TREATING SMALL-VOLUME WASTE STREAMS: THE DEVIL IS IN THE DETAILS

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ABSTRACT

Meeting Site Treatment Plan (STP) waste treatment deadlines can be a challenge, both from a regulatory and a technical perspective. This paper discusses several mixed waste (MW) types that have been particularly challenging:

- Septage
- Absorbed Oil
- Mock High Explosive (HE)
- Sealed Sources
- Explosives (Thermal Batteries, Timer-Drivers)
- Oil with High Mercury
- Spark Gap Tubes
- Manufactured Items <60 mm

Treatment issues for these wastes included potential biological activity and gas generation in the septage, high tritium activity in the absorbed oil, high barium nitrate concentration in the mock HE, determining if the sealed sources were in fact MW, ensuring the thermal batteries and timer drivers had been fired, the mercury concentration in the waste oil, high radioactivity in the spark gap tubes, and the fact that macroencapsulation was the only viable treatment for certain manufactured items that were not covered by the debris rule.

The septage, explosives, high mercury oil, and spark gap tubes have been successfully treated. Treatment plans have been developed for the remaining wastes listed above and are currently being implemented. Details concerning issues resolution, waste treatment, and lessons learned are presented in the following sections.

INTRODUCTION

While technically not a "small site", Sandia National Laboratories (SNL) in Albuquerque, New Mexico has a wide variety of small-volume MW streams. These wastes must be treated to fulfill the requirements agreed to by SNL, the Department of Energy (DOE) and the New Mexico Environment Department (NMED) and formalized in SNL's Site Treatment Plan (STP).

SNL began treating MW with the on-site neutralization and stabilization of acidic and basic liquids in 1994 under the treatability study provisions of the Resource Conservation and Recovery Act (RCRA). At that time, the SNL mixed waste inventory was 70 cubic meters. To date, over 175 cubic meters of stored, legacy and newly generated MW have been treated on-site and by commercial entities, as appropriate. On-site treatment is performed under RCRA Part B interim status. (SNL submitted its first RCRA Part B application to NMED in 1992.) Remaining legacy wastes will be treated by the end of 2005. On-site treatment currently includes physical separation, neutralization, stabilization, deactivation of water-reactive materials and oxidizers, and macroencapsulation. SNL has developed its on-site waste treatment capabilities because many of our waste streams do not meet treatment facilities' waste acceptance criteria and in-house treatment is usually more economical.

WASTE TREATMENT CHALLENGES

Radiological and RCRA characteristics of the eight waste streams discussed here are summarized in Table I. The wide variety of research activities at SNL can generate mixed wastes that present unique treatment challenges. These eight waste streams span the spectrum of technical and regulatory issues the SNL waste treatment team has dealt with over the past nine years. They were chosen with the hope that our experience will be a useful reference if these same types of waste are present at other DOE sites.

Table I Waste stream radiological and RCRA data

Waste Stream	Vol, m^3	RCRA Codes	Radionuclide(s)	TotalActivity, mCi
Septage	51	F002 F003 F005 TCLP Metals	U isotopes and decay products	E-09 per gram
Absorbed Oil	2.3	D006 D008 D009	H-3	E+05
Mock HE 900-10	0.36	D001 D003 D005	H-3 U-238 U-235 Cs-137	11.8 E-04 3.67 E-04 6.33 E-05 2.08 E-04
Sealed Sources	0.96	D006 D007 D008 D011	U-238 Ni-63 Ba-133 H-3 Ra-226 Sr-90 Pm-147	0.6 to 0.94/source
Explosives	6.6	D001 D003 D005 D006 D008	Activation Products	E-09
High Mercury Oil	<0.003	D006 D009	H-3	1.7 E-04
Spark Gap Tubes	3.3	D008 D011	Each tube has one of the following: Cs-137 Kr-85 Ni-63	 5.0 E-04 per gram 8.9 E-05 per gram 6.0 E-06 per gram
Manufactured Items <60 mm	<0.2/yr	D006 D008	Cs-137 Kr-85 Ni-63 Sealed source isotopes	E-09 to 100

Specific treatment issues associated with each waste stream, their resolution, and the types of treatment(s) implemented are discussed in the following sections.

