SULFUR POLYMER STABILIZATION/SOLIDIFICATION (SPSS) TREATABILITY OF SIMULATED MIXED-WASTE MERCURY CONTAMINATED SLUDGE

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ABSTRACT

The Environmental Protection Agency (EPA) is currently evaluating alternative treatment standards for radioactively contaminated high mercury (Hg) subcategory wastes, which do not require the removal of mercury from the waste. The Sulfur Polymer Stabilization/Solidification (SPSS) process developed at Brookhaven National Laboratory is one of several candidate technologies capable of successfully treating various Hg waste streams. To supplement previously supplied data on treatment of soils, EPA needed additional data concerning stabilization of high Hg subcategory waste sludges. To this end, a 5000 ppm sludge surrogate, containing approximately 50 wt% water, was successfully treated by pilot-scale SPSS processing. In two process runs, 85 and 95 wt% of water was recovered from the sludge during processing. At waste loadings of 46 wt% (30 wt% dry) sludge, the treated waste form had no detectable mercury (<10 ppb) in TCLP leachates. Data gathered from the demonstration of treatment of this sludge will provide the EPA with information to support revisions to current treatment requirements for high Hg subcategory wastes.

INTRODUCTION

The Environmental Protection Agency's (EPA) Land Disposal Restrictions (LDR) program currently lists technology-specific treatment standards for hazardous wastes containing greater than or equal to 260 ppm total mercury (Hg) (i.e. high Hg subcategory wastes). The treatment standards specify RMERC for high Hg subcategory wastes and IMERC if the high Hg subcategory wastes contain organics. RMERC requires retorting or roasting in a thermal processing unit, while IMERC specifies incineration. Both of these standards are based on the premise of recovering the Hg for recycling. In the case of radioactively contaminated wastes, the recovered Hg is typically still radioactively contaminated, and therefore cannot be recycled. EPA requires that this recovered, radioactively contaminated Hg undergo additional treatment, specifically amalgamation, prior to disposal. The Department of Energy (DOE) TRU and Mixed Waste Focus Area (TMFA), along with the Mercury Working Group (HgWG) chartered under the TMFA, are working with EPA to validate technologies that can directly treat radioactively-contaminated high Hg subcategory wastes without removing the mercury from the waste.

To date under this program, radioactively contaminated waste soil from Brookhaven National Laboratory (BNL) containing approximately 4,800 ppm of Hg and radioactively contaminated elemental Hg have been successfully treated by SPSS to meet a Hg Toxic Characteristic Leaching Procedure (TCLP) treatment goal of 0.025 mg/L or less.(1) These treated waste forms are now undergoing several additional evaluations at the University of Cincinnati (UC) and Oak Ridge National Laboratory (ORNL), using analytical protocols developed by faculty at Vanderbilt University and UC. These new protocols provide another methodology to predict how the treated waste form will behave in a variety of disposal environments.

To supplement the soil treatment results, BNL and several commercial technology vendors provided additional data for stabilization of high Hg subcategory waste sludges under this program. The data gathered from this treatability study for simulated mixed waste mercury contaminated sludge will assist EPA in their decision to revise current LDR regulations and allow alternative treatment technologies, such as stabilization, of high Hg subcategory wastes.

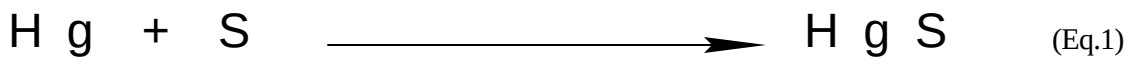
In BNL's Sulfur Polymer Stabilization/Solidification (SPSS) process, elemental mercury or mercury-containing wastes are reacted with sulfur polymer cement (a thermoplastic material composed of 95 wt% elemental sulfur) to form a stable mercury sulfide compound with significantly reduced leachability and, for elemental mercury, lower vapor pressure. The reacted mixture is then melted, mixed, and cooled to form a monolithic solid waste form in which the stabilized mercury sulfide particles are microencapsulated within a sulfur polymer matrix.

As in the demonstration on the BNL soils referenced above, this program had two major objectives. The first was to evaluate stabilization as an alternative process to RMERC and IMERC for DOE's legacy mixed waste. To that end, the process treated a high Hg subcategory surrogate waste to achieve a TCLP treatment goal of 0.025 mg/l or less. The second objective was to provide EPA with treated waste forms so that EPA can compare the proposed new analytical protocols to standard TCLP results. EPA will use these comparisons in their efforts to revise the LDR treatment standards for Hg-bearing hazardous wastes.

