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**WASTE CHARACTERIZATION FOR RADIOACTIVE LIQUID WASTE
EVAPORATORS AT ARGONNE NATIONAL LABORATORY - WEST**

Low Level, Intermediate Level, and Mixed Waste

By

Boyd D. Christensen

Operations Division

and

Michael A. Lehto Ph.D.

Operations Division

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Argonne National Laboratory B West

P.O. Box 2528

Idaho Falls, Idaho 83403-2528

ABSTRACT

Several facilities at Argonne National Laboratory - West (ANL-W) generate many thousand gallons of radioactive liquid waste per year. These waste streams are sent to the ANL-W Radioactive Liquid Waste Treatment Facility (RLWTF) where they are processed through hot air evaporators. These evaporators remove the liquid portion of the waste and leave a relatively small volume of solids in a shielded container. The ANL-W sampling, characterization, and tracking programs ensure that these solids ultimately meet the disposal requirements of a low-level radioactive waste landfill. One set of evaporators will process an average 25,000 gallons of radioactive liquid waste, provide shielding, and reduce it to a volume of six cubic meters (container volume) for disposal.

Waste characterization of the shielded evaporators poses some challenges. The process of evaporating the liquid and reducing the volume of waste increases the concentrations of RCRA regulated metals and radionuclides in the final waste form. Also, once the liquid waste has been processed through the evaporators it is not possible to obtain sample material for characterization. The process for tracking and assessing the final radioactive waste concentrations is described in this paper. The structural components of the evaporator are an approved and integral part of the final waste stream and they are included in the final waste characterization.

Samples are processed through the analytical chemistry lab to ensure that the liquid waste falls within acceptance criteria before the radioactive liquids can be shipped to the RLWTF holding tanks. In order to obtain a representative sample, all liquid samples are obtained after the tank volume has been circulated for a period of time. Particularly important to the sampling protocol is verification that the liquid does not exceed concentrations of RCRA regulated metals listed in 40 CFR §261.24 Table 1, *Maximum Concentration of Contaminants for the Toxicity Characteristic*. The pH of the liquid is measured to verify that it does not exceed limits of corrosivity listed in 40 CFR §261.22 and to ensure that the liquid will not damage the associated piping and components of the RLWTF. Radiological analyses are also performed to account for the inventory of specific radionuclides in the evaporators. If acceptance criteria parameters are not exceeded, the radioactive liquid is shipped for temporary storage in the holding tanks of RLWTF.

Prior to processing the liquid through the shielded evaporators, a one-liter sample is taken for each 100 gallons of liquid to be processed. These samples are poured into a Feedstock Sample Evaporator (FSE), which evaporate the liquid and leaves behind only solids in much the same manner as the full-size shielded evaporators. The residue solids in the FSE become a representative sample of the contents in the evaporators at the end of their useful life.

Once the analytical results have been returned on the residue samples from the FSE a hazardous waste determination can be made against the limits listed in 40 CFR §261.24 Table 1. Once those limits are found not to be exceeded and radiochemistry indicates that the isotopes present are within parameters required by the radioactive waste disposal landfill the shielded evaporators may be removed from service and prepared for shipping to the disposal facility. The evaporators are disposed of at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL).

As research programs have changed at ANL-W concentrations of regulated metals and radioactive nuclides have increased necessitating a method of tracking the regulatory status of the evaporators while they are in service. This paper will show the method ANL-W has developed to characterize this low-level radioactive waste stream.

INTRODUCTION

Aqueous radioactive liquid waste is generated primarily in three facilities as a result of 1) water washing hot cell equipment in spray chambers, 2) analytical chemistry procedures, and 3) general facility clean up/radiological decontamination at ANL-W. The liquid waste is processed on site in self-shielded evaporators, which also become the shipping and disposal container at the end of their useful life. Figure 1 is a schematic diagram of an evaporator, also known as Shielded Hot Air Drum Evaporator (SHADE). Operating history shows that a set of six evaporators has the capability to efficiently evaporate between 25,000 and 32,000 gallons (94,600 to 121,000 liters) of water. The evaporator set is approximately six cubic meters, giving considerable waste volume reduction over other methods of radioactive liquid waste disposal. The final waste consists of a radioactive dry-solid residue on a series of evaporator trays within a three ft.

diameter by five ft. tall cylindrical steel and concrete shielded disposable cask that can be disposed of as a contact-handled low-level radioactive waste.