Septage

SNL has a large number of remote sites on Kirtland Air Force Base that originally had their own septic systems. These sites were eventually hooked up to the base sewage system, and, beginning in 1995, site septic tank residues were cleaned out and packaged in 70-gal high-density polyethylene (HDPE) drums and 55-gal metal drums for treatment and/or disposal. Based on process knowledge and sampling, the contents of many of the septic tanks were radioactive (primarily uranium isotopes and tritium) and presumed to be hazardous, making the septage mixed waste.

The waste consisted of aqueous liquid with suspended solids that settle to the bottom in a sludge layer upon standing. Both the metal and organic contaminants concentrate in the sludge layer. Per cent solids in individual containers ranged from <10% to >90%.

After extensive characterization, it was determined that 240 drums from six sites exceeded RCRA volatile organic compound (VOC) concentration limits and required treatment. Ten drums contained RCRA metals above Toxicity Characteristic Leaching Procedure (TCLP) concentration limits and were stabilized on-site with Portland cement by Perma-Fix. Samples from all cemented drums passed TCLP.

Drums with high concentrations of VOCs were sent to Diversified Scientific Services, Inc. (DSSI, now Perma-Fix) for treatment in their energy recovery boiler in 2000-2001. The waste was pumped into four stainless steel tankers provided by DSSI for shipment, as shown in Fig. 1. Only waste that could be

Fig. 1 Pumping septage into tankers for shipment to Perma-Fix for processing.

forced through a 70-mesh screen could be sent to DSSI. Remaining solids (approximately 3 m^3) were sent to M&EC for thermal desorption. Desorbed liquid was sent to DSSI and treated solids were disposed of at Envirocare of Utah.

Challenges associated with the characterization and treatment of this waste were the potential presence of fecal coliform bacteria and gas generation in the drums from biodegradation. Analytical results for fecal coliform were negative. While the drums were in storage at SNL, 14 were fitted with relief vents to prevent internal gas buildup.

During waste sampling and pumping operations, the following safety measures were instituted:

- Operations personnel wore full-face, air purifying respirators with super cartridge.
- Spark-free tools were used for opening drums and sampling.
- Drum lid venting bungs were “cracked” and allowed to vent slowly before the entire drum lid was removed.
- Drums were opened using a protective drum safety net to prevent a potentially explosive lid release.
- Upon opening, drum air space was checked for hydrogen with a Lower Explosive Limit (LEL) meter, for VOCs with a photionization detector (PID), and for hydrogen sulfide with a hydrogen sulfide meter.
- Hydrogen sulfide was monitored continuously to ensure levels remained below 10 ppm (the National Institute for Occupational Safety and Health (NIOSH) exposure limit [1]) in the workers’ breathing zone.

A total of 57 of the 240 drums were sampled and 51 m^3 of waste were treated. It was recently determined that as many as nine additional sites may have septic systems that were missed in the original campaign. The fact that procedures are now in place to handle this waste stream will greatly expedite any sampling and treatment that may be required.

Absorbed Oil

Between January 1992 and October 1996, the Tritium Research Laboratory at SNL’s California site underwent decontamination and cleanup as part of a transition from a Category II non-reactor nuclear facility to a low-hazard, general-purpose laboratory [2]. Waste generated during this effort included vacuum pump oil contaminated with high levels of tritium, cadmium, lead and mercury from the tritium gas manifold system. This waste was sent to SNL in Albuquerque for treatment and disposal. Approximately 2.3 m^3 of the oil was absorbed onto unnamed absorbent or “diatomite.” The absorbent appears to be “kitty litter”, and the absorbed oils contain no free liquids, with one exception. The oil was packaged in 15-gal plastic carboys. Tritium activity ranged from <0.01 to 7.5 Ci/carboy.