TECHNOLOGY DESCRIPTION

Sulfur Polymer Stabilization/Solidification (SPSS) is based on Sulfur Polymer Microencapsulation, a patented mixed waste treatment technology previously developed at BNL.(2) Sulfur Polymer Cement (SPC) consists of 95 wt% elemental sulfur reacted with 5 wt% of an organic modifier to enhance mechanical integrity and long-term durability. Prior testing conducted on sulfur polymer waste forms indicates excellent performance under anticipated disposal conditions.(3,4) During FY97, SPSS was developed at BNL as part of a DOE Mixed Waste Focus Area (MWFA) Quick Win Project, and used to treat 24.5 kg of BNL mixed-waste elemental mercury.(5) In FY98, SPSS was demonstrated as a pilot-scale process, successfully treating two 55 gallon drums of mixed waste Hg contaminated soils and 68 kg of mixed waste elemental Hg, excavated from the BNL Chemical Holes.(5) Newmont Mining, Inc. recently licensed SPSS for production-scale use on elemental Hg generated in gold mining operations.

SPSS mercury treatment (patent pending) is conducted in two stages. The first step is a reaction between mercury and powdered SPC, forming mercuric sulfide, as seen in Equation 1:



(Eq.1)

The second step involves melting the thermoplastic sulfur binder. On cooling, the reacted sulfide particles become microencapsulated within the inert sulfur matrix. Since the BNL SPSS process includes chemical stabilization of the mercury, yielding mercury sulfide, it meets EPA requirements for amalgamation, AMLGM.

Bench-scale development work for the SPSS process demonstrated that as much as 33 wt% elemental mercury could be successfully encapsulated. Even at this waste loading, the final waste form still meets EPA TCLP leaching criteria.(7) This ratio assures nearly a 12-fold molar excess of sulfur to mercury, facilitating a fast reaction of the mercury metal with sulfur. A small quantity (up to 2 wt%) of additive is

included to ensure the sulfide reaction.. Once the mercury is chemically stabilized, the mixture is heated at about 130°C until a homogeneous molten mixture is formed. It is then poured into a suitable mold where it cools to form a monolithic solid waste form.

Pilot-scale SPSS processing was accomplished using a 1-ft^3, oil-heated, vacuum capable, vertical cone mixer (Ross Mixers, Hauppauge, NY). Mixing action is provided by a 24-inch long auger screw, rotating up to 105 revolutions per minute (rpm), which also revolves orbitally around the wall of the vessel, at up to 2.5 rpm. The auger screw draws material upward from the base of the cone, resulting in thorough mixing. Feed materials are charged to the unit through a 6-inch diameter port on the cone lid. the auger screw drawing material upward from the base of the cone. A photograph of the mixer and process control equipment is shown in Figure 1. Heat is provided to the jacketed cone by a 9kW circulating fluid heat transfer system (Mokon, Buffalo, NY). A 5 cm (2 in) heated ball valve at the base of the cone is used to discharge the molten SPSS product.

Fig. 1. Vertical cone mixer and process controls with simulated sludge mixing in the foreground.

Off gas is captured in multiple stages: first it passes through a shell and tube heat exchanger cooled by a 3 ton chiller (Mokon), followed by a liquid nitrogen cryogenic trap and finally through HEPA and activated charcoal filters before venting to the atmosphere. Condensate is collected for analyses at the heat exchanger in an off-gas condensate vessel and at the cryogenic trap. A schematic of the off-gas system components is shown in Figure 2.

