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OAK RIDGE Y-12 PLANT

LOCKHEED MARTIN

FINAL DISPOSAL OPTIONS FOR MERCURY/URANIUM MIXED WASTES FROM THE OAK RIDGE RESERVATION

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**FINAL DISPOSAL OPTIONS FOR
MERCURY/URANIUM MIXED WASTES FROM
THE OAK RIDGE RESERVATION**

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SUMMARY

Laboratory testing was completed on chemical stabilization and physical encapsulation methods that are applicable (to comply with federal and state regulations) to the final disposal of both hazardous and mixed hazardous elemental mercury waste that is in either of the following categories:

1. waste generated during decontamination and decommissioning (D&D) activities on mercury-contaminated buildings, such as Building 9201-4 at the Oak Ridge Y-12 Plant, or
2. waste stored and regulated under either the Federal Facilities Compliance Agreement (FFCAgreement) between the Department of Energy-Oak Ridge Operations (DOE-ORO) and the Environmental Protection Agency (EPA) or the Federal Facilities Compliance Act (FFCAct) between DOE-ORO and the State of Tennessee.

Methods were used that produced copper-mercury, zinc-mercury, and sulfur-mercury materials at room temperature by dry mixing techniques.

Toxicity Characteristic Leaching Procedure (TCLP) results for mercury on batches of both the copper-mercury and the sulfur-mercury amalgams consistently produced leachates with less than the 0.2-mg/L Resource Conservation and Recovery Act (RCRA) regulatory limit for mercury. Headspace results showed that the copper-mercury and zinc-mercury amalgams had vapor pressures of mercury that were the same as that for elemental mercury (about 14 mg/m³), whereas that of the mercuric sulfide averaged 0.008 mg/m³. Free mercury analysis of the mercuric sulfide indicated that only 300 ppm of unreacted mercury (99.97% reaction yield) was present in the final product.

The results clearly showed that the reaction of mercury with sulfur at room temperature produces black mercuric sulfide, a material that is well suited for land disposal. The results also showed that the copper-mercury and zinc-mercury amalgams, although acceptable for land disposal in terms of regulation promulgated by 40 Code of Federal Regulations (CFR), had major adverse properties that make them undesirable for land disposal. In particular, they reacted readily in air to form oxides and liberate elemental mercury.

Another major finding of this study is that sulfur polymer cement is potentially useful as a physical encapsulating agent for mercuric sulfide. This material provides a barrier in addition to the chemical stabilization that further prevents mercury, in the form of mercuric sulfide, from migrating into the environment.

INTRODUCTION

The decontamination and decommissioning (D&D) of Building 9201-4 at the Oak Ridge Y-12 Plant will involve both the treatment of a wide variety of mercury-contaminated materials and the generation of a considerable amount of elemental mercury. Because of their acute toxicity, these materials can be health hazards. Because depleted uranium processing operations have also occurred in Building 9201-4, these materials may be contaminated with small amounts of depleted uranium (depleted of ^{235}U). No regulatory *de minimis* limit for radioactive contamination now exists; therefore, the current policy of Martin Marietta Energy Systems, Inc. (the managing entity for the Oak Ridge Y-12 Plant), is to classify material removed from Building 9201-4 as radioactive, regardless of its activity level.

The elemental mercury both removed from the building and recovered during decontamination of building materials is expected to be of reasonably high purity (>99% mercury by weight). As such, the mercury can possibly be transferred to private entities for resale for electrical applications, chlor-alkali production, or other uses. Even if the purity of the mercury is unacceptable for some applications, standard, inexpensive methods are available for processing the material into an extremely pure (>99.9999%) form. In particular, the processing would undoubtedly lower any uranium contamination that is present to <1 part per trillion.

Despite the fact that mercury contaminated with <1 part per trillion of depleted uranium would show no measurable radioactivity increase over background radiation, the material may still be classified as containing low-level radioactivity because of its origin. Thus, any private entity that received the material would need to be prepared to handle a material that is classified as containing low-level radioactivity. Because mercury is readily available, the low-level radioactivity classification may make it undesirable for a private entity to accept the material. If such is the case, the material may be classified as a waste. Evidence has shown that a significant portion of the waste elemental mercury does not fail the toxicity characteristic leaching procedure (TCLP). Only the mercury that "fails" (i.e., has a mercury concentration in the extract >0.2 mg/L) the TCLP test is considered a mixed waste because passage of the test removes the Resource Conservation and Recovery Act (RCRA)-hazardous designation from the waste.

