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Title: Nitrate Waste Treatment Sampling and Analysis Plan

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Nitrate Waste Treatment Sampling and Analysis Plan, Revision 2

1.0 PROJECT DESCRIPTION AND GOALS

This plan is designed to outline the collection and analysis of nitrate salt-bearing waste samples required by the New Mexico Environment Department- Hazardous Waste Bureau in the Los Alamos National Laboratory (LANL) Hazardous Waste Facility Permit (Permit). The sampling and analysis plan includes the following:

- A plan for which containers of waste will be sampled.
- The type of samples to be collected (e.g., solid and liquid).
- Sampling methods including a description of the methods and procedures that will be used to collect each type of sample.
- A description of the analyses that will be conducted to measure constituent concentrations and other characteristics of the waste.
- A description of the QA/QC procedures that include, but are not limited to, a description of all sample handling, labeling, and chain-of-custody procedures.

Nonradioactive surrogates for both remediated and unremediated nitrate salt-bearing waste were created as part of the development of the treatment methodology for nitrate salt-bearing waste. It is a requirement of the Permit to collect both pre-treatment and post-treatment samples from these waste streams. The objective of sampling and analyses conducted as a result of this plan is to comply with Permit requirements outlined below.

Permit Section 7.6(2) requires pre-treatment and post-treatment verification samples to be collected in accordance with the applicable subsections of Permit Attachment C.3.2.4 *Characterization Procedures Prior to and After Treatment of Mixed TRU Wastes.* The applicable subsections outline the following sample collection requirements.

- For pre-treatment sample collection and analysis, Section C.3.2.4.1 states the following: “Six remediated nitrate salt-bearing waste containers (including drum #68685) and the liquids from two unremediated nitrate salt-bearing waste containers will be sampled when the containers are opened within the glovebox in the TA-50-69 Indoor Permitted Unit. The samples will be analyzed at a LANL onsite analytical laboratory and will provide additional acceptable knowledge characterization information for these types of nitrate salt-bearing waste to confirm testing conducted with surrogate materials. Analytical results for this testing will be provided to the Department within 60 days of sample collection; the Permittees shall provide these results in the form of a table with a column indicating expected ranges for each analyte based on the Permittees surrogate waste testing.”
- Samples of treated waste (blended with water and zeolite) must be collected in accordance with Section C.3.2.4.2, “samples will be collected from a minimum of 1% of treated waste containers from each waste stream and analyzed at an onsite laboratory to confirm chemical composition when compared to that of the surrogates tested.”

These permit conditions require sampling and analysis of 1) untreated nitrate salt-bearing waste to ensure that the surrogates developed to test the treatment methodology were representative of the chemical constituents within the waste to be treated, and 2) post-treatment waste to verify the treatment methodology performs as tested.

1.1 Data Limitations

With the permit conditions in mind, the following limitations can be outlined:

- There are 60 remediated nitrate salt-bearing waste containers and 27 unremediated nitrate salt waste containers available for sampling.
- There have been samples of unremediated nitrate salt waste collected and analyzed previously.
    - Samples were collected from the top of two waste containers of untreated waste, and residuals from four empty parent containers of nitrate salt waste.
    - These containers represent waste generation years: 1980, 1981 (one salt sample and one residual sample), 1982, 1985 (two samples of residuals), and 1986. The 27 waste containers of unremediated nitrate salt waste represent waste generation years 1979-1986
- It is not yet known the final number of treated waste containers that will be generated and the number will not be known until the conclusion of the treatment process, therefore, assumptions must be made about the total number of treated waste containers for collection of the post-treatment waste samples.

1.2 Sample Selection

A biased approach was used to choose waste containers for pre-treatment sample collection and post-treatment sample collection.

1.2.1 Pre-treatment Sampling

Pre-treatment solid samples of remediated nitrate salt-bearing waste were chosen using the following considerations. Table 1 summarizes the container numbers and choices outlined below.

1. The two containers that are sampled daily for headspace gas concentrations were chosen because one containers is specifically called out within the permit condition and the other exhibits the highest concentration of carbon dioxide (CO_2) within headspace gases.
2. Three containers that exhibit higher concentrations of CO_2 in headspace gases.
3. The most full of the three remediated nitrate salt-bearing waste containers marked “Beryllium contaminated”.

Pre-treatment liquid samples of unremediated nitrate salt waste will be collected from containers that represent waste generation years 1979 and 1984. These are the two waste generation years that have not already been sampled.

1.2.2 Post-Treatment Sampling

Post-treatment solid samples will be collected from random batches of treated waste throughout the generation of the first daughter container generated from the following parent waste containers:

1. The first container of remediated nitrate salt-bearing waste treated.
2. Container number 68685.
3. The container marked Beryllium contaminated.
4. The first container of unremediated nitrate salt-bearing waste treated.

