This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

Physical and Chemical Measurements Needed to Support Disposition of Savannah River Site Radioactive High Level Waste Sludge

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Abstract

Radioactive high level waste (HLW) sludge generated as a result of decades of production and manufacturing of plutonium, tritium and other nuclear materials is being removed from storage tanks and processed into a glass waste-form for permanent disposition at the Federal Repository.

Characterization of this HLW sludge is a prerequisite for effective planning and execution of sludge disposition activities. The radioactivity of HLW makes sampling and analysis of the sludge very challenging, as well as making opportunities to perform characterization rare. In order to maximize the benefit obtained from sampling and analysis, a recommended list of physical property and chemical measurements has been developed. This list includes distribution of solids (insoluble and soluble) and water; densities of insoluble solids, interstitial solution, and slurry rheology (yield stress and consistency); mineral forms of solids; and primary elemental and radioactive constituents.

Sampling requirements (number, type, volume, etc.), sample preparation techniques, and analytical methods are discussed in the context of pros and cons relative to end use of the data. Generation of useful sample identification codes and entry of results into a centralized database are also discussed.

Background

The Savannah River Site HLW sludge is stored in large (from 0.75 to 1.3 million gallons) waste tanks until it can be removed and processed at the DWPF. The sludge is highly radioactive, which makes it both difficult and expensive to sample and analyze. In addition, the solids are comprised primarily of precipitated oxides/hydroxides of iron and aluminum. As such, they settle to the bottom of the waste tanks and do not mix without the input of multiple high powered mixers.

Sampling of the slurried waste is conducted using ‘grab sampling’. The tank contents are thoroughly mixed and then a stainless steel bottle is lowered into the sludge and allowed to fill. The bottle is retrieved and placed into special containers for transport to a ‘hot cell’ where it can be opened. The type of characterization can vary from very simple, such as a few physical property measurements to an extensive study of the sludge composition and behavior.

Introduction

The characterization program of HLW sludge started even before the waste was sent to the first tank in November of 1954. Over the next three decades a tremendous amount of basic research and development was conducted and a facility to turn HLW into 10 foot long glass logs had been designed. In the eighties, the ground-breaking ceremony for the new facility changed the process from one that was on paper to one that was actually being built. We knew that making sense of all the information we had generated and actually removing the sludge and making it into glass was going to be a time, energy, and money intensive process. We sympathized with those future engineers and scientists who were going to make it happen at some point in the far distant future and tried our best to record everything that could be important.

SRS started incorporating the HLW into glass in 1996. The site has processed 4 large batches of sludge through the facility. Recently, all of the data collected on the sludge batches was compiled. The reader (in the year 2007) of these numerous reports can not help but be keenly aware of the weeks and months of hard work that has gone into getting the data that can now be read about in a couple of hours. One of the things that was hard to appreciate back in the eighties was the value of recording all of the mundane information about a sample, such as its date, type, location, tank conditions. Now, having spent weeks reading through old log notes and reports trying to pin down this information, it is clear how important this seemingly trivial information would become.

In accessing all of the sludge information, it became obvious that the average waste management engineer had a limited understanding of the laboratory analyses described in the technical reports. The most important reason for writing this paper is to provide an introduction to the sample processing and analysis typically encountered for sludge samples. The information should also be useful for project managers who need to understand and justify the need for the given number and volume of samples.

The second purpose is to begin to document the preliminary thinking about how to best manage the information collected in these reports. The information had to be collected from the original reports because we currently do not have a comprehensive electronic database of the information. In looking at what it would take to put this information into a database, it quickly became obvious that it would be a difficult task. The reason for this becomes apparent when you think of how the data is generated. An example of the flow of gathering data and the amount of data generated is given below.

Assume that three samples are taken from a waste tank. The first tier of information is fairly straight-forward.

Sample 1	Sample 2	Sample 3
TkXX-1	TkXX-2	TkXX-3

Next, perform triplicate physical property measurements on each sample. As shown in the table below, we now have (7 x 9) or 63 results, and we haven’t even started the analysis of the data. The second tier is not quite straight-forward, but is still manageable.

Sample	TkXX-1-A	TkXX-1-A	TkXX-1-A	TkXX-1-B	TkXX-1-B	TkXX-1-B	TkXX-1-C	TkXX-1-C	TkXX-1-C
Slurry density	X	X	X	X	X	X	X	X	X
Supernate density	X	X	X	X	X	X	X	X	X
Wt % TS	X	X	X	X	X	X	X	X	X
WT% IS	X	X	X	X	X	X	X	X	X
WT% DS	X	X	X	X	X	X	X	X	X
WT% SS	X	X	X	X	X	X	X	X	X
WT% OS	X	X	X	X	X	X	X	X	X

(TS = Total Solids, IS = Insoluble Solids, DS = Dissolved Solids, SS = Soluble Solids, OS = Oxide Solids)
See Reference 1 for more information.

