Nondestructive Assay of TRU Waste Sludge at Los Alamos National Laboratory

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ABSTRACT

Nondestructive assay (NDA) measurements of Transuranic (TRU) sludge waste at Los Alamos National Laboratory (LANL) shares many of the same measurement complexities that have been encountered at other DOE sites. The sludge matrix is highly attenuating to both gamma rays and neutrons, the homogeneity of matrix and source material inside the drums cannot be verified for every drum, there are no representative standards for sludges, and independent tests intended to ascertain the accuracy of the measurements are not characteristic of the waste form.

At LANL, a single instrument has been used to explore the appropriateness of both passive neutron and quantitative gamma ray methods for measuring sludge drums. The passive neutron approach uses the Reals coincidence count rate to establish plutonium mass and other parameters of interest for TRU waste. The quantitative gamma ray method assumes a homogeneous distribution of matrix and source material and assays the drum with a calibration based on the known density of the matrix. Both methods are supplemented by a simultaneous isotopic measurement using Multi-Group Analysis (MGA) to determine the plutonium isotopic composition.

This report will discuss the two methods in detail. Included in the discussion will be descriptions of the setup parameters and calibration techniques for the instrument. Then an evaluation of the measurement results, including a summary of the checks and tests that are applied to sludges, will be presented. Finally, a brief discussion of the conclusions that can be drawn from the tests will be offered.

INTRODUCTION

Nondestructive assay (NDA) techniques measure radiation emitted from nuclear materials without altering their physical or chemical state. For measurements of transuranic waste entrained in sludges, some of the NDA techniques used to measure radioactive materials include passive neutron analysis in which the spontaneously fissioning neutrons are measured, active neutron analysis where the induced fission signal is determined, and gamma analysis. Gamma analysis may be performed in a segmented fashion or by measuring the entire sludge monolith.

Active matrix attenuation correction is often applied to segmented methods. The techniques offer several advantages over radioanalytical techniques when applied to waste measurements of sludges (typically packaged in 55 gal drums) including reduced exposure to measurement personnel and waste handlers, reduction of contamination risks, faster turnaround of results, and elimination of the need for sampling.

Unfortunately, NDA measurements of sludges are accompanied by a number of measurement difficulties that have the potential for affecting measurement accuracy. For active and passive neutron measurements, the large hydrogen content in sludged waste acts as a strong moderator and attenuator of the neutrons. Neutron measurements are also affected by limitations in neutron matrix correction methodologies such as the Add-a-Source (AAS) method because the interrogating neutrons from the AAS source cannot penetrate deeply into the interior of the sludge drum. Gamma-ray measurements are problematic because the sludge matrix is highly attenuating to the most commonly used gamma rays in nuclear materials. This means that even active gamma attenuation correction methods have limited value in correcting for matrix absorption. Both gamma and neutron techniques are negatively affected by one other difficulty that is inherent to sludge measurements but not generally present in matrices that are more amenable to NDA analysis. Homogeneity of source and matrix material must be assumed for sludge measurements in order that NDA methodologies be considered reliable.

The purpose of this report is to describe the methods used to measure sludge waste at Los Alamos National Laboratory (LANL) in detail. Included in the discussion will be descriptions of the sludge waste matrix, instrument setup parameters, calibration techniques, and analysis restrictions for the methods. Then an evaluation of the Performance Demonstration Program (PDP) test results will be presented. Finally, a brief discussion of possible areas of improvement for sludge measurements will be offered.

SLUDGE WASTE

The "sludge" waste streams considered for this paper originated from throughout the Los Alamos National Laboratory research complex. The waste stream [1] consists of homogeneous dewatered solidified inorganic materials generated from Nov 1979 through Dec 1987. The primary origination facility for this waste stream is the TA55 Plutonium Facility complex where several hundred different plutonium processes have been conducted. Processes included chloride operations, metal operations, nitrate operations, pyrochemical processes, ^{238}Pu heat source operations, and special operations. Other sites contributing to the waste included a nuclear reactor, a Van de Graff facility, the Chemistry and Metallurgy Research Laboratory, a cryogenics facility, a radiochemistry research facility, and various other buildings, sites, and complexes. The waste from the various sites was piped or trucked to a central facility called the Radioactive Liquid Waste Treatment Facility (RLWTF) where it was treated, dewatered, and discharged into 208-liter drums with plastic liners. Approximately 10 pounds of dry Portland cement was placed under the sludge and another 10 pounds on top for moisture absorption. Subsequently, many 208-liter drums were over packed into 320-liter drums because of pinhole leaks or indications of rust in the primary container. There are approximately 3750 208-liter drums and 1240 320-liter drums totaling 1178 cubic meters of this waste form at LANL.