Disposal of elemental mercury mixed wastes is strictly regulated. In 40 CFR, Part 268.42, Table 3, the technology-based standard of amalgamation (AMLGM) is given for radioactive hazardous mixed elemental mercury waste (EPA waste code D009). Table 1 of 40 CFR, Part 268.42, defines AMLGM as "Amalgamation of liquid, elemental mercury contaminated with radioactive materials utilizing inorganic reagents such as copper, zinc, nickel, gold, and sulfur that result in a nonliquid, semi-solid amalgam and thereby reducing potential emissions of elemental mercury vapors to the air." As discussed in Ref. 1, this particular treatment *must* be used for the given waste if the land disposal restrictions (LDR) are to be satisfied. This fact does not imply that the mercury characteristic toxic hazard is controlled simply by using any amalgamating material and process. Only a TCLP (Method 1311 from EPA Publication SW-846) extract of the amalgam can be used to determine whether the amalgam is a mixed or a low-level treatment residue. If the amalgam "passes" (i.e., has a mercury concentration in the extract not exceeding 0.2 mg/L) the TCLP test, it is considered a low-level treatment residue; if it fails TCLP, it is designated as a mixed treatment residue. Note that the mercury concentration limit in the extract is obtained from the table of constituent concentrations of waste extracts (CCWE) in 40 CFR, Part 268.41, Table CCWE.

The amalgamation process specified in 40 CFR indicates that zinc, copper, nickel, gold, sulfur, or other suitable inorganic reagents may be used for amalgamation. No processing

requirements, however, are listed in the regulatory definition. In general, the solubility of the elements listed in the definition of AMLGM in mercury is low, and precipitates form quite readily under different processing conditions. The implication in the definition is that the amalgams are considered to be the crystalline compounds that precipitate out of the solutions of mercury and these elements, not the solutions themselves. Therefore, the authors note here that the amalgams in the definition do not adhere to the rigorous scientific definition of amalgams as "solid solutions of mercury and one or more other metals."

The objective of this task is to determine a suitable disposal method for elemental mercury and other mercury compounds removed from Building 9201-4 during D&D activities. Because other waste mercury of similar origin (associated with radioactive sources) exists on the Oak Ridge Reservation (ORR), the authors expect that the disposal methods developed and recommended in this study will also be used for this other material.

The technology required for preparation of the amalgams described in this report is both relatively simple and in direct contrast to the regulatory and administrative aspects of the project. The technology required for waste disposal of the material is less well developed. A conversation² on October 12, 1993, between officials from the Oak Ridge Y-12 Plant and the Tennessee Department of Environment and Conservation (TDEC) clarified the posture of the State of Tennessee on the treatment of radioactively contaminated elemental mercury. The State official indicated that the State's primary focus is on the air emissions resulting from the mercury and its compounds; therefore, any final waste form (i.e., any material deemed an amalgam) for the mercury should minimize the air emissions first. This suggestion does not imply that reduced leachability is insignificant; the State of Tennessee simply considers it a secondary concern for the final waste form. Thus, a suitable disposal method both complies with the EPA treatment and concentration-based standards and can be permitted for use by the State of Tennessee (air emission considerations and leachability).

Earlier efforts characterized the extent of mercury contamination in Building 9201-4 and suggested decontamination techniques.³ The chemical and physical properties of mercury and common mercury compounds are generally well known⁴, and several specific studies related to disposing of mercury¹ or treating mercury-contaminated materials^{5,6} have been performed. In particular, Ref. 1 discusses amalgamation of radioactively contaminated elemental mercury waste. The objectives for this work differ from those of Ref. 1 chiefly in the scale of disposal operations required. The amount of radioactive mercury disposed in Ref. 1 was ~15 kg, whereas this study is aimed at developing disposal methods for up to several hundred metric tonnes of mercury.

SPECIFIC PROJECT OBJECTIVES

The objective of this project is to develop practical methods for treating radioactive hazardous mixed elemental mercury waste from Building 9201-4 that is generated in the decontamination of the building so that it may be disposed in an appropriate landfill. Any method that is found to be suitable for the treatment of this waste could also be applied in the treatment of mixed hazardous elemental mercury waste regulated under the Federal Facilities Compliance Agreement and the Federal Facilities Compliance Act. A self-imposed (and more stringent) objective is to develop final waste-form technologies for elemental mercury that meet the following requirements:

1. can be carried out at room temperature to avoid the obvious hazards associated with the increased volatilization of elemental mercury when thermal processes are used,
2. produce products with consistent chemical and physical properties (i.e., products that consistently pass the TCLP test and produce mercury concentrations in the air consistently lower than elemental mercury), and
3. produce no sidestreams that need subsequent treatment.

CHEMICAL STABILIZATION EXPERIMENTS AND RESULTS

As discussed in the Introduction, amalgamation of uranium-contaminated mercury is necessary before its legal disposal can be executed. This amalgamation may be accomplished with either metals or nonmetals, and only the reactions of mercury with organic compounds are excluded. Similarly, the method of amalgamation is not specified. Because mercury reacts with a large number of chemical elements, in principle, many alternatives exist. The ultimate treatment selected, however, must be applicable to large-scale operations. The amalgamating reagent also must not be a toxic characteristic hazard and must combine with a relatively large amount of mercury. Based on these criteria, sulfur, copper, and zinc were chosen for experimental study as amalgamating agents for mercury.

