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DEVELOPMENT OF A CERTIFIED LOW-LEVEL WASTE STREAM FROM ANALYTICAL LABORATORY OPERATIONS AT LAWRENCE LIVERMORE NATIONAL LABORATORY

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ABSTRACT

Chemistry and Materials Science Environmental Services (CES) is LLNL's on-site environmental analytical laboratory, analyzing approximately 2500 samples annually generally for waste characterization purposes. Due to the lack of process knowledge for analyzed samples, the waste produced by CES has traditionally been characterized on a "worst-case" basis as RCRA-hazardous mixed waste. By instituting rigorous "up-front" waste characterization, including segregation of acutely/extremely hazardous materials, utilizing regulatory exemptions, and developing a novel radiological characterization strategy, CES was able to receive approval for a certified LLW waste stream, adequately characterized for disposal at the Nevada Test Site. In the 10 months of operating history, CES has diverted 33% of its waste (by mass) from mixed to LLW. This will result in significant cost savings and reduction in waste re-handling/personnel exposure.

INTRODUCTION

The management of wastes produced in analytical laboratory operations has always been a complex and involved undertaking. These labs do not produce a single homogeneous waste stream from a well-defined process, but many waste streams of different matrices contents, and characteristics. The waste from an analytical lab contains not only hazardous and radioactive constituents from the residual samples, but also hazardous and radioactive constituents added during the various analytical processes. Wastes may include varying amounts of residual samples, and samples may contain a nearly infinite variety of constituents. Finally, since any given sample arrives as partially characterized at best, and may be analyzed for only one or a few constituents, the completed analytical data may not completely characterize the sample.

At the Lawrence Livermore National Laboratory (LLNL), the on-site environmental compliance analytical lab is known as Chemistry and Materials Science Environmental Services (CES). CES analyzes approximately 2500 samples annually, performing over 12,000 individual analytical tests. CES performs a variety of United States Environmental Protection Agency (EPA), United States Department of Energy (DOE), and State of California certified methods, including organic analysis for volatile compounds, polychlorinated biphenyls (PCBs), and semi-volatile compounds, metals analysis with sample preparation via both total digestion and extraction, radiochemical analysis, including gross alpha/beta, tritium, gamma spectroscopy, and alpha spectroscopy, and basic general chemistry tests such as pH, normality, flashpoint, and oil and grease analysis. In performing these analyses, CES generates a wide variety of waste types and volumes. Table I below shows the approximate annual waste generation rate for different types of waste. Of these waste types, the water-miscible organic, oil, and non-water miscible solvent streams consist almost entirely of discarded samples, while the aqueous acid and basic streams consist of approximately equal parts discarded samples, and process solutions. The solid mixed waste contains approximately 60% lab trash and consumables, 30% empty sample and processing containers, and 10% residual solid samples.

Table I. Annual waste generation rate for different waste matrices from analytical laboratory operations at LLNL.

Waste Stream	Annual Generation Rate
Radioactive Aqueous Acid solutions	4500 liter/yr
Radioactive Aqueous Basic solutions	70 liter/yr
Rad. Water-miscible organics	70 liter/yr
Rad. Oils	70 liter/yr
Rad. Non-water miscible solvents	40 liter/yr
Solid mixed waste	3100 kg/yr

The waste streams identified above have a variety of disposal fates. The aqueous streams are typically treated on-site at LLNL by the Radioactive and Hazardous Waste Management Division (RHWM), resulting in the generation of mixed waste solids and clean water for disposal to sanitary sewer. The organic liquids are typically stored at RHWM, pending treatment at an offsite TSDF licensed to receive radioactive materials. Until the last several years, the fate for mixed solid waste was indefinite storage. In the last several years, an effort has begun to sample all newly-generated solid mixed waste, with the goal of disposal at the Envirocare of Utah site. Needless to say, the sampling and analysis of solid mixed waste is expensive and generates a significant quantity of new waste, and involves significant personnel exposure, so this solution is not without large drawbacks.

For CES, waste management has been a difficult and resource-intensive process for the 9+ year history of operations. For most of this period, CES solid wastes have been characterized on a "worst case" basis. In other words, because CES samples may contain radioisotopes, the waste is managed as radioactive. Since CES samples may contain hazardous constituents (primarily regulated metals and solvents), the waste is managed as RCRA-hazardous, and since CES samples may contain solvents that have been used in listed processes, the waste is managed as RCRA F-listed hazardous. In reality, when rigorous destructive analysis is performed on the solid wastes, they are typically found to contain only tens of mBq/g (pCi/g) concentrations of radioactivity, metals are almost never seen at regulated levels, and organic compounds (generally only acetone or similar solvents in the few cases detected) are typically at 1-10 part-per-million (ppm) levels.