2.0 SAMPLE COLLECTION

This sampling and analysis plan identifies the sampling and analysis requirements for the containers outlined in Section 1.2 and describes the sampling, analysis, and quality assurance/quality control (QA/QC) methods that will be used to demonstrate that the goals outlined in Section 1.0 of this plan have been met. Sampling activities will be conducted within a glovebox-contained environment at Technical Area 50, Building 69. All samples will be collected and analyzed in accordance with the procedures in Section 4 of this plan.

2.1 Sample Collection

Samples will be collected in accordance with the procedures identified herein which incorporates guidance from the Environmental Protection Agency (EPA), (EPA 1986, EPA 2002a, and EPA 2002b); DOE (DOE 1995); and other LANL-implemented and approved procedures for sampling and analysis as implemented by waste management personnel.

All tools used for sample collection of pre-treatment waste will be non-sparking tools because the waste being sampled is characterized as ignitable waste (EPA Hazardous Waste Number D001). Sample tools will be reused for samples within a single composite or for replicate samples only. Separate tools will be used for individual samples; therefore, a description of decontamination of sampling equipment is not included herein.

2.1.1 Solid Sampling

Pre-treatment grab samples will be collected from approximately the top, the middle, and the bottom of parent remediated nitrate salt-bearing waste containers as the solid waste is removed from the parent container into a bin, prior to treatment. Individual grab samples of the waste will be collected using a scoop or other tool as deemed appropriate by waste sampling personnel. The three grab samples from a single parent container will be placed in individual sample containers and then composited for analysis at the analytical laboratory. Composite solid samples will not be field mixed due to safety precautions, contamination control concerns, and to simplify the chain of custody process when grab samples are collected at different times. Grab samples will be placed in a vented 120 milliliter (mL) or larger Teflon container and sealed tightly with at least 30 grams (g) of material.

Post-treatment grab samples will be collected from at least three randomly chosen treated mixer batches during the generation of a single treated waste daughter container and will be composited for analysis at the analytical laboratory. At least three grab samples from three mixed batches will be collected. Individual grab samples of the waste will be collected using a scoop or other tool as deemed appropriate by waste sampling personnel. Composite solid samples will not be field mixed due to safety precautions, contamination control concerns, and to simplify the chain of custody process when grab samples are collected at different times. Grab samples will be placed in a 120 milliliter (mL) or larger Teflon container and sealed tightly with at least 30 grams (g) of material.

2.1.2 Liquid Sampling

Liquid samples will be collected from the containers outlined in Section 1.2.1 after removal into a container or bin within the glovebox containment. Liquid samples will be collected using syringes, pipettes, or other tool as deemed appropriate by waste sampling personnel. Samples will be collected in a 120 mL or larger Teflon container, sealed tightly with at least 5 mL of liquid.

2.2 Sample Documentation

Sampling personnel will complete and maintain records to document sampling and analysis activities. Sample documentation will include sample identification numbers, chain-of-custody forms, analysis requested, sample logbooks detailing sample collection activities, and shipping forms (if necessary).

2.2.1 Chain of Custody

Chain-of-custody forms will be maintained by sampling personnel until the samples are relinquished to the analytical laboratory. This will ensure the integrity of the samples and provide for an accurate and defensible written record of the sampling possession and handling from the time of collection until shipment to the laboratory for analysis. One chain-of-custody form may be used to document all samples collected from a single sampling event or day. The sample collector will be responsible for the integrity of the samples collected until they are properly transferred to another person. The EPA considers a sample to be in a person's custody if it is in a person's physical possession; in view of the person in possession; or secured by that person in a restricted access area to prevent tampering.

The sample collector will document all pertinent sample collection data. Individuals relinquishing or receiving custody of the samples will sign, date, and note the time on the analysis request and chain-of-custody form. A chain-of-custody form must accompany all samples from collection through laboratory analysis. The analytical laboratory will return the completed chain-of-custody form to the facility, and it will become part of the permanent sampling record documenting the sampling efforts. The LANL information management system for the Actinide Analytical Chemistry Group is Labware. Samples are logged and distributed into Labware for analysis. The Labware database tracks the sample while it is being analyzed, and will serve as the chain of custody once the analytical laboratory receives it.

2.2.1.1 Sample Labels and Custody Seals

A sample label will be affixed to each sample container. The sample label will include a unique sample identification number that will correspond to the information found in the sample logbook. A custody seal will be placed on the final outer bag that contains the sample container to detect unauthorized tampering with the samples. The labels with the unique identification number will be affixed by the sample collector before he or she enters the radiological area where the samples will be collected.

