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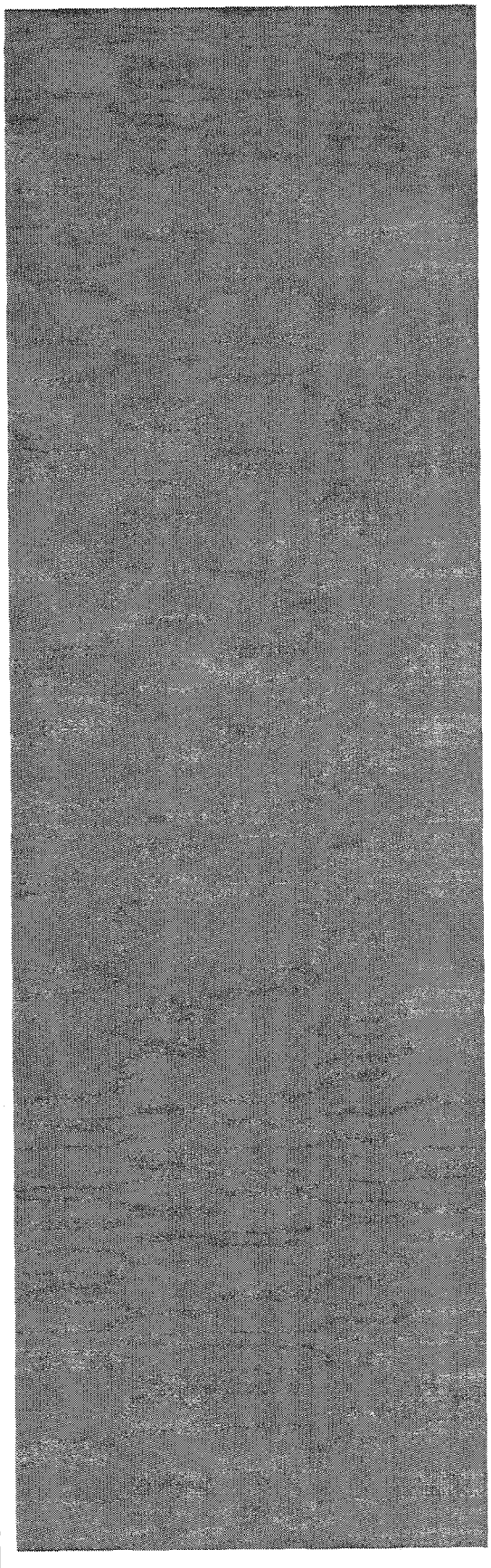

Disposition of Mixed Waste Organics at the Los Alamos Plutonium Facility

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by

S. B. Schreiber, S. L. Yarbro, E. M. Ortiz, F. Coriz, and S. Balkey

ABSTRACT

Twenty-six organic solution items totaling 37 L had been stored in the Plutonium Facility vault at the Los Alamos National Laboratory, some for up to 18 years. They were residues from analytical analyses of radioactive solutions. All items had a Resource Conservation and Recovery Act (RCRA) defined hazardous waste combined with special nuclear materials (SNM) and were stored as a mixed waste in a vault room pending disposition. Seventeen items had plutonium concentrations above established discard limits for organics. Due to their age, the containers were not suitable for long-term storage because a container failure would contaminate the vault area and personnel. Therefore, an aqueous-based flowsheet was developed to remove the plutonium so that the items could be discarded. The procedure was a wash with either sodium fluoride and/or potassium hydroxide solution followed by absorbing the discardable organic residues on vermiculite. When this approach did not work, permission was obtained to discard the items as a transuranic (TRU) mixed waste without further treatment. The remaining nine solution items were consolidated into two items, repackaged, and stored for future disposition. The overall effort required approximately four months to disposition all the items. This report details the administrative and regulatory requirements that had to be addressed, the results of processing, and the current status of the items.