LLNL has not traditionally been a large generator of mixed waste. From 2000-2003, LLNL generated an average of 240 containers per year, containing a total of 19,500 kg/yr of solid RCRA mixed waste. Of this waste, an average of 24% of the containers, and 56% of the mass of waste were generated by waste management operations, including the treating of liquid mixed wastes. During the same time period, CES operations generated an average of 93 containers per year, containing a total of 3086 kg/yr of mixed waste. If only programmatically-generated waste is counted (not including waste management and facility decommissioning), CES analytical laboratory operations produce 56% of the containers, and 51% of the mass of waste. Even when the RHWM-generated waste and one-time demolition wastes are included, CES analytical operations still represent 39% of the containers and 16% of the mass of solid RCRA mixed waste. When the costs of regulatory compliance, sampling and analysis, and eventual disposal are tallied, in addition to the potential for personnel exposure when handling and opening waste containers, it can be seen that any reduction in the generation of mixed waste is a highly desirable goal.

In an effort to minimize the generation of these extraordinarily costly and difficult to dispose of mixed wastes, a project was begun at LLNL in late 2001 to develop at least one certified low-level waste stream (LLW) from CES operations, free of hazardous constituents, and adequately characterized for disposal at the DOE's Nevada Test Site (NTS). For this project, a single waste stream was chosen: empty sample containers and other small bottles. This waste stream represents a large volume of waste containing only minute amounts of radioactivity, and it also poses the fewest regulatory and management challenges.

REGULATORY BACKGROUND

The keystone to the development of a LLW stream from CES empty containers is the use of the "empty container exemption" from federal hazardous waste regulation 40CFR261.7 and State of California hazardous waste regulation 22CCR66261.7. Both of these sections of law allow exemption of small empty containers from hazardous waste regulations under certain conditions. The exact wording of 40 CFR 261.7 section (a)(1) states

> (a)(1) Any hazardous waste remaining in either (i) an empty container or (ii) an inner liner removed from an empty container, as defined in paragraph (b) of this section, is not subject to regulation under parts 261 through 265, or part 268, 270 or 124 of this chapter or to the notification requirements of section 3010 of RCRA.

To meet this exemption, the containers must be small in volume (5 gallons or less, per California regulations), empty by "practices commonly employed," and not have formerly held federally-defined acutely hazardous materials (defined in 40 CFR 261.31, 261.32, or 261.33(e)) or state-of-California-defined extremely hazardous materials (22 CCR 66261.126 Appendix 10). Most of CES's sample containers are 50-500 ml plastic bottles, or 100-1000 ml glass jars, so the volume limitation was not a concern. CES chemists are taught during sample dumping/waste handling training that if a container cannot be emptied without leaving a residue (common with sludge and oil samples) that the containers are to be disposed of as mixed waste, rather than in the LLW stream.

In order to ensure that containers did not formerly hold an acutely hazardous (AH) or extremely hazardous (EH) sample, an upfront segregation is performed for these containers. Less than 1%

of CES samples meet this criteria, the most common being concentrated hydrochloric acid solutions, liquid mercury, and samples containing beryllium. When samples are delivered to CES, they are accompanied by a form called a Sample Hazard Assessment (SHA), which informs the lab if the sample contains particular hazards, such as high levels of radioactivity, high concentrations of volatile solvents, reactive chemicals, and inhalation hazards, such as beryllium. The SHA form is filled out by a trained Characterization Chemist from RHWM prior to sampling. For the purposes of this project, the SHA form was modified to add a check box to be marked if the sample may contain AH or EH materials. CES log-in personnel are trained to review this form, then label any sample bottles that contain AH/EH material with an orange sticker. These bottles are then segregated during sample dumping, and the empty containers are disposed of as mixed waste. In addition, CES log-in personnel are trained in the identification of AH/EH materials, and are capable of reviewing the sample description to determine if any samples contain AH/EH materials.

RADIOACTIVITY CHARACTERIZATION STRATEGY

In order to certify low-level waste for disposal, it is necessary to characterize the identity and quantity of radionuclides present. This is a non-trivial problem in that LLNL has a history of using a huge variety of radioactive isotopes, including both gamma emitters easily detected with non-destructive assay methods (depleted uranium (U-238), Cs-137, Eu-152, etc.) and non-gamma emitters (H-3, C-14, Pu-239, etc.), and CES wastes might contain any of these isotopes. Any radioactive characterization strategy must address both gamma emitters and non-gamma emitters, must be simple and cost-effective to use on the majority of containers that have only tens to hundreds of mBq/gm (pCi/gm – nCi/gm) amounts of contamination, yet must be able to identify and quantify occasional containers that have higher levels of activity. For this project, the following quantification scheme was developed:

- Assume that the radioactive contamination of the empty containers comes from the samples they used to contain.
- Determine the average distribution of radionuclides in CES samples.
- Determine a measurement technique for a scaling isotope in the distribution.
- Develop a method to identity and quantify isotopes in drums with non-standard radionuclide distributions.