Because of the many different research areas contributing to the waste, a very large range of isotopes are in the waste. The most prevalent isotopes by mass are U-235, U-238, Pu-239, Am-241, H-3, and Pu-238. The average weight percents and range of weight percents for the most prevalent isotopes are listed in Table I. There are over 35 other elements that may be present in trace amounts. These include uranium, strontium, cesium, americium, carbon, californium, curium, cobalt, europium, iron, gadolinium, sodium, neptunium, protactinium, promethium, antimony, silicon, technetium, thorium, and tin.

Table I. Average Weight Percents and Range of Weight Percents of the Most Prevalent Isotopes in Los Alamos Sludges.

Radionuclide	Average Wt%	Range of Wt%
U-235	37.0%	0 – 94%
U-238	37.0%	0 – 99.8%
Pu-239	25.6%	0 – 100%
Am-241	0.38%	0 – 100%
H-3	< 1.75%	0 – 1.75%
Pu-238	0.02%	0 – 100%
All Other Isotopes	Trace	NA

The approximate total activity for the waste stream is 552.1 Ci based on the total activities for Am-241, Pu-238, Pu-239, and U-235. On a drum basis, this equates to 0.11 Ci/drum, on average.

A manually operated sliding gate valve in the discharge chute from the sludge processing facility allows the operator to stop the discharge of dewatered sludge when a drum is full. Consequently, most drums are expected to be filled to 95%, or more, of capacity.

The average weight of a Los Alamos sludge drum is 209 kg. Assuming a tare weight of 30 kg, the net weight of a drum is 179 kg. Each drum contains approximately 0.208 m^3. Assuming a fill height of 95%, the average density of a drum is 0.9 g/cm^3.

The chemicals and solvents number over 197 compounds [1] that may be in the waste, including thrichloroethane, Acetone, Ammonium chloride, benzene, cadmium, chromium, diethyl phthalate, hydriodic acid, mercuric iodide, oxalic acid, selenious acid, sodium fluoride, toluene, xylene, and zinc oxide.

NDA METHODS USED TO MEASURE SLUDGE WASTE

The Mobile Characterization Services (MCS) HENC, shown in Fig. 1, is a hybrid NDA instrument based on the High Efficiency Neutron Counter (HENC) with an integrated gamma system. The basic HENC design was modified to incorporate gamma-ray spectroscopy capability. Thus the MCS HENC system integrates two NDA counting modes: passive neutron and gamma-ray assay.

Fig. 1. MCS HENC trailer showing conveyer assembly

High Efficiency, Add-A-Source, Passive Neutron Coincidence Counting Modality

The MCS HENC passive neutron counter employs neutron coincidence and multiplicity counting of 208-liter drums. The counter utilizes 113 He-3 proportional detectors, divided into 16 detector banks, arranged in a 4-π geometry about the assay cavity. The nominal assay cavity is 81 cm wide by 86 cm long by 102 cm tall. An Add-A-Source (AAS) Matrix Correction assembly has been incorporated into the counter for neutron moderation and absorption correction.

The neutron portion of the instrument is calibrated [2] using NIST-traceable standards to create a calibration curve that compares the coincidence count rate to the Pu-240 effective mass. The Pu-240 effective mass is related to the spontaneously fissioning isotopes of plutonium by the following equation:

$$m_{Pu240Eff} = 2.52m_{Pu238} + 1.0m_{Pu240} + 1.68m_{Pu242} \qquad \text{(Eq. 1)}$$

The calibration curve is used to calculate a Pu-240 effective mass value for neutron measurements of waste drums. These values, in turn, are combined with isotopic measurements and AAS corrections to determine the total plutonium mass.

Gamma-Ray Assay Modality

The gamma portion of the MCS HENC system uses a Broad Energy Germanium (BEGe) gamma-ray detector. This detector is mounted in one of the sidewalls of the counter perpendicular to, and pointing towards, the vertical axis of the sample drum in the counter cavity.