BACKGROUND

All work with actinide-containing materials requires analyzing radioactive solutions and has produced waste liquids for subsequent recovery or waste management. Recently, changing administrative requirements for "hazardous" materials, as defined by the Resource Conservation and Recovery Act (RCRA), required special storage and handling methods. In particular, Room A in the Plutonium Facility vault had been set aside to store analytical residues and other wastes that have hazardous materials content or are suspected to have been in contact with hazardous materials. However, most of the solutions being stored in Room A had been there for several years. Nearly 40% of the items had been in storage for at least a decade and over 80% had been in storage for more than five years. The age distribution is presented in Table I.

Table I
Solutions Age Distribution

Year Stored	No. of Items	Years in Storage
1980	1	18
1985	1	13
1987	1	11
1988	7	10
1989	8	9
1990	2	8
1992	1	6
1995	5	3

These items were not packaged for long-term storage, and the containers were deteriorating. During an inspection of one of the items containing alpha active plutonium-238 (RES-3135-L19), the outer bag crumbled while the item was being handled. Some contamination was released into an introduction hood. Most of the items were corrosive solutions stored in glass bottles with vented rubber stoppers that had the potential to leak. In fact, several of the stoppers had deteriorated to the point where solution was present in the secondary containment bag. In addition, as part of the RCRA Part B permit for handling the mixed waste items, an entire room within the vault was being dedicated to segregating and storing these twenty-six items. This was clearly not an efficient use of valuable vault space. Therefore, it became important to disposition these items quickly.

When the RCRA-permitted storage area had first been established and the items initially relocated to Room A, they were divided into two categories based upon the amount of special nuclear materials (SNM) present in each. The criteria was the FY89 Nuclear Materials Economic Discard Limits (EDL) that represented the SNM concentrations in residue matrices below which production of new SNM was more economical than SNM recovery. For organic solutions the limit was 6 g/L so items below this amount were declared a waste and those above were stored for subsequent SNM recovery. See Table II for a summary of each item by SNM content, volume, waste determination, and RCRA waste code.

DISPOSITION OF NONWASTE ITEMS

For the seventeen items not declared a waste, a procedure was proposed to attempt to remove the SNM so that the remainder of the item could be discarded. The flowsheet, based on work described by Maraman and Mullins (1), is presented as Fig. 1.

The item is introduced into the glove box, and the liquid is removed from the glass bottle or container. The liquid, typically black and viscous (similar to used motor oil) is then gently mixed in a Teflon separatory funnel with a 1:2 volume ratio of 1.7 M NaF to organic. The sodium fluoride should form a strong complex with the actinides present that will transfer from the organic phase to the aqueous phase. The solution is allowed to settle and separate. The aqueous phase is nondestructively assayed using a solution assay instrument (SAI) inside the glove box, and the organic is assigned an SNM

Table II
Solutions Waste Determination and Characteristics

Item Identification	SNM (g)	Volume (L)	Waste Determination	RCRA Waste Code
CLS1ORG-492	<1	0.48	Y	
CMCICPP00	4	1	Y	
CMCICP2	<1	2	Y	
CMC5119E5	5	2	Y	
CMC712801	1	0.30	Y	
CMC97861	8	2	Y	
SOLCLS15119-F4	5	2	Y	
SOLCLS15135-G6	1	0.01	Y	
SOLCLS15119-J6	<1	2	Y	
CMCICPP01	7	1	N	D002, D019
CMCICPP02	4	0.50	N	D002, D019
CMCICP1	11	2	N	D019
CMC5133A4	33	1.25	N	D019
CMC5133B7	24	2	N	F003, D019
CMC5133N3	40	2	N	D002
CMC5133S1	30	2	N	D002, D019
CMC5133V9	20	2	N	D002
CMC5133X2	34	2	N	D002, D019
CMC712860	10	1	N	D002, D019
SOLCLS15133-F5	36	1	N	D019
RES-3135-L17	3	<1	N	D002
RES-3135-L18	3	<1	N	D002
RES-3135-L19	2	<1	N	D002
RES-5131-J3	18	<1	N	D002
RES-5131-J4	18	<1	N	D002
STD-A	1	<1	N	