Determination of radionuclide distribution

The first assumption made in the waste characterization strategy was that the empty container waste stream would be contaminated with the same radionuclides, in the same relative ratios, as the original samples. Analytical results were available for 13 containers of CES sample dumping waste produced during the time period 1995-2000. These containers included 5 aqueous waste containers, 5 solid and soil waste containers, and 3 organic waste containers. The analyses performed on these samples included gross alpha/beta, tritium, and gamma spectroscopy. Several of the later samples also have alpha spectroscopy results. The average radioactivity concentration was determined for each sample matrix: solid, aqueous, and organic.

A search of the CES database showed that CES performed 10,430 individual analytical tests between 10/99 and 10/00. These tests were sorted by matrix to generate the results in Table II.

Table II. Breakdown by matrix of samples analyzed at CES from 1999-2000.

Matrix	% of total samples
Solid	53
Aqueous	37
Organic liquid	10

The average analytical results for each matrix were then multiplied by the percentage of total samples for that matrix, then the results were normalized to the U-238 activity in order to generate the results in Table III. Assuming that the waste streams produced at LLNL are substantially the same over the past several years, the radioactivity present in the lab trash would be expected to be present in the same activity ratios as the original samples.

Table III. Activity ratio for radionuclides found in CES samples, normalized to U-238.

Isotope	Ratio to Dep-U activity
H-3	8.65E+00
U-238	1.00E+00
Eu-152	3.5E-02
Cs-137	1.7E-02
Am-241	1.33E-02
Th-232	6.00E-03
Pu-239	1.0E-03
Np-237	7.2E-04
Co-60	4.3E-04

Measurement of scaling radionuclides

Once a radionuclide distribution had been developed, the next step was to develop a measurement technique for one of the isotopes in the distribution, in order to scale the results to a given container. Gamma spectroscopy was performed on the first five drums of the LLW stream, and the results were indistinguishable from background. For the setup and count time used, the calculated minimum detectable activity (MDA) value for U-238 was approximately 37 kBq/drum (1 µCi/drum). Each drum was also surveyed using a NaI(Tl) "microR" meter, and the results were again indistinguishable from the background of 7-8 microR/hour. Using this data, it was decided that all drums of LLW would only be surveyed via microR meter, and those within a factor of 3 of the local background would be assigned an activity of 37 kBq (1 µCi) of U-238. The assigned value of 37 kBq (1 µCi) U-238 would then be multiplied by the distribution in the table above to determine the activity of non-gamma emitting isotopes.

In order to identify and quantify any containers with higher levels or non-standard isotope distributions, it was decided to perform gamma spectroscopy on any drum that exceeds 3 times the local background, as determined by microR meter. Any detected isotopes would be reported at the measured value, and the U-238 measured value (or MDA for U-238 if not detected) would be used to scale the isotopes in the table above, as for normal drums.

DOCUMENT DEVELOPMENT, TRAINING AND QUALITY ASSURANCE

At LLNL, the documentation of a certified Low-Level Waste stream is done using a Process Knowledge Evaluation form, or PKE. The PKE includes information on the waste matrix and contents, expected rate of generation, radioactive and hazardous constituents, and the methods used to quantify the radioactivity in the waste. Since the proposed CES waste stream will convert a significant quantity of waste from mixed to LLW, and will probably be audited extensively, the documentation requirements were stringent, resulting in a very long and complex PKE. While an average PKE for LLW at LLNL is typically 6-10 pages long, and is approved in approximately 1 month, the CES LLW PKE is 52 pages long, and includes copies of the applicable regulations, a CES standard operating procedure that describes the segregation of waste containers, training records for this standard operating procedure, as well as a memo documenting the radioactivity characterization strategy. Development and approval of this document took greater than 18 months, and required many hours of work by several dedicated individuals from both Radioactive and Hazardous Waste Management (RHWM) and CES.

The first document to be developed was the radioactivity characterization strategy memo, which outlined how drums of empty containers would be assayed for radioactivity. This memo required approximately 20 hours of work to develop, spread over several weeks of time. It was written by the CES Deputy Program Leader for Lab Operations, and was reviewed independently by a Radiological Characterization Analyst (RCA) from RHWM.

Next, the CES standard operating procedure for sample dumping and container disposal was written, which took approximately 60 hours of work over several months of time. This also included modifying the Sample Hazard Assessment (SHA) form to insert a check box for potential AH/EH materials. These documents were written by the CES Deputy Program Leader for Lab Operations, but as they are safety-related documents, they required significant quality assurance and environment, safety, and health review and approval, and were externally reviewed by both an RCA and the LLNL Waste Certification Official (WCO). Finally, technicians from RHWM developed a 1-hour training course to train CES employees on both the sample segregation and PKE requirements. In addition, all CES employees who generate LLW must be current in LLNL's institutional training requirements for both hazardous waste generation and certification, and certified LLW generation and certification. The development of RHWM's training course took approximately 20 hours of work, spread over approximately 2 months.