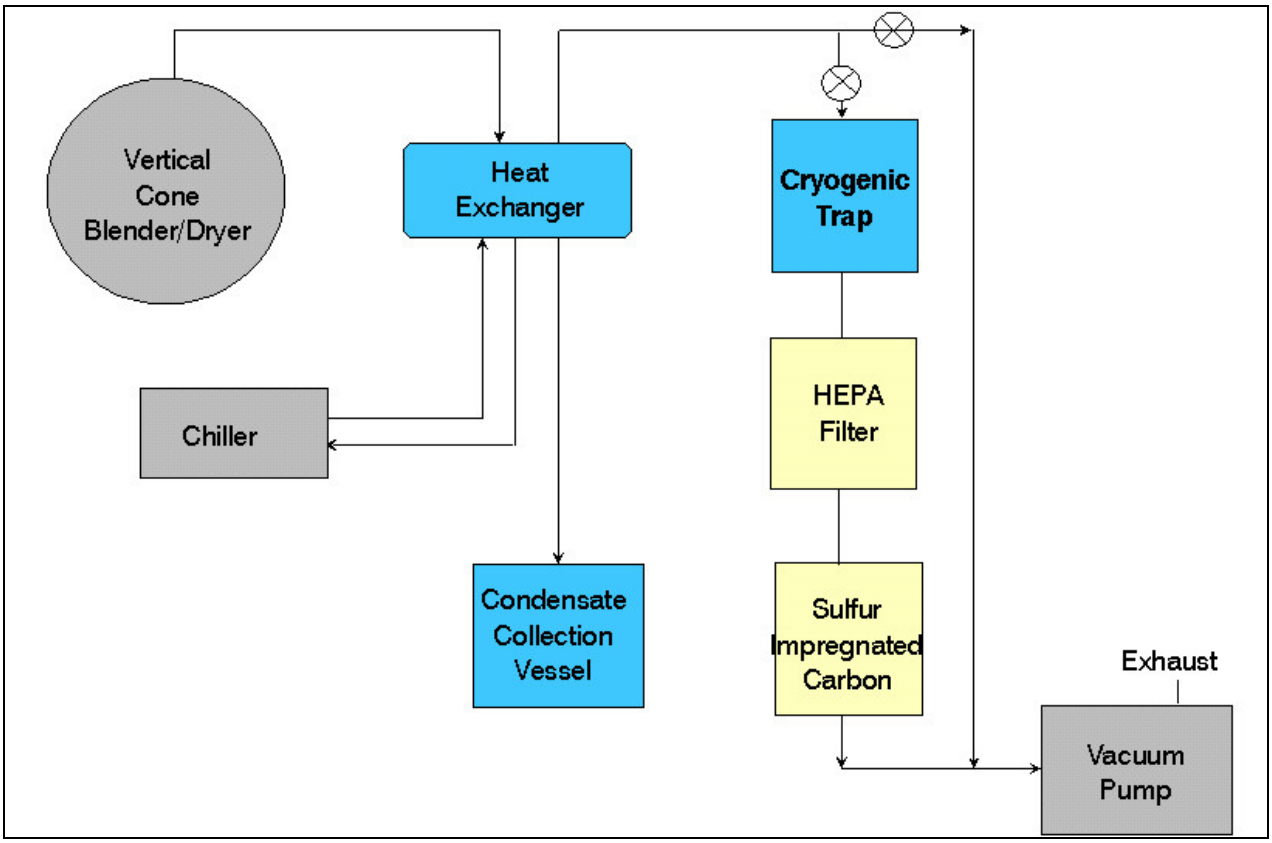


Fig. 2. SPSS off-gastreatment components.

WASTE DESCRIPTION

The waste to be treated was a sludge surrogate containing 5,000 ppm of mercury, in the form of elemental mercury and the compounds listed in Table I. Four inorganic compounds comprised the bulk of solids in the sludge: diatomaceous earth (20 wt%), and aluminum hydroxide, ferric chloride, and sodium chloride (10 wt% each). The remaining 49.5 wt% of the sludge weight was water. Each component was individually pre-packaged for surrogate consistency at the ALTER Facility of the University of Cincinnati (UC). (UC is conducting stabilization technology evaluations for EPA.) At BNL, gross and net weights of these compounds were verified prior to their addition to the appropriate quantity of water.

Two batches, 50 lb each, were prepared, as given in Table I. The first lot, containing mercury compounds, was used for bench-scale formulation verification tests and final pilot-scale demonstration.

The second batch, prepared without mercury contaminants, was used for initial pilot-scale processing to determine mixing characteristics, corrosivity effects, and dewatering parameters in the Ross mixer system.