F003 - spent nonhalogenated solvents
D002 - characteristic of corrosivity (pH <2)
D019 - carbon tetrachloride

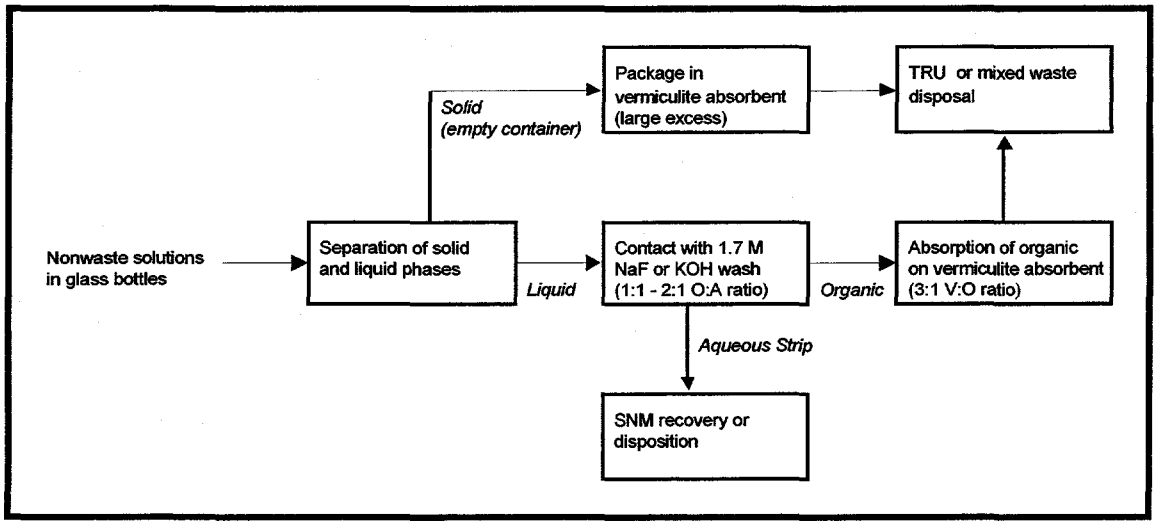

Fig. 1. SNM Recovery Flowsheet for Nonwaste Items

value by comparing the difference to the entering value. The organics are then mixed with a 3:1 ratio of vermiculite to liquid in a new stainless steel container for disposal as transuranic (TRU) solid waste. Any solids that are removed from the container to facilitate organic removal are dried, then nondestructively assayed by thermal neutron counter (TNC) for eventual discard as solid waste. The original container is filled with vermiculite to absorb any residual liquid and sent to TRU waste. The recovered SNM in the aqueous strip solution is sent for routine recovery or disposition, as appropriate based upon its concentration, using existing aqueous recovery operations in the Plutonium Facility.

When the flowsheet was implemented, it was hard to remove the SNM from the organic phase because of the extreme age, degradation, and variability of the organics. Just getting the organic sludge out of the container was difficult because in several instances it had solidified and could not be physically separated or washed out. Initially, the sodium fluoride wash was used in a 1:2 ratio with the organic. This was later increased to a 1:1 ratio. Problems encountered at this step in the process were the formation of an emulsion or a three-phase solution that could not be separated. The result was poor organic and aqueous phase separations that in turn resulted in poor SNM recovery from the organic. When the potassium hydroxide wash was used (as an alternative complexant) in a 1:1 ratio with the organic, better phase separation was observed, but the SNM was still not efficiently removed from the organic.