Once all the documentation was completed, the finished PKE was submitted to both an RCA and the WCO for final approval. Due to the extensive interactions of these individuals with the PKE authors, the final PKE was approved within a few months of submittal.

The final PKE is maintained at the LLNL WCO office, where, as with all LLNL PKEs, it is subject to routine surveillance and audit. New CES employees are trained on the requirements of the PKE and the CES procedure for sample dumping as part of routine new employee training. This training is documented and maintained with the employees CES training records.

WASTE GENERATION DATA/OPERATING EXPERIENCE

During the time period 2000-2003, CES operations generated an average of 93 drums of RCRA mixed waste, containing 3090 kg of waste material per year.
Generation of LLW began in February of 2004. From February 2004 through the first week of January 2005, 51 drums of RCRA mixed waste containing 3060 kg of material have been generated. In the same time period, 13 drums containing 1495 kg of certified LLW have been generated. By instituting the LLW stream, 20% of waste containers, and 33% of waste mass have been diverted from mixed waste. This is an impressive savings in multiple areas; cost, personnel exposure, regulatory oversight, and even further waste generation. At LLNL, newly generated mixed waste is destructively sampled and analyzed, with the eventual goal of disposal at Envirocare of Utah. Newly generated mixed waste is tracked, sorted into populations, sampled under a specific sampling and analysis plan or data quality objective (DQO), and analyzed by CES (in the process generating more waste). The data is used to generate disposal profiles, finally the waste is transported to the disposal site. The cost savings of reducing the quantity of mixed waste includes not just disposal cost, which is $7 per cubic foot of LLW versus $40 per cubic foot of mixed waste, but also all the regulatory and management costs associated with the activities above. In addition, since sampling of mixed waste involves a sampling team opening and sorting containers of potentially hazardous materials, any reduction of mixed waste involves a significant reduction in potential personnel exposure. At LLNL, it is conservatively estimated that the costs of managing a drum of mixed waste is $5200 more than managing a drum of LLW. Given the CES generation rate of 93 drums of mixed waste, and assuming 20% of these drums may now be managed as LLW, this represents a potential cost savings of $97,000 per year.

The upfront segregation for AH/EH materials has progressed smoothly. There have only been ~30 samples (~1% of the total) during this time that have been AH/EH, and the vast majority were properly identified before sampling ever occurred. In several cases, samples which were not identified prior to sampling as AH/EH by the sampling team were identified upon receipt by CES chemists, labeled, and segregated during sample dumping. In all cases, the empty bottles containing potentially AH/EH materials were disposed of as mixed waste.

CES chemists have been taught to dispose of any suspicious containers, including those with sludge or oil residue, as mixed waste, rather than LLW. The CES chemists generating the waste are taught to err on the side of conservatism when discarding items as LLW. Still, well over 90% of empty sample and process containers are now disposed of in the LLW stream. The full drums of empty containers are backfilled with absorbent to immobilize any small traces of liquids left in the containers, and to ensure that the containers meet the NTS Waste Acceptance Criteria (WAC).

While this process was originally intended to deal with empty sample containers, it is beginning to be used for other waste items, including process containers used in the chemical processing of samples, and counting planchettes which are used to mount alpha/beta samples. These planchettes are used to hold liquid samples (which are then dried to form solid counting samples) and contain nearly weightless residues, and therefore meet the definition of empty containers.

CONCLUSION

The largest single programmatic source of newly-generated mixed waste at Lawrence Livermore National Laboratory (LLNL) is the on-site environmental compliance analytical lab, Chemistry and Materials Science Environmental Services (CES). CES typically generates approximately 100 drums of mixed waste per year, containing approximately 3100 kg of waste. In an effort to minimize the generation of this expensive and difficult to deal with waste, a certified low-level waste stream (LLW), free of hazardous constituents, and adequately characterized for disposal as LLW at the Department of Energy's Nevada Test Site (NTS) was developed for CES operations. By utilizing the empty container exemption in state and federal hazardous waste laws, as well as up-front segregation of samples of acutely/extremely hazardous materials, a waste stream of empty sample and process containers has been developed. Generating the necessary paperwork, and receiving approval for this waste stream took nearly two years and a great deal of work. In the 10 months that the stream has been in use, the CES program has diverted 33% (by mass) of its mixed waste to LLW, with hopes of increasing the amount that will be diverted in the future. Comparing the costs of managing LLW versus managing mixed waste, this represents a potential cost savings of nearly $100,000 per year, as well as reduced personnel exposure and regulatory burden.

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