Table I. MER04 Sludge Surrogate Formulation

Component	Nominal Wt. %	Batch 1 Net Wt. (gm)	Batch 2 Net Wt. (gm)
Mercury			
Elemental	0.15	34.11	
Phenyl-mercuric chloride	0.05	16.14	
Mercuric Nitrate	0.10	32.29	
Mercuric Oxide	0.10	32.29	
Mercuric Chloride	0.10	32.29	
Diatomaceous Earth	20.0	4,508	4,540
Aluminum Hydroxide	10.0	2,266	2,270
Ferric Chloride	10.0	2,261	2,270
Sodium Chloride	10.0	2,265	2,270
Water	49.5	10,888	11,202
Total Sludge		22,335	22,552

For each batch, inorganic chemicals were added to deionized water in a 45 liter polyethylene container. (Approximately 3 liters of water were kept separate prior to mixing, to use as rinse water, where needed.) The soluble salts (first $FeCl_3.6H_2O$, then NaCl) were dissolved in de-ionized water, followed by addition of the insoluble compounds, $Al(OH)_3$ and diatomaceous earth. A vertically mounted commercial coring drill motor (shown in Fig. 1) was used to turn a steel mixing blade (double-fluted, approximately 12" diameter x 6" high). The sludge thickened significantly after approximately ? of the diatomaceous earth was added, requiring slow addition of the remainder. Approximately 15 minutes were required to complete addition of the four major constituents, after which the batches were stirred another 15 minutes to ensure homogenization. Batch 1 continued to be stirred an additional 15 minutes while the 5 mercury compounds were added. There was no visible difference between the mercury-loaded and nonhazardous batches. The sludge was very corrosive however, as evidenced by its severe attack on the mixing blade; the pH of the sludge was measured to be 0.98. A photograph of mercury-spiked MER04 surrogate sludge is shown in Figure 3.

Fig. 3. MER04 sludge surrogate prior to SPSS treatment.

SPSS PROCESSING AND RESULTS

Bench-Scale Process Verification Tests

A series of bench-scale tests were carried out to establish waste loading limits for pilot-scale SPSS processing and the effect of additives on TCLP leachability. Optimal waste loading was determined by preparing test batches using one of the two 1-Liter grab samples of the previously prepared hazardous sludge surrogate. Initial batches were prepared at waste loadings of 70 wt% dry surrogate, the maximum loading identified in soil stabilization with SPSS. Batches were reacted with powdered sulfur polymer cement (SPC) and then heated to remove water from the sludge. Bench-scale processing involved treating maximum 200 gm batches in a Rotovap distillation apparatus, trapping the evaporated condensate to assure that no mercury was lost during drying. Once dry, the batch was heated to melt free SPC in the mixture, thereby microencapsulating the reacted sludge powder. Due to the fine particle size of this surrogate however, the 70 wt% mixture could not be wetted/encapsulated. Thus, increments of SPC powder were added until the mixture became fluid. While mixtures started to become workable with hand mixing at about 45 wt% dry surrogate, batches were not fluid enough to use an electric mixer until diluted to <35 wt% waste loading. An optimal process formulation of 30 wt% dry surrogate was recommended for pilot-scale processing based on product workability. This corresponds to a total waste loading of the hydrated, original waste surrogate of 46 wt%.

After the workability of the molten mixture was determined, bench-scale tests were conducted to determine optimal use of additives to reduce mercury leachability in the final waste form. As the additive

reacts not only with mercury but all readily soluble cations in the aqueous sludge, three formulations were prepared containing one half, one, and two-times the stoichiometric amount of additive calculated for the batch. The stoichiometric quantity was based on the total mercury plus total iron in ferric chloride. TCLP results of 30 wt% dry (46 wt hydrated) surrogate waste forms containing 1.49, 4.47 and 5.96 wt% additive showed decreasing amounts of mercury in the leachates, approximately 500, 40, and 10 ppb, respectively. To meet the current UTS leachability limit for mercury, twice the calculated stoichiometric mass of additive (6 wt% of the final waste form) was recommended for the pilot-scale formulation.

Pilot-Scale Processing

Using formulations derived in the bench-scale tests, BNL conducted pilot-scale treatment of MER04 sludge surrogate using the vertical cone mixer described earlier. Two batches were processed as previously noted, the first without mercury compounds and the second with. The first batch formulation was based on processing 40 lb of wet sludge surrogate. Actual sludge added was 18.44 kg (40.66 lb). The second batch contained slightly less sludge surrogate, 15.88 kg (35 lb), due to surrogate material removed for bench-scale testing and pre-treatment grab sampling. The amount of additive also varied slightly for the two batches, 4 wt% for the first versus 6 wt% (two times the calculated stoichiometric amount required) for the second, since the first batch was primarily intended to address processing issues. Compositions of the two process batches are given in Table II.