Three items were processed using the described flowsheet: CMCICPP01, CMC5133B7 and CMC5133V9. The work was labor intensive and time consuming, requiring several weeks to handle just these items. The aqueous wash solutions that were collected contained water soluble organics, probably degradation products from radiolysis of the original organic matrices, which impeded subsequent recovery operations. The process was generating additional bottles, containers, and sample vials to handle the solutions. The result was that the approximately 3.5 L of wash solution produced contained only 4 g of SNM that represented a recovery efficiency of less than 8%. Thus, the flowsheet was unsuccessful in removing the SNM from the organic matrices and was generating more waste, both liquid and solid, which would also have to be dispositioned. Therefore, the decision was made to disposition the remainder of the items as waste without further SNM recovery efforts.

A formal request was made to the responsible agency, the Nuclear Programs Division of the Department of Energy's (DOE) Albuquerque Operations Office (AL), by using the recently established plutonium disposition methodology (PDM). The PDM approach was developed in 1995 when the DOE determined that the EDL was no longer a valid discriminator because plutonium, and thus SNM, production had been terminated. The PDM approach considers twelve criteria of which the principle relevant ones were worker safety, waste minimization, cost, proliferation potential, and regulatory concerns (2).

As a result, the organic solution items were absorbed on vermiculite. The major driver was the radiolytic decomposition that was severely degrading the packaging. With a total SNM content of 318 g (approximately 250 g of plutonium-239 with lesser amounts of neptunium, uranium, and other plutonium isotopes), the safety

concerns were considered significant enough not to require recovery of the SNM. This is particularly true because it was demonstrated to be relatively inefficient with the matrices involved. Other technical options evaluated, including a hydrothermal process and a more established cementation process, were each determined to be incompatible for treating the organic items.

Researchers at Los Alamos had recently completed a series of laboratory-scale tests with hydrothermal processing for the treatment of radioactive combustible materials. Hydrothermal processing although an emerging technology at the Plutonium Facility, was not a viable option in this case because during the time frame that was required for dispositioning these organic solutions, it was still in a developmental stage. Recent experiments with the technique, however, have shown the complete destruction of radioactive combustible materials, on a small scale, to carbon dioxide (CO_2) and water (H_2O) with 30 wt % hydrogen peroxide (H_2O_2) as an oxidant at 540^{0}C and 46.2 MPa. Cementation using Portland cement was not viable because the waste must be uniformly distributed to be encapsulated in the final matrix. Obviously, an organic solution is not readily emulsified in the aqueous solution that is required to form the cement monolith.

From a regulatory standpoint, these items were considered to be "newly generated waste" and were allowed to be processed according to the flowsheet presented in Fig. 2. It was determined that they would maintain their RCRA designations and be disposed of as a mixed waste.

For these items, a waste disposal form was completed, and the absorption process was observed by qualified waste management personnel to ensure that the final product was certified. The vermiculite absorbent and organic were mixed in the approximately 3:1 ratio within a stainless steel dressing jar. The treated waste and empty glass containers were subsequently bagged out and managed as routine solid wastes. As such, these items have been systematically removed from the Plutonium Facility and are being managed as certified TRU mixed waste for ultimate disposition to the Waste Isolation Pilot Plant (WIPP) when it becomes available.

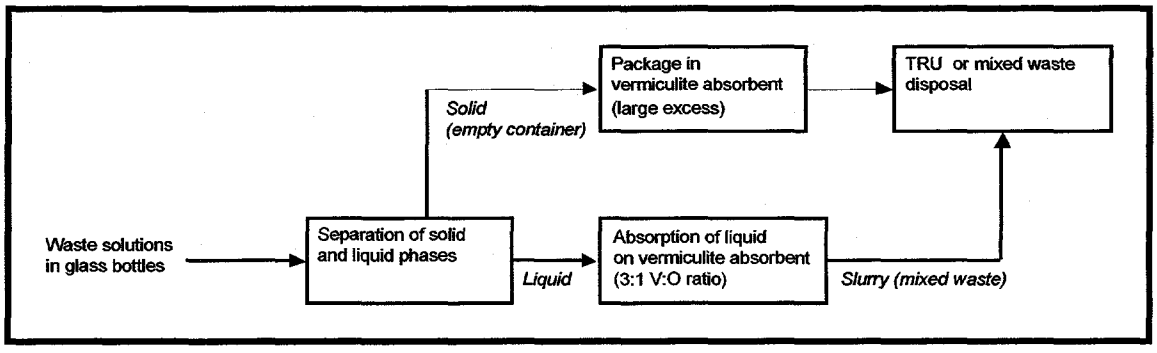

Fig. 2. Disposition Flowsheet for Declared Waste Items.