SULFUR AMALGAMATION

The most stable compound formed between mercury and sulfur is mercuric sulfide (HgS). It exists in two stable forms—the black cubic tetrahedral form, which is most commonly obtained when soluble mercuric salts and sulfides are mixed, and the red hexagonal form found in nature as cinnabar. Black mercuric sulfide can be converted to red sulfide by heating it in a concentrated solution of alkali polysulfide. Both forms are insoluble in water ($K_{sp, red} = 3.0 \times 10^{-53} M^2$ and $K_{sp, black} = 1.9 \times 10^{-15} M^2$) and in acidic solutions. However, in alkaline solutions that contain excess sulfur anions, mercury's solubility from the HgS may be augmented by the following mechanism:

A common method of forming HgS from mercury is to dissolve the mercury in hydrochloric acid, neutralize it to form an aqueous solution of mercuric chloride (HgCl₂), then precipitate HgS by the addition of sodium sulfide. The mixture can then be separated by filtering or centrifugation to produce fairly pure HgS. This method is not reasonable on a large scale because of the limited solubility of HgCl₂ in water and the creation of secondary aqueous streams, which undoubtedly would contain at least small amounts of mercury contamination. Therefore, the method studied by this task was the direct reaction of elemental mercury and elemental sulfur. Thermodynamic data show a Gibbs free energy value of -11.1 kcal/mol for black HgS, indicating that a direct reaction between the elements is favorable. Also, experiments have shown that the reaction rate is quite rapid, with the vast majority of the mercury being converted to HgS after only a 2-h residence time.

The following procedure was developed and used to make the HgS for this study.

1. Begin with -60 mesh sulfur powder.
2. Beat the sulfur powder in a paint shaker with 7/16-in. stainless steel milling balls for 1 h.
3. Add elemental mercury to the beaten sulfur (using a 50 wt % excess of sulfur).
4. Shake longitudinally for 1 h.
5. Shake transversely for an additional hour.

Results of X-ray diffraction on the product indicated that HgS was the material formed.

To characterize the HgS made by this method, 4 ostensibly identical 1-kg batches were made. Each batch was sampled and analyzed for mercury concentration in the TCLP extract, free mercury, and equilibrium mercury headspace content. Table 1 shows both these results and results for some commercially produced black HgS.

Table 1. Analysis results from four batches of HgS material prepared by the method described in this report. Also shown are analysis results for commercial HgS

Batch number	TCLP Hg (mg/L)	Elemental Hg (ppm)	Reaction yield (%)	Headspace Hg (mg/m ³)
S1	<0.0008	362	99.96	0.007
S2	<0.0008	246	99.98	0.006
S3	<0.0008	250	99.98	0.008
S4	<0.0008	337	99.97	0.012
Average	<0.0008	299	99.97	0.008
SC	<0.0008	10	-	0.005

The TCLP results were determined by extracting each batch of material in accordance with Method 1311, which is found in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, EPA Publication SW-846. The resulting leachate was then sampled and analyzed for total mercury by cold cathode atomic absorption. The results (shown in Column 2 of Table 1) are in mg/L of the leachate, which is the usual reporting method. By way of comparison, the regulatory limit for disposal of mercury-contaminated (nonradioactive) material is 0.2 mg/L. Thus, the TCLP values are a factor of 250 below the RCRA regulatory limit. The fact that no mercury was leachable by the TCLP method is not surprising because the solubilities of both HgS (the main mercury-containing species in the batches) and elemental mercury in water are exceedingly low.

The elemental mercury results were determined using one stage of a sequential extraction method developed by Lockheed Environmental Systems and Technologies Company (LESAT), the contractor for the Environmental Monitoring Systems Laboratory-Las Vegas.⁷ The stage of the extraction method used in this study separated elemental mercury and metallic mercury amalgams from mercury sulfide based on solubility differences in a nitric acid solution. The procedure for this extraction stage is as follows:

1. For each of the 4 batches of HgS, weigh out two 0.5-g samples in separate centrifuge tubes.
2. Add 12.5 mL of 1:3 (by volume) 70% HNO₃ + H₂O solution to each centrifuge tube. Cap the tube, and mix the contents thoroughly.
3. Loosen the cap on the centrifuge tube, and heat the mixture for 30 min in a 90°C water bath with occasional mixing.
4. Centrifuge the liquid for 5 min. Decant the liquid into a bottle.