The detector is mounted such that it can be withdrawn from the counter side wall when required. The detector is firmly positioned in the sidewall upon reassembly for routine gamma ray assays.

The spectrum from the BEGe gamma detector is processed by the acquisition electronics that are controlled by an external system computer. Both the passive neutron and the gamma-ray signals are processed and analyzed by the Canberra NDA 2000 waste assay software package.

Additionally, the BEGe gamma-ray detector is used to measure the plutonium isotopic composition of the waste during each drum assay. Determination of the plutonium and Am-241 isotopic distribution is performed with Multi Group Analysis (MGA) software under the control of NDA 2000. This measurement is performed concurrently with the quantitative gamma ray measurement.

The gamma calibration [2] method requires both an energy calibration and an efficiency calibration. The energy calibration is straightforward and requires that the unique peaks associated with known radionuclides fall within a specified energy range. The efficiency calibration requires measurement of gamma ray count rates from isotopes of known activity at energies between 60 keV and 1400 keV as a function of the density of the matrix material. Five matrix drums were used to establish the efficiency calibration: foam, homasote®, particle board, inorganic sludge surrogate, and sand. The densities of the matrix drums range from 0.002 g/cc to 1.64 g/cc. Am-241/Eu-152 line sources that extend the full axial length of the 208-liter drums are used for the calibration. The sources are placed in a configuration such that, when the drums are rotated during the calibration measurements, the sources resemble a uniform source distribution. With this information, measurement of an unknown source in similar matrices yields the activity of each isotope. Generally, the quantitative gamma method is used to assay sludge waste.

For the sludge waste stream, the most important assumption underlying the measurements is that the radioactive isotopes and matrix materials are homogeneously distributed throughout the drum volume. The assumption about radioactive isotopes is necessary because nearly total attenuation of both neutron emissions and gamma rays occurs for isotopes near the center of the drum. The matrix material must be presumed to be homogeneous because the AAS neutrons cannot penetrate to the center of sludge drums and, consequently, interrogate only the outer portion of the sludge monolith.

SLUDGE TEST RESULTS

PDP tests were used to evaluate the efficacy of the sludge calibration on MCS HENC.
The results of those tests are shown in Tables II through V. Table II indicates the overall results for the system for PDP Tests 10B, 11A, and 12A. In the Table, the last column (Pass/Fail) refers to whether the series of test measurements met (Pass) or did not meet (Fail) the PDP accuracy and precision [3]. Tables III through V indicate the positioning of the sources during each of the indicated tests.

Table II. Sludge PDP Results for the MCS HENC At LANL for Cycles 10B, 11A, and 12A. %R Refers to the Average Percent Recovery of the Six PDP Measurements. %RSD Refers to the Relative Standard Deviation in those Measurements.

Matrix Type	PDP Cycle	Avg Meas TRU α-Ci	Known TRU α-Ci	%R	%RSD	Pass/Fail
Sludge	10B	0.0301	0.0720	41.80	3.36	Fail/Bias
Sludge	11A	0.458	0.2714	168.60	12.91	Fail/Fail
Sludge	12A	1.01	1.0699	94.25	3.30	Pass/Pass

The MCS HENC failed the bias portion of PDP Sludge Test 10B. This was the first instance that the system was tested for this waste stream. The positioning of the sources indicates that the radioactive material was nearly uniformly distributed in Tubes 2, 3, and 4 for the tests. The total plutonium plus Am-241 loading in the drum was 0.072 α-Ci which corresponds to approximately 0.91 g of plutonium. Corrective actions were not pursued after the Test 10B PDP failure because there was no perceived need to measure sludge waste at LANL at that time.

Table III. Summary of Source Locations for Cycle 10B Sludge Measurements at LANL. Cycle 10B was Conducted during April 2004

Sludge Drum	Nominal Activity (TRU α-Ci)	Tube	Height
NTP-0085	0.0244	2	8
NTP-0092	0.0243	3	8
NTP-0099	0.0233	4	6
Drum Total	0.0720		

The MCS HENC failed both the bias and precision portions of the PDP cycle 11A that was conducted during Oct 2004. The source locations for cycle 11A, shown in Table IV, indicate that the preponderance of the plutonium resided in Tube 4 for the test. The total source activity in the drum was 0.2714 α-Ci, corresponding to 3.41 g of plutonium. Again, resolution of the failure was not initially pursued because the instrument was not to be used to assay sludge waste at the time. However, prior to the next PDP Cycle, an imperative to measure sludge waste at LANL had arisen and it became necessary to resolve the cause(s) of the two failures.