DISPOSITION OF WASTE ITEMS

The nine declared waste items were to be treated with a newly developed hydrothermal process to destroy the organic constituents and thus eliminate the RCRA component. The resulting solely radioactive material could then be dispositioned as radioactive waste by routine methods rather than being handled as a mixed waste. However, the cost and time required to deploy and operate a unit of the appropriate size to handle the ~12 L of waste could not be justified. Although the technique had been successfully demonstrated on a pilot scale to destroy pure organic materials, more development would be required to handle organics mixed with metallic impurities. As configured, the metals would oxidize and remain in the reactor. Alternatively, the SNM impurities would have to be quantitatively removed before the hydrothermal treatment, which negates most of the advantages of the process. Thus, the pressing safety concerns of the inadequate packaging did not allow time for this approach to be developed and demonstrated. The alternative of simply sorbing the solutions on vermiculite, as had been done with the nonwaste items, was rejected for regulatory reasons.

Thus, the waste solutions were transferred into a permitted glove box for dispositioning. The nine items were consolidated into two items with like characteristics. The solutions were placed in a coated glass bottle that was placed in a plastic bag and then nested in vermiculite absorbent within a secondary tin can. The secondary can was removed from the process line in a filter-vented polyethylene bagout bag that was placed within a filter-vented stainless steel vault can. Each of the two items was placed in a vented stainless steel 55-gallon drum that was stored within a plastic overpack "doghouse" for spill containment within a designated waste storage area of the Plutonium Facility. The future of these solutions is unknown but they are no longer in the Room A vault space and are very conservatively packaged for indefinite storage. See the following sequence of photos for the packaging of the waste items (Figs. 3–7).

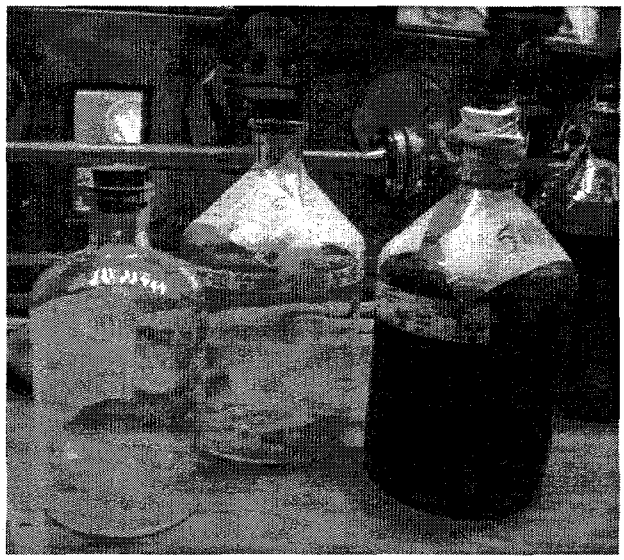

Fig. 3. Organic waste solutions in original containers.

Fig. 4. Consolidated organic waste solutions in coated glass containers.