Next, determine individual and tank averages (4 x 7) or 28 results.

Sample	TkXX-1-A, Avg	TkXX-1-B, Avg	TkXX-1-C, Avg	TkXX-Avg
Slurry density	X	X	X	X
Supernate density	X	X	X	X
Wt % TS	X	X	X	X
WT% IS	X	X	X	X
WT% DS	X	X	X	X
WT% SS	X	X	X	X
WT% OS	X	X	X	X

So far, we have (63 + 28) or 91 results and we haven't even addressed 'data qualifiers'. There are notations that tell the person using the sample results important additional information, such as if it is a replicate, field blank, below detection, etc. Add a place to hold data flags (which are notations to indicate data that should not be used due to various reasons such as cross-contamination) and we now have 182 pieces of information.

Next, dissolve some of the solids for chemical and radiochemical analysis. Generally, two dissolution methods are used – sodium peroxide fusion performed at ~650 ºC in an open Zr crucible and a hydrofluoric, nitric, and hydrochloric acid digestion performed at ~100 ºC in a sealed Teflon vessel.

Sample	TkXX-1-A-Na	TkXX-1-A-Acid	TkXX-1-B - Na	TkXX-1-B - Acid	TkXX-1-C - Na	TkXX-1-C – Acid
Mass of solids	X	X	X	X	X	X
Volume of diluents	X	X	X	X	X	X
Conversion Factor	Calculate	Calculate	Calculate	Calculate	Calculate	Calculate

Next, submit some of the liquid for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis. Assume that triplicate samples of each dissolution solution are submitted.

Sample	TkXX-1-A-Na-1	TkXX-1-A-Acid-1	TkXX-1-1 – Na-2	TkXX-1-2 – Acid -2	TkXX-1-C – Na -3	TkXX-1-C – Acid -3
Ag	X	X	X	X	X	X
Al	X	X	X	X	X	X
As	X	X	X	X	X	X

……….on down through Zr for a total of 52 analytes.

This adds (6 x 54) or 324 results. Include the detection limit for each one and the number expands to 648. Next, add data qualifier flags. Note that some of the values may have to be rejected due to contaminants introduced in the sample preparation. This adds another 324 results. Add information about the error associated with each determination.

Repeat the above for the remaining chemical and radioisotope methods.

It now becomes obvious that there can be hundreds of lines of data associated with one tank sampling event. Standardized databases, protocols, data analysis assumptions, and so forth should be developed so as to make good use of all of this information, however, this task has not yet been attempted for sludge. Data analysis at this level usually requires a statistician and is usually beyond the skill of the waste management engineer or project manager.

Generally, the ‘best’ value is determined by the scientists at the Savannah River National Laboratory (SRNL) after they have analyzed the characterization information and documented it in a report.

Information is lost in the process, however, as the engineer looking at only the ‘best’ value can not know if it was generated as a result of one sample or more, and if it was one determination or an average of several. When it comes time to compile all of the historical information and make an estimate of the inventory of the tanks, the waste management engineer cannot determine how much weight to give to each result and that can lead to misunderstandings of the data.

Sampling Requirements

A thorough characterization of the sludge slurry in a HLW tank can be performed using as little as approximately 300 mL of sludge slurry. The sample size is mainly a function of the volume of sludge needed to measure the rheological properties of the sludge. Settling data will require a larger volume of sludge, on the order of one liter.

Sample Identification

The first order-of-business is to record all of the information relevant to the sample identification. The information listed in Table 1 will seem to be obvious at the time the sample is being processed in the SRNL Shielded Cells, but years later simple information such as the tank level and sampling date will be hard to determine and reference. Tracking down this seemingly mundane information can takes hours or even days of digging through old records.

The measurements should be performed in the order listed in Table 1.

Table 1. Sample Identification Information

ITEM	PURPOSE
Sample Number	Assign a unique sample number based on the naming conventions described in Section X.
Other Sample ID Numbers	Record the number assigned by the tank farm
Tank	Record the number of the HLW tank that was sampled, along with any significant information
Date Tank Sampled	Record the date the samples were taken
Tank Liquid Level	The tank liquid level is important for estimating the inventory in the tank and should be recorded along with a reference.
Type of Sample	Record whether the sample was a ‘dip’, a ‘pump’, or a 3-liter.
Date Sample Received	Record the date the sample was unloaded into the cells

As can be seen in the above discussion about sample results, the identification label of the various samples, subsamples, determinations and associated data can be quite involved. It is desirable to have a way to easily sort out the results, so that the difference between a value that is an average of 6 determinations by two methods can be distinguished from one that is the sole result of 1 determination and one method. A standardized method to identify the samples and results and to set up the data tables in an electronic database has not yet been developed and is recommended.