Table IV. Summary of Source Locations for Cycle 11A Sludge Measurements at LANL for the MCS HENC Assayed in 2004.

Sludge Drum	Nominal Activity (TRU α-Ci)	Tube	Height
NTP-0064	0.0025	1	5
NTP-0071	0.0023	2	8
NTP-0099	0.0233	3	7
NTP-0106	0.2433	4	10
Drum Total	0.2714		

Success for the PDP sludge tests came during Cycle 12A. The source locations for cycle 12A, shown in Table V, indicate that most of the activity resided in the sources placed in Tube 4. Unlike the previous tests, however, the majority of the activity (> 60%) was due to Am-241 rather than Pu-239. The source with the large Am-241 loading was NTP-0012 and was located in Tube 4.

Table V. Summary of Source Locations for Cycle 12A Sludge Measurements at LANL for the MCS HENC Assayed during April 2005.

Sludge Drum	Nominal Activity (TRU α-Ci)	Tube	Height
NTP-0064	0.0025	1	5
NTP-0071	0.0023	1	15
NTP-0085	0.0245	2	5
NTP-0092	0.0244	2	15
NTP-0001	0.0443	3	5
NTP-0099	0.0233	3	15
NTP-0012	0.7050	4	5
NTP-0106	0.2436	4	15
Drum Total	1.0699		

The remainder of the discussion in this section summarizes the discoveries made about the sludge measurements, MCS HENC, and the PDP matrix drums as the LANL NDA team came to understand the reasons for the failed PDP test Cycles 10B and 11 A and applied those lessons to the PDP Cycle 12A measurements.

Upon failure of Cycle 11 of the PDP tests for the sludges, several studies [4] were undertaken to determine the reasons for the failure. The studies included a reassessment of the sludge PDP measurements, reevaluation of the calibration for the MCS HENC, and a determination of the geometric response of the instrument to discrete sources in a sludge matrix. Reassessment of the PDP measurements and calibration included a check of the calculations of all calibration parameters and assumptions, evaluation of the matrix drums that were used for calibration, and an examination of the properties of the calibration standards. In reassessing the PDP measurements, it was determined that the self absorption correction in the gamma software for the MCS HENC should not be implemented when a source is present in the outer tube (Tube 4) of the PDP sludge drum. For these measurements, the self-absorption correction over corrects the assay result because the analysis assumes that the measured signal has been attenuated by the sludge whereas, when the source is in the outer tube, very little attenuation has taken place.

Evaluation [4] of the matrix drums that were used for calibration identified a second problem peculiar to sludge measurements. As indicated above, five matrix drums were used to establish the efficiency calibration of the MCS HENC: foam, homasote®, particleboard, inorganic sludge surrogate, and sand. The matrix drums each have nine plastic tubes positioned vertically in a spiral configuration in the matrix at different radial distances from the drum axis. The calibration reference materials consist of six line sources that extend the full length of the drums and were loaded in a manner such that the response, upon rotation of the drums during the calibration measurements, represented a uniform distribution of radioactive sources. Each line source has a mixture of ~ 10μCi of Am-241 and Eu-152 evenly distributed along the length of the source. During the reevaluation, it was identified that the sludge drum, unlike the other four, was only 74% full of matrix material. Since 26% of the activity from the reference materials protruded beyond the matrix, this fraction led to an overestimation in the instrument's efficiency at the sludge density.

It was also determined from the source manufacturer during the reevaluation [4] that, although the six line sources used as reference standards for the calibration each had a nominal activity of 10 μCi, self-absorption within the standards reduced that activity by an important factor. The self-absorption came about due to the presence of epoxy, aluminum, and PVC between the Am-241 and Eu-152 sources and the gamma detector. The epoxy attaches the source material to the outer aluminum sheathing of the standards isolates the standards from the environment. The aluminum sheathing, in turn, is separated from the matrix material in the drum by PVC tubes. The reevaluation results demonstrated that the actual activity of the standards should have been reduced by, approximately, 18% for gamma rays at 60 keV and 3% at 1408 keV from the certificate values due to the additional attenuation from these three materials.

