidation state
$FeCl_2$	iron chloride
IC	Ion Chromatograph
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
M&TE	Measuring and Test Equipment
NIST	National Institute of Standards and Technology
NP	(SNL/WIPP) Nuclear Waste Management Procedure
$PbCl_2$	lead chloride
pcH	the negative, common logarithm of the molar concentration of H^+
pH	the negative, common logarithm of the activity of H^+
SEM	Scanning Electron Microscopy
SOP	Standard Operating Procedure
SP	(SNL/WIPP) Activity/Project Specific Procedure
TP	Test Plan
UV-Vis	Ultraviolet-Visible (spectrophotometry)
WIPP	Waste Isolation Pilot Plant
XRD	X-ray Diffraction

2 REVISION HISTORY

This is revision 0 of this test plan (TP).

3 PURPOSE AND SCOPE

The objective of this TP is to experimentally determine the concentration of aqueous complex species composed of iron(II) (i.e., iron in its +2 oxidation state) and organic ligands. Organic ligands of interest are EDTA, citrate, acetate, and oxalate. These ligands are capable of mobilizing actinides by forming soluble complex species with the actinides. Iron(II) also forms soluble complex species with these organic ligands, and, thus, iron(II) is expected to be bound with those organic ligands, decreasing the availability of organic ligands. The inventory of iron exceeds that of actinides significantly. Experimental variables are concentration of iron(II) and organic ligands, ionic strength, and pH of solutions. UV-Visible spectrophotometer (UV-Vis) will be used to determine the concentration of the complex species. Spectrophotometers use light to measure chemical concentrations (Harris, 1987). Solutions containing both Fe(II) and the organic ligand of interest will be investigated using the UV-Vis, and the absorbance data will be processed to determine the concentration of the aqueous complex species. When necessary, due to their redox stability under atmospheric condition, manganese(II), magnesium(II), and/or lead(II) will be used as analogue for Fe(II) to develop analytical methods. If necessary, additional experiments that use potentiometric titration of the solutions and other spectroscopy techniques (e.g., Raman, Nuclear Magnetic Resonance, etc.) would be performed to support the UV-Vis measurements.

4 EXPERIMENTAL PROCESS DESCRIPTION

This section describes the experiments that Sandia National Laboratory (SNL) will use for the measurement of the concentration of aqueous complex species composed of iron(II) and organic ligands. Experiments that contain iron(II) will be conducted in anoxic glove boxes to minimize the oxidation of iron(II).

4.1 Overall Strategy and Process

The following tasks will be performed in the order listed. Additional procedures and deviations of the procedure from those listed below shall be recorded in the corresponding Scientific Notebooks.

Task 1: Prepare $FeCl_2$ and organic ligands solutions from properly selected salts.

Task 2: Prepare mixture by combining two solutions above in prescribed ratios in high ionic strength media (NaCl and/or $MgCl_2$). Check if any precipitation occurs.

Task 3: Scan the individual solution and mixtures using UV-Vis to obtain the absorbance vs. wavelength plot.

Task 4: Measure and record the absorbance as functions of ionic strength and solution pH. Measure concentrations of components in the solution when necessary due to unexpected chemical reactions, such as dilution, oxidation, and/or precipitation, etc.

4.2 Sample Control

Sample control for the experiments carried out under this TP will conform to SNL Nuclear Waste Management Procedure NP 13-1, "Control of Samples and Standards." The reader should check the website for SNL's Nuclear Waste Management Procedures at https://nwmp.sandia.gov/onlinedocuments to ensure that the latest version of this and other procedures cited below are used for the work described in this TP.

If and when samples are not in the possession of individuals designated as responsible for their custody, they shall be handled and stored with documentation specified by SNL/WIPP Activity/Project Specific Procedure Form SP 13-1-1, "Chain of Custody."

4.3 Data Quality Control

4.3.1 Measuring and Test Equipment

Calibration of all of the measuring and test equipment (M&TE) used for the experiments conducted under this TP will conform to NP 12-1, "Control of Measuring and Test Equipment."

Any computerized data processing required for this TP will conform to NP 9-1, "Analyses."

4.3.2 Data Acquisition System

Data-collection procedures are specific to individual instruments. For details regarding a specific instrument, see the activity/project specific procedure (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 submitted to the SNL/WIPP Records Center according to NP 17-1, "Records."

Scientific notebooks for all of the work performed under this TP will be established and maintained according to NP 20-2, "Scientific Notebooks."

4.4 Data Identification and Use

All calculations conducted under this TP will be documented in a scientific notebook (see Subsection 4.3.2 above), which will be technically and QA reviewed periodically according to NP 6-1, "Document Review Process," and NP 20-2, "Scientific Notebooks." These reviews will be documented on the Document Review and Comment (DRC) Form NP 6-1-1.