Evaporating the liquid has a concentrating effect, resulting in residue with a higher concentration of radioactive isotopes and RCRA regulated metals than the feed wastewater. Due to evaporator design and radiological exposure concerns, direct sampling of the evaporators is virtually impossible, yet good data must be obtained in order to show compliance with all applicable waste acceptance criteria.

DISPOSAL CONSIDERATIONS

Care must be taken throughout the operational life of the evaporators to ensure that the final waste product will meet the waste acceptance criteria of the receiving facility, i.e., RWMC. Presently, the RWMC is the best disposal option for the evaporators for several reasons: first, the unusual package is unique; second, undesirable shipping problems (i.e., greater expense, operator radiation exposure, added transportation risks) would be encountered if the evaporators were shipped to a remote location. No practical storage or disposal options exist for these evaporators should they become a mixed waste.

For these reasons every effort is made to meet waste acceptance criteria for the RWMC and at all costs avoid generating transuranic or mixed waste.

FACILITY OPERATION

The RLWTF receives liquid waste primarily from three radiological facilities at ANL-W. Each of these facilities has liquid waste hold-up tanks that are filled from day-to-day facility operations. Once the facility hold-up tank is filled, the tank contents are circulated and sampled. During the sampling and analysis process the tank inlet is isolated to prevent liquids being added that would not be represented by the sample. This first sample is used as a screening sample. If the sample indicates high levels of fissile material, transuranic isotopes, or RCRA-regulated metals, the batch will be prohibited from RLWTF. If levels are low, the waste-water batch is pumped through underground piping to the RLWTF holding tanks.

Analytes of interest in the screening sample are:

- RCRA-regulated metals, expressed as µg/ml,
- mass of uranium, expressed as grams per batch,
- mass of plutonium, expressed as micrograms per batch,
- ¹³⁷Cs, expressed in micro curies per ml of liquid waste,
- solids suspended in the liquid, expressed as grams of solids per batch,
- pH.

Table I shows the current administrative limits placed on liquids entering the RLWTF.

Table I Administrative Limits on Liquids Destined for the RLWTF

Analyte	Limit
plutonium	7500 μ g/1000 gal
uranium	1.5 g/1000 gal
RCRA Regulated Metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver)	Limits Listed in 40 CFR §261.24 Table 1
pH	>5 and <10

Once in RLWTF, the batch is again circulated, sampled, and analyzed prior to processing. RCRA regulated metals that are not detected or detected at very low levels in the first screening sample do not require confirmatory analysis from a second sample. Analytical results obtained from this second sample are used to calculate radioactive isotope curie inventory, which will become part of the waste stream profile for evaporator disposal. At the same time, samples are taken from the batch that will comprise a composite sample representative of the residue solids at the end of the evaporators' useful life. For each 100 gallons liquid in the batch a one-liter sample is drawn. For example, for an 800-gallon batch eight liters would be drawn off to become part of the composite sample. Those liquid samples are poured into the FSE, which evaporates the liquid and leaves only solids behind in much the same manner as the full-scale production evaporators.

This process is repeated for each batch of radioactive liquid generated. The evaporator set is considered "full" when one of three conditions occurs: 1) The evaporation rate drops off to inefficient levels due to the large amount of solids removed in the liquid evaporation process and collected in the evaporator trays (generally this is at approximately 250,000 g of solids), 2) Concentrations of RCRA metals approach the limits imposed by 40 CFR §261.24 Table 1, or 3) Radioactive isotope concentrations approach the performance assessment concentration limits listed in the INEEL Reusable Property, Recyclable Materials, and Waste Acceptance Criteria manual (RRWAC), Table 4.5.5-1.

Once the evaporators are filled, the FSE is opened and a subsample is removed for analysis. The sample in the FSE is the residue solids from one liter for each 100 gallons processed through the full-scale evaporators. This sample is representative of all residue within the evaporators. A representative sample is obtained by removing material from all strata of the residue in the

evaporator tray. This sample is used to characterize concentrations of leachable RCRA-regulated metals.

Waste characterization consists of evaluating concentrations of RCRA metals and radioactive isotopes. After waste characterization is complete the evaporators are disconnected from the facility systems and the tops are capped with concrete, forming a sealed and shielded package ready for disposal in a radioactive waste landfill.