Sampling and analysis on a select number of the absorbed oils showed that the oils are high in several TC metals, although all passed the TCLP. About one-third of the absorbed oils do not meet the land disposal restrictions universal treatment standards for one or more metals. Further treatment will be performed. Bench-scale tests have shown that a blend of the waste with Petroset II® and Portland cement and enough water to obtain a slurry stabilized the metals such that the treatment standards were met.

Plans continue to sample all of the oils and treat all of them that do not meet the treatment standards. Some of the waste is high in tritium. License limits of the receiving laboratories will be investigated in concert with the SNL/NM Sample Management Office to ensure that samples may be properly transported and received.
The treatment of absorbed oils will be scaled up to drum scale from the bench-scale tests already performed. The treatment is expected to be performed using on-site glove boxes or glove bags in which the waste and stabilizing mixture will be combined. When the treated waste drum is closed and removed from the glove boxes, a motorized drum rotator will be used to blend the ingredients.

The waste containing a free liquid will probably be treated in part or in total using Nochar absorbent.

Mock HE 900-10

Mock explosives are non-detonating materials "bearing similar physical properties (texture, density, cohesion, etc.) to an explosive material … Mock explosives are used to represent explosives for purposes such as dry run testing of equipment. DOE (Department of Energy) mock explosives are normally pink in color."[3]. Mock HE 900-10 is a pink solid consisting of (by weight) 48.0% pentaerythritol, 46.0% barium nitrate, 2.8% nitrocellulose and 3.2% chloroethylphosphate. It is used to mimic the mechanical properties of PBX-9404. "Mock HE 900-10 is difficult to ignite and will not propagate a detonation, but it is definitely an exothermic material."[4].

SNL has to dispose of approximately 560 pounds of mock HE 900-10 contaminated with pCi/g levels of tritium. The issues with this waste are the high concentration of barium nitrate, an oxidizer with a TCLP metal that is only slightly soluble in water (8.7 g/100 mL at 20^{o} C [5]), and the nitrocellulose, which exhibits the characteristic of reactivity. The most economical treatment for this waste would be to stabilize an aqueous suspension with Portland cement or another stabilization agent that may be more suitable for high concentrations of barium in the presence of organics, such as Gubka. Bench-scale studies will be required to determine both the optimum agent and the optimum amount of water required to produce a waste form that passes TCLP for barium. Stabilization would also remove the reactivity characteristic of the nitrocellulose.

If it is not possible to produce an acceptable solid waste form due to the high concentration of pentaerythritol, an alternate (and more expensive) approach would be to dissolve the mock HE in a methanol-water solution and send the liquid to Perma-Fix for treatment in their energy recovery boiler. Barium nitrate is soluble in water (relatively large volumes will be required) and insoluble in alcohols; pentaerythritol is soluble in both solvents; nitrocellulose is at least somewhat soluble in methanol and insoluble in water; and chloroethylphosphate is <1% (by weight) soluble in water and soluble in methanol [6]. Bench-scale studies would need to be performed to optimize the relative amounts of water and methanol, since the solubility of the pentaerythritol in a methanol-water mixture is not known.

Given that either treatment process is expected to be rather time-consuming, SNL is negotiating to have the mock HE treated by Perma-Fix of Florida.

Sealed Sources

The challenge associated with the disposition of SNL sealed sources that have been declared waste is to determine if they are in fact "mixed waste". Table II summarizes data for sealed sources that were submitted for disposal and were initially categorized as mixed waste. Of the 200+ sources listed in Table II, 82 were reclassified as low-level waste (LLW) based on a re-examination of existing data. Seven more may be declared LLW, pending further evaluation, and the remainder will be macroencapsulated.