4.5 Equipment

A variety of M&TE will be used for the work described in this TP. A complete list of this M&TE, including serial numbers, will be established and maintained in the scientific notebooks.

The user(s) of all of the equipment specified below will follow the appropriate SP and/or user's manual for each instrument.

4.5.1 Weighing Equipment

Several balances are available for use in the work described in this TP. Balance calibration checks will be carried out daily or prior to use, and will be recorded in the balance calibration records. These calibration checks will use National Institute of Standards and Technology-(NIST-) traceable weight sets. These NIST weights are in turn calibrated periodically by the SNL calibration laboratory.

4.5.2 Liquid measurement Equipment

Standard laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times for the work described in this TP. In addition, several adjustable Eppendorf pipettes are available. The pipettes will be calibrated periodically using a calibrated balance, and will be recorded in a scientific notebook. The accuracy of all pipettes used for this work must be within ± 1%.

4.5.3 Other Analytical Equipment

Centrifuge. A floor model Beckman centrifuge will be used for phase separations prior to chemical analyses of solutions. The user will weigh opposing buckets on a balance prior to use of the centrifuge to ensure that the weight is distributed uniformly. Cumulative spinning time will be recorded in a logbook to determine decommissioning time.

Chemical analyses. Five instruments are available for chemical analyses: (1) a Carey model 300 ultraviolet-visible (UV-Vis) spectrophotometer, (2) a DIONEX model 3000 ion chromatograph (IC), (3) a Perkin Elmer NexIon model 300D inductively coupled plasma-mass spectrometer (ICP-MS), (4) a Perkin Elmer Optima model 3300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES), and (5) a UIC carbon (C) analyzer. The ICP AES and the ICP-MS are the two primary instruments that will be used for this study. The user will calibrate all analytical instruments according to the SP and/or user's manual prior to use.

Mineralogical analyses. A Bruker model AXS D-8 X-ray diffractometer will be used for X-ray diffraction (XRD) analysis. This will be the primary method used for solid-phase characterization. An internal standard will be used periodically to verify the positions of diffraction lines.

An Olympus model BX60 polarizing microscope and a JEOL model JSM 5900LV scanning electron microscope (SEM) may also be used.

Ovens and furnaces. Ovens and furnaces will not be used because they cannot be placed inside the glove box(es) that will be used for redox control. Instead, these experiments will be performed at ambient laboratory temperatures.

pH meters and autotitrator. All pcH measurements carried out for this work will use pH meters and autotitrators. A Mettler model MA235 pH/ion analyzer (or equivalent hand-held models) and a Mettler model DL25 autotitrator will be used. Electrodes will calibrated daily or before use (whichever is less frequent) with two pH buffers chosen to bracket the expected pcH of the solutions being tested. NIST-traceable pH buffers will be purchased from chemical-supply companies, and the lot numbers and expiration dates of the buffers will be recorded in a scientific notebook. Calibration of electrodes will also be recorded in a scientific notebook.

5 TRAINING

All personnel involved in the experiments described in this TP will be trained to ensure that they are qualified for their assigned work. This requirement will be implemented according to procedure NP 2-1, "Qualification and Training." Specifically, the following NPs and SPs will apply:

- NP 6-1, Document Review Process
- 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
- CPG-CHEM-TWD-2011-001: ES&H Standard Operating Procedure (ESH SOP) for Activities in the Sandia National Laboratories/Carlsbad Programs Group Laboratory, Building NPHB
- SOP for Oxygen Deficiency Hazard Alarm Response for Carlsbad (Building NPHB)
- SP 13-1, Chain of Custody
- TWD 001: Safety Management of Bruker Analytical X Ray Systems D8 Advanced X-Ray Diffractometer

6 HEALTH AND SAFETY

All of the health and safety requirements that pertain to the experiments described in this TP and the procedures that will be used to implement these requirements are described in SNL/WIPP environmental safety and health (ES&H) standard operating procedures (SOPs). Each of these ES&H SOPs describes the hazards associated with this work and the procedures required to mitigate these hazards, including all of the training requirements for personnel involved in these experiments. Additional SOPs may be implemented to meet SNL's ES&H requirements. However, any additional SOPs that may be required would not necessitate revision(s) of this TP.

7 PERMITTING AND LICENSING

There are no permitting or licensing requirements specific to the experiments described in this TP.

8 REFERENCES

Harris, D. C., 1987. *Quantitative Chemical Analysis*. W. H. Freeman and Company, New York.