WASTE ACCEPTANCE CRITERIA

Waste acceptance criteria for mixed waste disposed of at the INEEL RWMC are detailed in the INEEL Reusable Property, Recyclable Materials, and Waste Acceptance Criteria manual (RRWAC). Of particular interest here is the restriction of 1) RCRA characteristic or listed hazardous waste(1), 2) radioactive waste that exceeds greater than Class C concentrations(2), and 3) waste that exceeds RWMC mandated "performance assessment" concentrations(3). The performance assessment criteria are based on Energy Department classifications of radioactive waste. Radioactive waste classifications are expressed in concentrations of curies per cubic meter, or nanocuries per gram of waste for transuranic isotopes. Of the 18 isotopes or groups listed in the performance assessment only five have been detected in the ANL-W evaporators at reportable concentrations; ^{137}Cs , ^{241}Pu , ^{90}Sr , uranium isotopes, and transuranic isotopes as a group.

Other waste acceptance criteria outside the scope of this paper are not discussed here, but can be found in the latest revision of the INEEL RRWAC, section 4.5.

RADIOLOGICAL CHARACTERIZATION

Prior to processing each batch of liquid waste the batch is circulated, sampled, and analyzed. The concentrations of ^{137}Cs and ^{90}Sr , and the mass of uranium and plutonium are usually the radionuclides of greatest interest. They are sampled to assure they meet Performance Assessment concentrations listed in the disposal site=s waste acceptance criteria. Other radionuclides listed in the performance assessment are not typically found above the reporting limit concentrations.

Analytical results for ^{137}Cs and ^{90}Sr are returned as $\mu\text{Ci/ml}$, and the specific radionuclide inventory for each batch is calculated by

$$\text{concentration } (\mu\text{Ci/ml}) \times \text{ml of water} = \text{total } \mu\text{Ci} \quad (\text{Eq. 1})$$

Analytical results for plutonium and uranium isotopes are returned in μg of plutonium or grams of uranium per batch. Ratios of plutonium and uranium isotopes are known through previous analyses and process knowledge. Through the use of specific activity values for each plutonium and uranium isotope the total nanocurie value for each batch can be calculated.

The nuclide source term is tracked as an isotopic curie inventory with each batch=s contribution

being added to the previous total inventory. Figure 2 illustrates how ANL-W personnel track radionuclide inventory. The following equations examples show how radionuclide concentrations are calculated for both transuranic isotopes and non-transuranic.

for non-transuranic isotopes

$$\frac{\text{Curies present}}{\text{Volume(m}^3\text{)}} = \text{Ci/m}^3 \quad (\text{Eq. 2a})$$

example

$$\frac{2.67 \text{ Ci Cs-137}}{6 \text{ m}^3} = 0.446 \text{ Ci/m}^3 \quad (\text{Eq. 2b})$$

for transuranic isotopes

$$\frac{\text{nCi present}}{\text{Mass (g)}} = \text{nCi/g} \quad (\text{Eq. 3a})$$

example

$$\frac{4.63 \text{ E+ } 06 \text{ nCi Pu-241}}{308400 \text{ grams}} = 15 \text{ nCi/g} \quad (\text{Eq. 3b})$$

These calculations are repeated for each isotope of concern in the performance assessment found in this waste stream. The concentration is then divided by the concentration limit for that isotope in the performance assessment giving a fraction of the performance assessment limit. The sum of the fractions of all isotopes must be less than one in order to comply with performance assessment criteria. Tracking the nuclide inventory in this way allows the facility to monitor our new source term with each additional batch processed, or choose not to process a batch if the concentrations would cause us to exceed allowable concentrations.

At the end of evaporator life the total isotope inventory is used to calculate isotopic concentration In terms of nCi/g for transuranic isotopes and Ci/m³ for other isotopes.

RCRA METALS ANALYSIS

At the end of the evaporator useful life, a hazardous waste determination must be made before the evaporator can be shipped to the radioactive waste disposal site. Hazardous wastes are prohibited from disposal in any of the facility liquid waste systems so the hazardous waste determination is made by looking for toxicity characteristic metals in the evaporate residue. Over years of samples and process knowledge ANL-W has found that of the eight RCRA toxicity characteristic metals, only four are routinely found at significant levels in the evaporators: chromium, lead, cadmium, and mercury.

The FSE is used as the source for the RCRA metals sample. Since the evaporators cannot be sampled directly the FSE was installed to provide a surrogate sample. The sample is analyzed

for the potential RCRA-regulated metals. Chromium, lead, and mercury have been found to be very insoluble in the residue matrix. It has been concluded that even if the total ppm levels of these metals are high, they do not readily leach out of solution in the sampling protocol. However, cadmium leaches out of the sample matrix under the conditions of the Toxicity Characteristic Leaching Procedure (TCLP) at a much higher rate. Even moderate levels of cadmium in the radioactive liquid, once concentrated in the evaporators, may become a limiting factor in useful evaporator life since no alternate disposal options exist for the shielded evaporators as a mixed waste.