Table II. SPSS Batch Compositions For Pilot-Scale MER04 Sludge Surrogate Treatment

	Batch 1 - no mercury		Batch 2 – 5000 ppm mercury	
	Net weight (gm)	Weight percent**	Net weight (gm)	Weight percent
Sludge surrogate	18,444		15,876	
Solids*	9,283	30.0	8,136	30.0
Water*	9,161		7,739	
Powdered SPC	20,422	66.0	17,368	64.0
Additive	1,238	4.0	1,617	6.0
Total (wet basis)	40,104		34,861	
Total (dry basis)	30,943	100.0	27,122	100.0

*Calculated quantities, based on weights given in Table I.
**Based on final (dewatered) SPSS product.

Procedures developed during mercury-contaminated soil treatability studies were followed, namely with regards to addition and mixing of SPSS components, heating to remove water from the process batch, and melting of SPC to microencapsulate the stabilized sulfide compounds. Reaction time for this mixture was significantly reduced however, due to the aqueous sludge medium; 15 minutes of mixing was considered adequate to complete the sulfide reaction. Off-gas controls and worker industrial hygiene (mercury vapor) monitoring ensured containment of vapors during processing.

Wet sludge surrogate, in approximately 4 kg aliquots, was added to most of the dry SPC charged to the mixer, creating a pasty mustard-colored mix, which became significantly more fluid with increased mixing time. The remainder of the SPC was then added, forming a dry mixture, which became more fluid as it mixed. After approximately 30 minutes of mixing, the batch had apparently reached a stable consistency. At this point the powdered additive was added, instantly changing the color of the batch

from yellow to black as the powder contacted the sludge. On completion of additive addition, the batch had turned completely black in color, the mixture once again thickened, and an immediate exotherm to about 30 °C was noted. The system was sealed by replacing the gasketed window to the 6" port, and the chamber pumped to ~20" vacuum to evacuate air and moisture vapor from the system.

With the chiller-cooled condensate trap operating and the liquid nitrogen trap filled, the vacuum pump was once again opened to the system and the hot oil setpoint temperature raised to begin dewatering the sludge. Steady state was achieved after about 90 minutes, with a batch temperature of 115 °C (slightly below the melting point of SPC, 119 °C) and a pressure of ~20" vacuum. It was also at this point that the first sign of condensate was noted in the collection vessel.

For the first process run, the system operated consistently and flawlessly during dewatering of the sludge. System parameters, i.e., vessel temperature, oil bath and setpoint temperature, vessel pressure, screw/orbital drive loads, and condensate levels, were recorded at 30-minute intervals. The batch appearance gradually changed from wet and fluid to a damp, lumpy mixture, then finally to a dry powder. Vessel temperature was consistent throughout the drying phase, varying only between 81.4 and 82.8 °C. Dewatering continued for 14 hours for the first batch, until the condensate collection rate slowed to zero. Approximately 8,250 mL of liquid was collected in the chiller trap. At this point, the hot oil setpoint was raised to its maximum setting, 185 °C, to quickly melt and discharge the batch. The final condensate volume was approximately 8,780 mL. No appreciable amount of liquid was collected in the liquid nitrogen trap.

Several mechanical problems in the vacuum pump were encountered during processing of the second batch, increasing the drying time to almost 24 hours. Otherwise, processing parameters were similar to those of the first batch. When the molten mixture was discharged, three, one-liter-size jars of material were collected from bottom, middle, and top of the batch for subsequent preparation of TCLP samples. Material was also discharged into 2" diameter thin-wall aluminum tubes, to be cut as cylindrical monoliths. These were also collected at various stages of the batch discharge. Balance of the molten product was collected into a metal shipping pail. Approximate volume of the treated product was 5 gal for each batch. It is worth noting that discharge of the molten mercury-spiked batch was more difficult than the first batch tested. This was attributed to the use of a larger percentage of additive than was used in the mercury-free batch. The use of fine powders for the simulated sludge resulted in significantly different viscous behavior compared to the soil studies run previously (5), and small changes in fine powder chemical composition appears to influence the viscous properties as well.