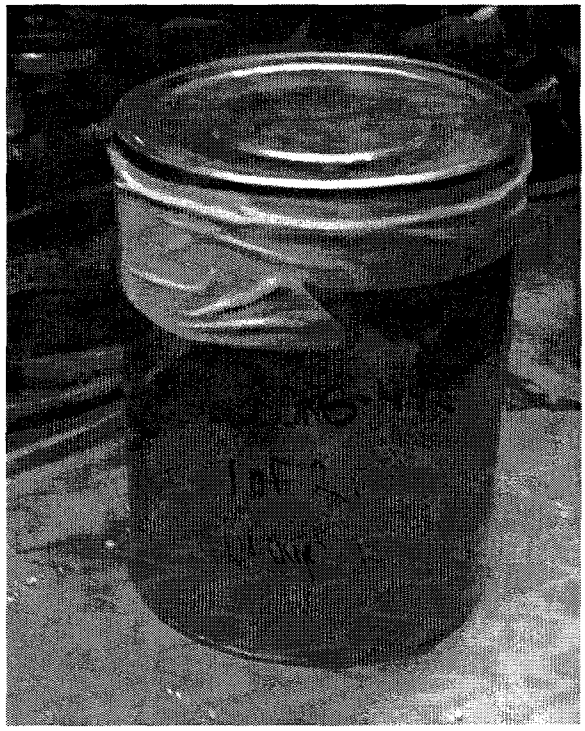

Fig. 6. Sealed secondary can.

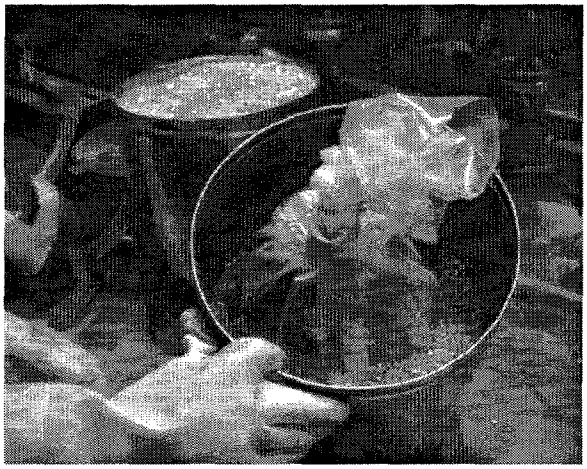

Fig. 5. Coated glass containers packed in vermiculite and secondary can.

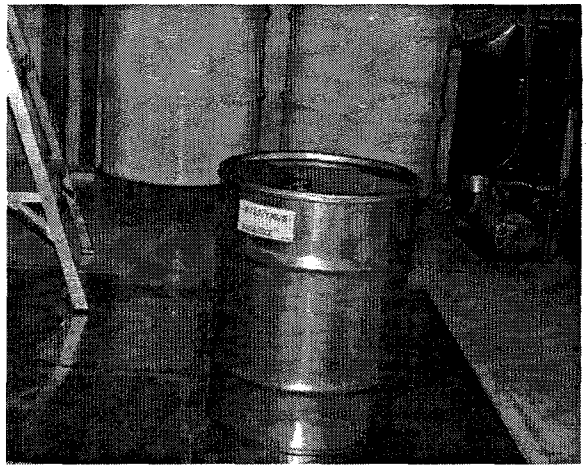

Fig. 7. Vented stainless steel 55-gallon drum.

SUMMARY AND CONCLUSIONS

Twenty-six organic solution items previously stored in Room A of the Plutonium Facility vault were dispositioned to prevent further degradation of the containers, to preclude any contamination of the vault area, and to recover valuable vault storage space. The entire effort required approximately four months from the time the first item was removed from the vault for inspection until all the items were completely dispositioned, from March through June of 1998. A flowsheet was developed and implemented to treat the solutions that had not previously been declared wastes because of their SNM content. When it did not work, the PDM was employed to reevaluate the need to recover the SNM in these items, and a formal decision was made to discard the items.

The result is that the previous application of the FY98 EDL split the items into two categories. Those previously designated as recoverable were reevaluated and finally discarded as a TRU mixed waste and in the normal course of waste handling were removed from the Plutonium Facility. Those previously designated as waste items have been consolidated and repackaged but are still being stored within the Plutonium Facility.

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