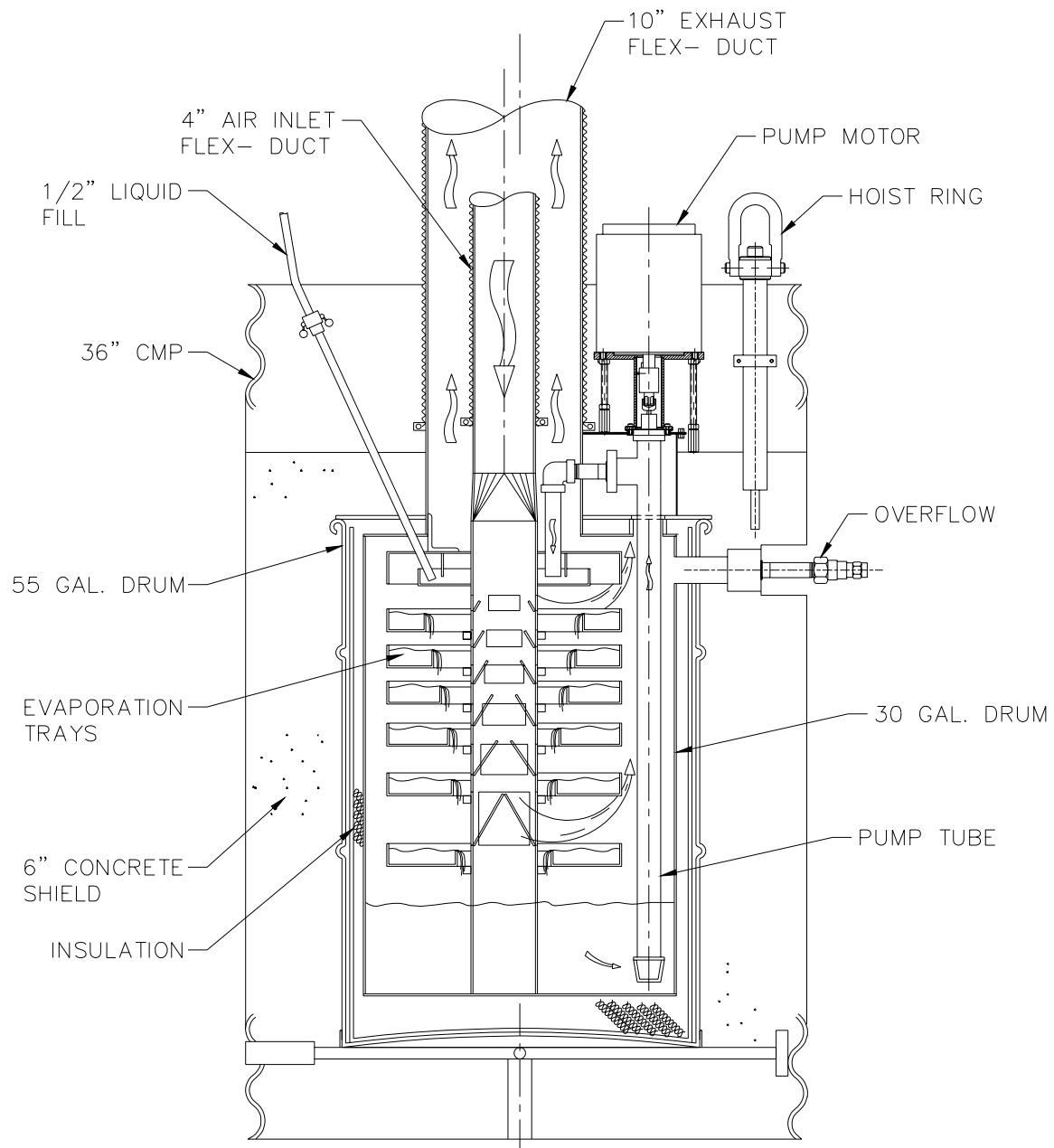
RCRA metals are measured first for total metal content using atomic absorption measurement methods. If the total content parts per million (PPM) is 20 times the RCRA regulated TCLP limits of 40 CFR §261.24 Table 1, then the TCLP must be run to determine leachable metals concentration.