TCLP Qualification of SPSS Processed MER04 Sludge Surrogate Waste

TCLP samples were made by remelting the subsamples collected from Batch 2. The molten SPSS product was then poured into Teflon molds (Figure 4) to create small pellets, approximately 8 mm (5/16") diameter by 8 mm (5/16") high, which meet the size requirement of the TCLP test while maintaining the integrity of the encapsulated product. Approximately 3,500 gm of sample were palletized then combined to form a composite of top, middle, and bottom material from the batch. Prior to shipment of samples to UC and ORNL, representative material was shipped to a certified testing laboratory for TCLP pre-certification. Test results, using extraction fluid #1 (pH 4.93 ± 0.05), yielded no measurable mercury (<10 ppb).(8)

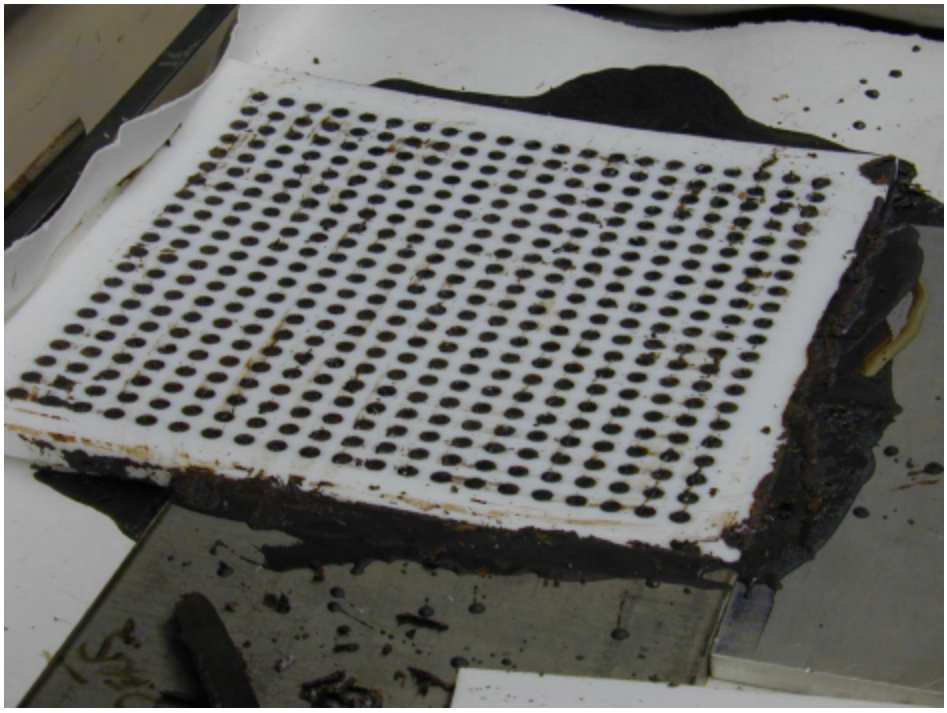


Fig. 4. SPSS treated MER04 sludge cast as 8mm diameter pellets.

DISCUSSION AND CONCLUSIONS

This study investigated application of SPSS for direct stabilization/solidification treatment of a simulated high mercury subcategory waste, in this case, a sludge waste containing 5000 ppm Hg. Bench-scale treatability tests concluded that maximum waste loading of the dry sludge was limited to 30 wt% (46wt% of the original sludge), based on physical mixability issues, not the leachability of mercury from the final waste form product. By way of comparison, BNL soil contaminated with similar concentrations of Hg were successfully treated by SPSS at a total waste loading of 60 wt%. TCLP testing of the SPSS treated MER04 simulated mixed-waste Hg contaminated sludge yielded a mercury concentration of < 10 ppb, below UTS criteria of 25 ppb.

Pilot-scale processing of surrogate sludges was successfully demonstrated, first for a surrogate waste containing no mercury, then for a surrogate containing 5000 ppm mercury. For the non-hazardous batch, mixing and dewatering were very well controlled, recovering approximately 96 wt% of the added water. For the mercury batch, several vacuum pump failures occurred, likely causing the slightly lower observed yield of condensed vapor of 85 wt%.

SPSS is a proven, cost-effective, robust process that can successfully treat a broad range of mercury wastes including elemental Hg, and Hg contaminated soil, sludge and debris. For radioactively contaminated Hg (i.e., mixed waste) it enables direct treatment of the waste to meet stringent EPA and disposal site acceptance criteria without generating separate radioactive and mixed waste residuals that require treatment prior to disposal.

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