Table II Disposition of sealed sources designated "mixed waste"

Waste Description	Comments	Disposition
Metal assembly with uranium source.	Assembly is old enough that it probably does contain lead and/or silver solder. Not able to verify composition.	Macroencapsulate
Two Ni-63 electron tube sources	MW determination is pending visual examination. Sources may be the same as one that is known to be LLW.	If the same as the known source, dispose as LLW. If not, microencapsulate.
Alphatron Model 530	A 3-year-old Web reference to an Alphatron 530 indicated it was made by NRC Equipment Corp., which apparently no longer exists. Item is old and validation data is unavailable; therefore have to assume it contains lead and/or silver solder.	Macroencapsulate
Ni-63 source originally coded D008	Item consists of a 1-micron thick plating layer composed of 19% Ni-63 and 81% Ni-62 on an 8-mil thick Ni substrate. No lead is present.	Reclassify and dispose of as LLW.
Leeco Instruments RG 75K ion gauge; Ni-63 wire.	Web search determined Leeco Instruments no longer exists; based on age, have to assume lead and/or silver solder is present.	Macroencapsulate
23 Ba-133 sources, originally coded D008 and D011	Sources are encapsulated in epoxy beads sealed into stainless steel bolts with epoxy. No lead or silver is present.	Reclassify and dispose of as LLW.
Two uranium foil sources coded D011	Uranium foils can have a silver backing.	Macroencapsulate
57 Titanium tritide sources, originally coded D003	Memo to file states that since tritium is a by-product material [10 CFR Part 30.71, Schedule B], and, in this case, is not associated with any hazardous constituents, it is not subject to RCRA [7].	Reclassify and dispose of as LLW.
Five Ra-226 sources encased in concrete. Removed from on-site landfill	Waste packages will be subject to real-time radiography to determine if electronics are present. Since items are already macroencapsulated, they should not require further treatment.	If only sources are present, dispose of as LLW. If electronics are present, dispose of as MW.
Ra-226 source on silver backing	Based on dimension data, source probably contains ~400 mg silver, which makes it MW.	Macroencapsulate
99 pulse circuit thyratron triggers	Memo indicates components will fail TCLP for cadmium and lead.	Macroencapsulate
Sweeny static meter RS02521; 3M Model 703 static meter	The Sweeny static meter is the predecessor of the 3M model. 3M will take both meters back for disposal; however, SNL shipping and receiving will not ship waste.	Macroencapsulate
Sr-90 sources from spark gap tubes; total number not given; two packages	Due to high dose rates, it is not practical to visually examine this waste for a MW determination.	Macroencapsulate
Berthold Sr-90 source #LB6701-10N, originally coded D008	Berthold stated source contains no lead.	Reclassify and dispose of as LLW.
Mixed gamma source	Source is adsorbed onto a silver zeolite substrate that is 37% silver by weight.	Macroencapsulate
Pm-147 source	Source contains silver and is wrapped in a 1"x4" lead sheet.	Macroencapsulate

Explosives

The SNL inventory of mixed waste and waste-like materials contains a small volume of items with both an explosive constituent and a radioactive constituent. These materials normally result from one of the following activities:

- Excavation of landfills where explosive switches and other components with explosive subassemblies were buried in the past. The items came in contact with radioactively contaminated soil and decontamination of these items by normal washing or extraction techniques is not feasible due to cracks, seams, and voids in the components.

- Radiation hardening testing on a variety of explosive components that resulted in activation. Most of these activated components carry a security classification.

Disposal of these items requires deactivation of the explosive constituent. DOE’s Explosive Safety Manual recommends a thermal method for deactivation of explosives. The manual requires “final decontamination by thermal techniques shall be done by subjecting the item to sustained heating at a temperature at least 60º C higher than required for decomposition of the most thermally stable explosive substance present.” [8]

SNL built a small, heavy-walled steel cylinder, known as an inerting chamber or “boom box”, with the capability to safely contain the detonation of 25 gm TNT, or equivalent. Prior to the first use the unit was subjected to a 125% overpressure test. The unit is equipped with fail-safe features such as temperature override shutoff, dual controls, and constant monitoring during operation.