EXTENDING USEFUL EVAPORATOR LIFE

As a waste minimization consideration and financial responsibility, it is in ANL-W's best interest to maximize the life of the evaporators. This is accomplished in two basic ways. First, in some cases gross solids and contamination can be filtered out of the waste water before it leaves the facilities. The downside that must be weighed against benefits is that filtration could produce mixed, transuranic, or remote-handled waste filters. The second way to maximize evaporator life is by careful management of the waste coming into the RLWTF and balancing concentrations of RCRA metals, radioactive isotopes, and total solids coming into the facility in such a way that no regulatory levels are exceeded.

CONCLUSION

Processing radioactive liquid waste in the RLWTF results in a residue with higher concentrations of RCRA-regulated metals and radioactive isotopes than the liquid waste going into the system. Therefore, it is necessary to have a method of tracking these concentrations while the evaporators are in service in order to prevent the generation of mixed or transuranic waste. This can be accomplished by tracking isotope inventories and monitoring concentrations of RCRA-regulated metals in the waste water being processed in the facility. RCRA-regulated metals are monitored through sampling of each batch, and a final composite sample at the end of evaporator life to confirm that regulatory limits are not exceeded. Past experience has shown that moderate concentrations of metals with higher solubility in the waste water may become a limiting factor in the useful life of the evaporators.



SHADE INTERNAL STRUCTURE

FILE NAME: 798-030.DWG
SHERRI L. PALMER 1-25-99

Figure 1 Shielded Hot Air Drum Evaporator (SHADE)

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Weight of waste	339620	g
Volume of SHADES	6	M ³
Plutonium present	6010	micro g
Uranium present	0.6	g
¹³⁷ Cs present	5.43	Ci
⁹⁰ Sr present	3.89	Ci

								sum of fractions	0.5097
PLUTONIUM									
isotope	fraction	% activity	sPa (Ci/g)	g/Ci	g of iso.	% by wt.	nCi present	RRWAC fraction	
²³⁸ pu	0.149	0.3840453	17.1	0.0584795	0.0087135	0.041054	4.22E+04		
²³⁹ pu	1	2.5774849	0.0621	16.10306	16.10306	75.87057	2.83E+05		
²⁴⁰ pu	1.03	2.6548095	0.227	4.4052863	4.5374449	21.378455	2.92E+05		
²⁴¹ pu	36.3	93.562703	103	0.0097087	0.3524272	1.6604827	1.03E+07		
²⁴² pu	5.11E-04	0.0013171	3.93E-03	254.45293	0.1300254	0.612623	1.45E+02		
²⁴¹ am	0.318	0.8196402	3.43	0.2915452	0.0927114	0.4368154	9.00E+04		
Tot	38.797511	100			21.224382	100	1.10E+07		
							nCi/g TRU isotopes	2.08E+00	0.2082
							nCi/g ²³⁴ Pu	3.03E+01	0.1211
URANIUM									
isotope	fraction	% activity	sPa (Ci/g)	g/Ci	g of iso.	% by wt.	Ci present	Ci per m ³	
²³² u	1.70E-05	4.54E-04	22.4	0.0446429	7.589E-07	9.487E-08	1.28E-08	2.13E-09	
²³³ u	4.75E-07	1.27E-05	9.65E-03	103.62694	4.922E-05	6.153E-06	3.56E-10	5.94E-11	4E-09
²³⁴ u	3.74	1.00E+02	5.23E-03	191.20459	715.10516	89.393585	2.81E-03	4.68E-04	0.01336
²³⁵ u	8.91E-05	2.38E-03	2.16E-06	462962.96	41.25	5.1565638	6.68E-08	1.11E-08	7.4E-07
²³⁶ u	1.70E-04	4.54E-03	6.17E-05	16207.455	2.7552674	0.3444294	1.28E-07	2.13E-08	
²³⁷ u	8.72E-04	2.33E-02	81638	1.225E-05	1.068E-08	1.335E-09	6.54E-07	1.09E-07	
²³⁸ u	1.36E-05	3.64E-04	3.33E-07	3003003	40.840841	5.1054158	1.02E-08	1.70E-09	4.3E-08
Tot	3.74E+00	100			799.95132	100	2.81E-03	4.68E-04	0.0134
BETA EMITTERS									
isotope							Ci present	Ci per m ³	
¹³⁷ Cs							5.425375	9.04E-01	0.1130
⁹⁰ Sr							3.889993875	6.48E-01	0.0540

Figure 2 Sample Batch Isotope Calculations

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REFERENCES

- 1 40 CFR §261.21-33
- 2 10 CFR §61.55 Radioactive Waste Classification
- 3 INEEL Reusable Property, Recyclable Materials, and Waste Acceptance Criteria manual (RRWAC) Table 4.5.5-1.