Analytical Requirements

For better planning of sludge removal and glass processing, the compositions of sludge in Specifically targeted waste tanks must be adequately characterized. To this end, laboratory analysis of representative targeted samples offers a mean of acquiring the necessary characterization information.

Samples taken from each tank must meet the conditions for representativeness and randomness, however, this aspect of sampling is outside the scope of this paper. A minimum of three independent samples should be taken and processed [Ref 2].

Physical Characteristics

Upon receipt, the sample will be visually inspected, photographed, and composited into labeled containers in the cells (if needed to obtain adequate sample volume).

A portion of the sample will then be used to perform a rheological study and/or a settling study, if requested.

A portion of the sample will be used to determine the following physical characteristics:

- Wt% total solids
- Density of the dried solids
- Wt% insoluble solids
- Wt% soluble solids
- Wt% dissolved solids
- Wt% calcine solids @ 1100^{o}C
- Calcine factor @ 1100^{o}C

Supernatant Characterization

A sample of the free liquid (supernatant) will be filtered to remove insoluble solids and the following will be determined:

- Density of the supernatant
- Ion Chromatography (IC) for: Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, $C_2O_4^{2-}$, CHO_2^-
- Titration for: Free OH^-, total base, CO_3^{2-}
- Carbon Analysis (TIC/TOC) for: total inorganic carbon/total organic carbon
- Gross Alpha and Gross Beta
- Gamma Pulse Height Analysis
- Suite of Radionuclides – Co-60, Ru-106, Sn-126, Sb-125, Cs-134, Cs-137, Ce-144, Eu-154, Eu-155, Am-241
- Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) Suite of isotopes - Tc-99, Ru-101, Ru-102, Ru-103, Ru-104, Ag-107, Ag-109, Sm-151, Th-232, U-233, U-234, U-235, Np-237, U-238, Pu-239, Pu-240, Am/Pu-241, Pu-242, Am-243, Cm-244
- Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES)-Suite of elements – Ag, Al, B, Ba, Ca, Cd, Ce, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, P, Pb, S, Sb, Si, Sn, Sr, Ti, U, V, Zn, Zr
- Radiochemistry/special counting methods: Sr-90, Se-79, I-129
- Thenoyltrifluoroacetone Separation/Alpha Spectroscopy and Beta Counting
- Alpha Pulse Height Analysis for: Pu-238 and Pu-239/240
- Beta counting for: Pu-241

Sludge Characterization

The dried sludge solids from the total solids determination will be used. Two dissolutions will be performed, one using aqua-regia and one using a sodium peroxide fusion method.

Any difficulty in dissolving the solids should be documented. Dissolved sludge solutions will be analyzed in duplicate for the following:

- Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)
- Suite of isotopes - Tc-99, Ru-101, Ru-102, Ru-103, Ru-104, Ag-107, Ag-109,Sm-151, Th-232, U-233, U-234, U-235, Np-237, U-238, Pu-239, Pu-240,Am/Pu-241, Pu-242, Am-243, Cm-244
- Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES)
- Suite of elements – Ag, Al, B, Ba, Ca, Cd, Ce, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, P, Pb, S, Sb, Si, Sn, Sr, Ti, U, V, Zn, Zr
- Gross Alpha and Gross Beta
- Gamma Pulse Height Analysis
- Suite of Radionuclides – Co-60, Ru-106, Sn-126, Sb-125, Cs-134, Cs-137, Ce-144, Eu-154, Eu-155, Am-241
- Radiochemistry/special counting methods: Sr-90, Se-79, I-129
- Thenoyltrifluoroacetone Separation/Alpha Spectroscopy and Beta Counting
- Alpha Pulse Height and Analysis for: Pu-238 and Pu-239/240
- Beta counting for: Pu-241

Conclusions and Recommendations

The recommended path-forward consists of the following.

1. A minimum of three independent samples should be taken in order to provide characterization data for a tank. Replicates of analytical measurements are less important in reducing characterization uncertainty than analyzing independent samples [2]; therefore, a cost-benefit analysis should be performed before replicates are considered.

2. A standardized characterization sample request form should be developed.

3. A standardized sample identification system should be developed.

4. Tables with standardized formats for reporting results should be developed to facilitate future entry of this information into an electronic database.

References

[1] Q. L. Nguyen, "Sludge Characterization Proposal," Savannah River Site, LWO-PIT-2006-00019, Rev. 0, August 2006.

[2] B. A. Hamm, et. al., "Utilizing Statistics to Determine How Much Sampling and Analysis is Warranted to Support Savannah River Site (SRS) High Level Waste (HLW) Sludge Batch Preparation", May 2000.