The inerting chamber, including closures and bolts, was machined from 17-4PH stainless steel and hardened to condition H1025. At that condition this material retains most of its strength to temperatures as high as 370° C and is thus well suited for this application. The chamber consists of an 18” long cylinder with an 8” I.D., and two heavy walled, machined end covers. (See Fig. 2.) Each cover is attached to the cylinder with eight ½” bolts. One end cover is removed every time an item is installed or removed. The second cover was machined with male pipe thread penetrations to provide a mechanism for evacuating and purging the chamber as necessary and feed-throughs for electrical heating elements and thermocouples. This end plate is not removed except for maintenance. The endplates are sealed to the cylinder using conflat style sealing rings made of copper. The interior of the cylinder contains a flat rectangular steel plate connected to three heating elements.

The atmosphere within the inerting chamber is controlled by an evacuation/purge system using ultra-high purity nitrogen. This is done to minimize the afterburn of any deflagration or detonation products.

Once the item is sealed in the inerting chamber, the temperature is increased at 30ºC/minute until a predetermined temperature (depending on the explosive contained in the component) is reached. To ensure complete decomposition, the item is held at this temperature for at least two hours.

The device has been used at SNL to treat debris items with an internal explosive component and to treat pressed pellets of explosive. Explosives and/or pyrotechnics that have been treated include:

Pentaerythroltetranitrate (PETN)
Titanium / Potassium Perchlorate (TiKP)
Hexanitrostilbene (HNS)
5-Cyanotetrazolatopentaaminecobalt (III) perchlorate (CP)
Cyclotetramethylene tetranitramine (HMX)

Fig. 2 SNL “boom box” used to inert explosively reactive mixed wastes and materials

The inerting operation does not inflict enough damage to provide sanitization of classified components and the treatment residue is managed as classified material, if appropriate. Additional treatment follows for components that contain RCRA regulated metals, as well as explosives.

High Mercury Oil

SNL had two bottles of used vacuum pump oil with high concentrations of mercury. One bottle held 872 g of oil that contained 198 ppm barium, 6.5 ppm cadmium, 4 ppm lead, 0.5 ppm silver and 540 ppm mercury. The second bottle held 29 g of oil with 4.13 ppm mercury. The combined samples were contaminated with 17 μCi of tritium. In 2001, this oil was shipped to Dr. K.T. Klasson at Oak Ridge National Laboratory to be used in a treatability study to evaluate a stabilization method for oil with >260 ppm mercury. The technology used Self-Assembled Mercaptan on Mesoporous Support (SAMMS), a sorbent powder developed by Pacific Northwest Laboratory for stabilization of RCRA metals, followed by stabilization with Nochar N990, an oil stabilization agent formulated for stabilization of vacuum pump oil [9]. While not all approaches to mixing oil, SAMMS and Nochar worked equally well, mixing SAMMS and Nochar using equipment similar to a drum roller, adding oil to the container, and allowing it to be absorbed produced a solid waste form where all samples successfully passed TCLP for mercury [9].

Spark Gap Tubes

Spark gap tubes (SGTs) are switches used in many weapons components. Debris-size (i.e., >60 mm) SGTs are currently being macroencapsulated on site at SNL/NM (Fig. 3). The SGTs treated up to this time contain Cs-137, Ni-63 or Kr-85 sources. The presence of the sources prevents off-site commercial treatment, due to their level of radioactivity.