2.2.2 Sample Logbook

All pertinent information on the sampling effort must be recorded in a bound logbook. The information must be recorded in ink and any cross-outs must be made with a single line with the change initialed and dated by the author. The sample logbook will include the following information:

a. container number
b. the sample location (including position within container)
c. suspected composition
d. sample identification number
e. volume/mass of sample taken
f. purpose of sampling
g. description of sample point and sampling methodology
h. date and time of collection
i. name of the sample collector

j. sample destination and how it will be transported
k. observations
l. name(s) of personnel responsible for the observations

2.3 Sample Handling and Storage

Samples will be collected and containerized in appropriate pre-cleaned sample containers. Samples will be triple-contained (e.g., vial or container, Ziploc bag, then another Ziploc bag). The final outer bag will be decontaminated to free-release radiological levels, and a custody seal will be placed on the outer bag. Sample containers and quantity of sample required for all analyses are described in Section 2.1 above.

2.4 Packaging and Transportation of Samples

All packaging and transportation activities will meet safety expectations, QA requirements, DOE orders, and relevant local, state, and federal laws (including 10 CFR and 49 CFR). Appropriate facility documents establish the requirements for packaging design, testing, acquisition, acceptance, use, maintenance, decommissioning, and for on-site and intra-site shipment preparation and transportation of general commodities, hazardous materials, substances, waste, and defense program materials. This sampling and analysis plan does not include the transportation of waste samples off-site.

3.0 SAMPLE ANALYSIS REQUIREMENTS

Samples will be analyzed for the constituents listed in Table 2. These constituents are determined to be applicable constituents that will aid in determining the chemical constituents to the comparison values developed for each of the waste types being sampled (i.e. remediated nitrate salt-bearing waste, unremediated nitrate salt liquid, and treated waste). Samples will be analyzed by the Actinide Analytical Chemistry Group using the methods and instrumentation outlined in Table 3.

3.1 Analytical Laboratory Requirements

The analytical laboratory at the Chemical Metallurgy Research (CMR) Facility will perform the detailed qualitative and quantitative chemical analyses specified in Section 3.2. The analytical laboratory will have

a. a documented comprehensive QA/QC program;
b. technical analytical expertise;
c. a document control/records management plan; and
d. the capability to perform data reduction, validation, and reporting.

The selection of the analytical testing methods identified in Table 3 is based the physical form of the waste, constituents of interest, and information requirements (e.g., waste classification).

3.2 Quality Assurance/Quality Control

All sampling and analysis will be conducted in accordance with the QA/QC procedures and methods defined by Actinide Analytical Chemistry Group procedures because the samples will be analyzed by an internal laboratory. These QA/QC procedures follow requirements outlined in QA-1 (Actinide Analytical Chemistry Quality Assurance Program, C-AAC 2015). Laboratory QC is required to ensure continuing precision, accuracy, and sensitivity of analytical measurements are consistent with customer requirements. Acceptance limits for QC measures must be specified as part of the customer's overall data quality objectives, and corrective actions must be taken when these limits are not met. Examples of such

quality measures should include, but are not limited to, instrument calibration; and internal QC samples, such as surrogate samples, spiked samples, replicates, duplicates, blanks, reference control samples, and standards.

The Actinide Analytical Chemistry Group management and workforce are committed to good professional practices and to the quality of its testing, services, and analytical chemistry results to customers. The Actinide Analytical Chemistry Group shall be familiar with and implement this QA program and all associated quality procedures that make up the program to ensure customer quality requirements are met. Information on the evaluation of the QC results is also described below.

3.3 Data Reduction, Verification, Validation, and Reporting

Analytical data generated by the activities described in this sampling plan will be verified and validated. Data reduction is the conversion of raw data to reportable units, transfer of data between recording media, and computation of summary statistics, standard errors, confidence intervals, and statistical tests.

3.4 Data Reporting Requirements

Analytical results will include all pertinent information about the condition and appearance of the sample as received. Analytical reports will include:

a. a summary of analytical results for each sample;
b. results from QC samples such as blanks, spikes, and calibrations;
c. reference to standard methods or a detailed description of analytical procedures; and
d. raw data printouts for comparison with summaries.

The laboratory will describe the analysis in sufficient detail so that the data user can understand how the sample was analyzed.

4.0 COMPARISON TO SURROGATE ANALYTICAL DATA

The data obtained from analysis of the samples will be compared to the values outlined in Table 4. Ranges and concentrations in Table 4 have been developed using information discovered during extensive nitrate salt-bearing waste surrogate development and testing.

If analysis of a sample is shown to be outside of the range, or illustrate a property not expected for the waste, the possible reason for this deviation will be analyzed and the need for more sampling and analysis will be evaluated.

5.0 RECORDS

Records generated as a result of this sampling and analysis campaign will be kept as part of the Facility Operating Record in accordance with LANL Hazardous Waste Facility Permit (NMED 2010).

6.0 REFERENCES

C-AAC, 2015. QA-1, R.10: Actinide Analytical Chemistry Quality Assurance Program, Effective: 01/29/2015.