Because the gamma calibration at the sludge density was incorrect due to matrix fill height and self-attenuation within the calibration sources, the multi-density efficiency calibration was recalculated using the corrected source activity and omitting the sludge matrix from the efficiency calibration. No changes were made to the neutron calibration.

The study [4] also examined source placement in the PDP sludge matrix drum. This characteristic was identified as the largest source of error in PDP test measurements of the sludge matrix. Specifically, the study indicated that if the bulk of the plutonium in the PDP test standards was placed in the outer tube (Tube 4) of the PDP sludge drum, then the neutron results were acceptable while the gamma results were biased high. Conversely, if the bulk of the plutonium in the PDP test standards was placed in the tube at the volume averaged position (Tube 3), then the gamma results were acceptable but the neutron results were biased low.

When results of the studies referenced above were merged with later studies performed over a period of seven months with the instrument, it was found that the percent recovery (%R) for gamma measurements of test sludge drums averaged 69% when the source was in Tube 3. For neutron measurements, the average %R was 19% when a source was located in Tube 3. With the source positioned in Tube 4, the average %R for the gamma measurements was 150%. For the neutron result, it was 124%. There is little data on the accuracy of the gamma and neutron measurements when a source is placed in either Tubes 1 or 2. However, preliminary evidence suggests that both the gamma and neutron signals are severely attenuated. There was no substantial change in these results when the sources were placed at different axial locations in the same tube.

These results are reasonable insofar as a high gamma bias comes about when most of the plutonium mass is in the outer tube because the efficiency calibration corrects the raw count rate under the assumption that the plutonium signal results from a homogeneously distributed source whereas, when the source is in Tube 4 of the PDP sludge drum, the signal is coming only from a single source that is attenuated only slightly by the sludge matrix. The neutron signal is acceptable in this case because, in general, only a small fraction of the spontaneously fissionning neutron pairs from the sources are detected in sludges. Even when most of the plutonium is in Tube 4 of a PDP sludge drum, the signal remains small because at least one of the neutrons in the pair is usually absorbed by the sludge. By contrast, when the bulk of the plutonium mass is in Tube 3, this configuration is most akin to a uniformly distributed radial source, and the gamma efficiency calibration is appropriate for this arrangement. But most of

the neutron signal is absorbed within the matrix when the source is in Tube 3 and it evidences a low bias.

In order to minimize these source position biases during subsequent sludge measurements, several additional review criteria were applied to ensure acceptable results for the Cycle 12A PDP sludge measurements. The criteria are also applied to both sludge waste and future PDP test measurements. First, the heterogeneity of the source distribution is evaluated based on the ratio of the Pu-239 peaks at 413 keV and 129 keV. If the 413/129 ratio is greater than 3.75, then the source distribution in the waste or PDP drum is considered to be too heterogeneous and neither the neutron or gamma result are used. If the ratio is less than 3.75 but greater than 2.0, then the gamma result is used. If the ratio is less than 2.0, then the neutron result is applied. Finally, if the peak ratio is less than 2.0 and the neutron/gamma plutonium mass ratio is less than 0.5, then the gamma result is selected. When the Cycle 12A PDP sludge data were reanalyzed using these criteria, the results were within the program's acceptance criteria for bias and precision.

CONCLUSIONS

Several important lessons were learned from the MCS experience of measuring sludge drums. First, certificate values on reference materials can be slippery, Two, matrix fill height plays an important role in calculating the calibration constants. Three, for the MCS HENC and presumably for other similar instruments, if the majority of the source material is in Tube 3 of a PDP-type sludge drum, the gamma measurement is likely to meet the PDP test bias acceptance limits but the neutron result will be biased low. When the source material is in Tube 4, the neutron result meets the PDP test bias acceptance limits while the gamma result is too high. It can be concluded that the sludge matrix drum and discrete sources used for the PDP tests biases NDA results because all of the techniques assume homogeneity of matrix material and radioactive sources. This assumption is violated by the PDP sludge matrix drum which have large holes in the matrix and by the PDP sources which provide highly heterogeneous source distributions.

The 413/129 ratio test is useful for predicting the location of discrete sources in drums However, the test may not provide useful results when sources of approximately equal masses are placed in different tubes. The usefulness of the test has not been fully evaluated for these cases.

In-depth modeling may be a useful tool to better understand source location effects in PDP sludge and waste measurements.

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