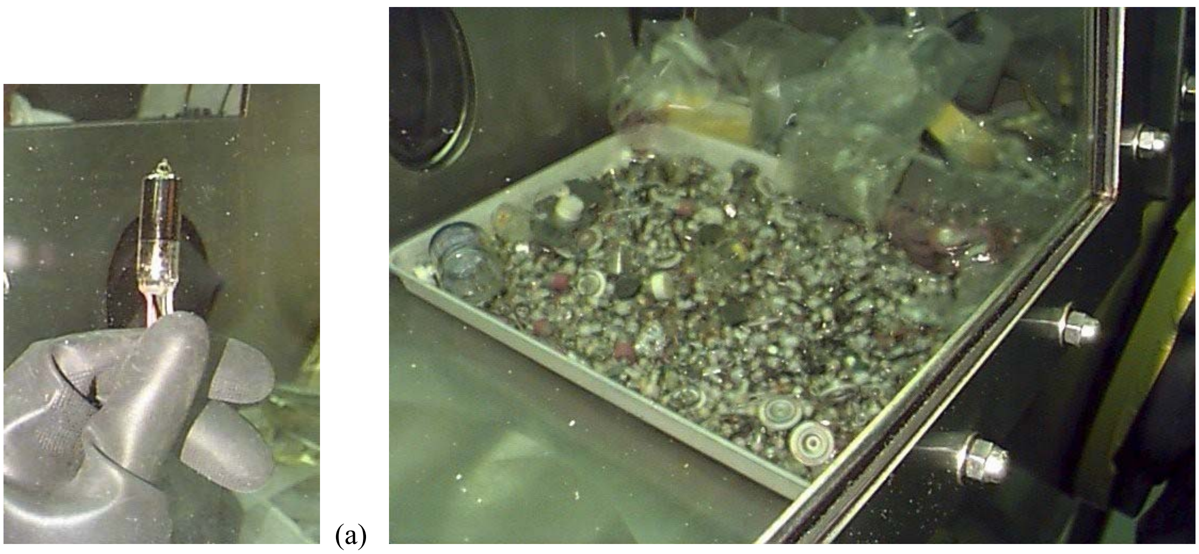
Fig. 3 Waste spark gap tubes ready for macroencapsulation at SNL

The macro unit is a commercial extruder using low-density polyethylene (LDPE). The basic macro technology we are using was developed by RMI Environmental Services, Ashtabula, Ohio. SNL/NM has modified the equipment and procedures to reduce cracking, voids, and other flaws in the waste forms.

The final waste form fits inside a 55-gallon drum and contains 15-20 gallons of debris waste. The treated waste remains in storage at SNL/NM in compliance with the land disposal restrictions and the SNL/NM Site Treatment Plan pending disposal off site as mixed waste.

Manufactured Items <60 mm

Part 262.2 of Section 40 of the Code of Federal Regulations defines debris as “solid material exceeding a 60 mm particle size that is intended for disposal and that is: A manufactured object; or plant or animal matter; or natural geologic material.” SNL has several “manufactured object” waste streams containing items that are <60 mm in any dimension, (see Fig. 4) but for which macroencapsulation is the only viable treatment. These include sealed sources, switch tubes and thermocouples. Ordinarily, one would shred small items such as these and then stabilize the shredded material; however, the levels of radioactivity associated with these wastes are high enough that shredding is not reasonable from a safety standpoint. SNL is currently working with the Environmental Protection Agency (EPA) to obtain an exemption that will allow the macroencapsulation of manufactured items <60 mm in any dimension.



(a) (b)

Fig. 4. (a) A spark gap tube <60mm in any dimension and (b) typical spark gap tube waste requiring macroencapsulation

SUMMARY

The preceding discussion has provided a synopsis of the wide variety of small-volume mixed waste streams that the SNL Radioactive and Mixed Waste Management Facility has treated over the past nine years. The critical lesson that this experience has provided is that the devil is indeed in the details. Whether it is issues of technical feasibility, personnel safety, or regulatory compliance, attention to detail and checking to ensure that all potential “show stoppers” have been considered can often mean the difference between an apparently insurmountable roadblock and successful treatment and disposal.

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