DOE 1995. *DOE Methods for Evaluating Environmental and Waste Management Samples*. DOE/EM-0089T, Rev. 2. Prepared for the U.S. Department of Energy by Pacific Northwest Laboratory, Richland, Washington.

EPA 1986 and all approved updates. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. EPA-SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, U.S. Government Printing Office, Washington, D.C.

EPA 2002a. *RCRA Waste Sampling Draft Technical Guidance Planning, Implementation, and Assessment*. EPA530-D-02-002, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C. August 2002.

EPA 2002b. *Guidance on Choosing a Sampling Design for Environmental Data Collection for Use in Developing a Quality Assurance Project Plan*. EPA/240/R-02/005, December 2002. (http://www.epa.gov/quality/qs-docs/g5s-final.pdf)

LANL 2015b. *LANL Waste Management*. P409, Rev. 5. Los Alamos National Laboratory, Los Alamos, NM. July 2015.

NMED 2010 and all approved updates. Los Alamos National Laboratory Hazardous Waste Facility Permit. New Mexico Environment Department, Santa Fe, NM. November 2010.

Table 1

Summary of Containers Selected for Pre-treatment Sampling

Container type	Container number	Reason for Choice
Remediated nitrate salt-bearing waste	68685	Specifically required by Permit Section C.3.2.4.1 and headspace gas concentrations sampled daily
Remediated nitrate salt-bearing waste	69490 (SB50522)	Headspace gas concentrations sampled daily
Remediated nitrate salt-bearing waste	69553	Exhibits higher concentrations of CO_2 in headspace gas
Remediated nitrate salt-bearing waste	94068	Exhibits higher concentrations of CO_2 in headspace gas
Remediated nitrate salt-bearing waste	69208 (SB50069)	Exhibits higher concentrations of CO_2 in headspace gas
Remediated nitrate salt-bearing waste marked “Beryllium contaminated”	69559	Is the most full container that is marked “Beryllium contaminated”
Unremediated nitrate salt-bearing waste	S793724	Representative of a waste generation year that has not been previously sampled
Unremediated nitrate salt-bearing waste	S844602 (69907)	Representative of a waste generation year that has not been previously sampled

Table 2

Constituents of Concern within Pre- and Post-Treatment Nitrate Salt Waste Containers

Category	Specific Constituents
Metals	Silver, Arsenic, Barium, Cadmium, Chromium, Mercury, Lead, Selenium
Anions	Nitrate (NO_3-), Nitrite (NO_2-) Chloride (Cl-), Fluoride (F-), Oxalate (C_2O_4-)
Other Major Elements	Sodium, Potassium, Aluminum, Calcium, Iron, Magnesium

Table 3

Summary of Analytical Methods

Analyte	Test Methods/ Instrumentation
Major and minor elements (metals)	Inductively coupled plasma atomic emissions spectroscopy (ICP-AES) and mass spectrometry (ICP-MS)
Anions	Ion chromatography
Radionuclides	Nondestructive assay by gamma spectroscopy, FRAM (a software analysis tool), and Spectral Nondestructive Assay Platform (SNAP)
pH	Potentiometric pH method
Moisture content	Loss on ignition 110 degrees Celsius (^{o}C)
Combustible content	Loss on ignition 600 ^{o}C
Major chemical composition and form	X-ray diffraction , micro X-ray fluorescence and other methods as determined useful depending on the sample

Table 4

Expected Chemical Constituents/Properties of Pre- and Post-Treatment Nitrate Salt-Bearing Waste

Analyte	Expected Range within Waste Stream	Unit
Nitrate	20-70	%
Lead	0-40	%
Water	10-30	%
Sodium	0-25	%
Aluminum	0-10,000	ppm
Calcium	0-10,000	ppm
Iron	0-10,000	ppm
Magnesium	0-50,000	ppm
Potassium	0-10,000	ppm
Arsenic	0-1	ppm
Barium	0-10	ppm
Beryllium	0-1	ppm
Cadmium	0-100	ppm
Chromium	0-1000	ppm
Copper	0-1000	ppm
Gallium	0-1000	ppm
Mercury	0-1	ppm
Nickel	0-1000	ppm
Selenium	0-1	ppm
Silicon	0-1000	ppm
Silver	0-1	ppm
Chloride	0-1000	ppm
Fluoride	0-1000	ppm
Nitrite	0-10,000*	ppm
Oxalate	0-1	%
Sulfate	0-2,500*	ppm
pH of moistened solid	0-7	pH
Organic Matter	5-90	%

* Expected ranges for these constituents were updated in Revision 2 of this plan based on analysis results of the first three pre-treatment samples collected in 2017 (See EPC-DO: 17-306, EPC-DO: 17-356, and EPC-DO: 17-408).
An expected range for organic matter has also been added to Revision 2 of this plan for completeness.