5. Repeat steps 2 through 4 for each sample, combining the second extract with the first. For each sample, 25 mL of decant contain the dissolved elemental mercury that was present in the HgS.

By knowing the mercury concentration in the decant and the volume of the decant, one may calculate the amount of free mercury that was present in each of the 0.5-g samples of HgS. The two intrabatch data points were then averaged in all four cases, giving an average free mercury content for each of the four batches. Because elemental mercury was the limiting reagent in the preparation of the HgS, the free mercury remaining in the reaction product (Column 3 of Table 1) can be used to calculate the reaction yield. In all 4 cases, the reaction yield was near 100%, indicating that the amount of excess sulfur, the mixing method, and the mixing time were appropriate. The commercial HgS showed a significantly lower elemental mercury content, probably because it was prepared by a precipitation/washing technique.

The headspace analysis was performed by allowing 100-g samples of each batch to equilibrate with the vapor phase in a vessel for 72 h, expanding the vapor into a gas sampling tube, then analyzing the gas in the sampling tube for total mercury using an ultraviolet detection method. Column 5 of Table 1 shows the results. By way of comparison, the immediately dangerous to life and health (IDLH) level for mercury is 28 mg/m^3 , the vapor pressure of mercury at 22°C is 14 mg/m^3 , and the threshold limit value (TLV) for mercury is 0.05 mg/m^3 .

The fact that HgS produced by the dry mixing method had a significantly higher headspace concentration than the commercially produced HgS demonstrates that some occluded elemental mercury probably remains in the product. This finding is consistent with the free-mercury results.

One option for ridding the in-house HgS entirely of free mercury is the use of surfactants. One such surfactant is a bacterial lysate that has been proven to be a dispersant for elemental mercury. The following two factors apparently slow down the kinetics of the reaction:

1. as more of the HgS is produced, the probability of collisions between molecules of the two elements is reduced; and
2. as the stainless steel balls continue to reduce the size of the spheres of elemental mercury through impacts, the surface free energy (surface tension) of the spheres is apparently high enough to inhibit the formation of interfaces with the sulfur molecules.

A longer residence time and/or a higher input of mechanical energy would be logical attempts at finishing the conversion of mercury to HgS without the surface-tension complication. Without the formation of interfaces between the mercury and the sulfur, collisions will have no effect, thereby leaving a finite amount of unconverted elemental mercury in the system. The addition of the biodispersant (provided by the Biology Division of the Oak Ridge National Laboratory) after the two elements have shaken together for 2 h, followed by additional residence time, may allow the conversion to be completed. An additional option is to finish the conversion to HgS with microwave energy.

COPPER AMALGAMATION

The laboratory procedure that was developed to make the copper amalgam is as follows.

1. Begin with fine copper powder (-325 mesh).
2. Wash the copper with 1 N nitric acid (HNO_3) (about 1 mL/20 g of powder).
3. Mill the washed powder in a laboratory shaker with stainless steel balls for 10 min.
4. Add the elemental mercury in about 62.5-wt % amounts.
5. Mill the mixture for 45 min with the stainless steel balls.
6. Stir what is now a phase that has a butter-like texture.
7. Mill the mixture for an additional 45 min.
8. Either allow the mixture to harden as a solid mass or crush it into a powder.

Material made by following the preceding procedure produced a clay-like material that hardened overnight into a hard mass. Samples analyzed by X-ray diffraction confirmed that the predominating phase that was present was a compound having the empirical formula Cu_7Hg_6 . This stoichiometry dictates a maximum waste loading of 73 wt % mercury in contrast to 86 wt % in HgS . TCLP results on four 1-kg batches of this material and headspace analysis were performed in a manner similar to that done for the mercury-sulfur batches. No free-mercury analysis was performed because of the tendency of the mercury-copper amalgam to dissociate when in contact with nitric acid.

The analytical results for the mercury-copper batches is summarized in Table 2.

Table 2. Analysis results from four batches of Hg-Cu prepared by the method described in this report

Batch number	TCLP Hg (mg/L)	Headspace Hg (mg/m ³)
C1	0.08	8
C2	0.02	12
C3	0.10	14
C4	0.08	10
Average	0.07	11

ZINC AMALGAMATION

The laboratory procedure developed to make the zinc amalgam is as follows.

1. Begin with fine zinc powder (-325 mesh).
2. Wash the zinc with 1 N HNO_3 (about 1 mL/20 g of powder).

3. Mill the washed powder in a laboratory shaker with stainless steel balls for 10 min.
4. Add the elemental mercury in about 45-wt % amounts.
5. Mill the mixture for 2 h with the stainless steel balls.

Material made by the preceding method was first sent for X-ray diffraction. The analysis confirmed that the predominating phase that was present was a compound having the empirical formula HgZn_3 . This stoichiometry dictates a maximum waste loading of 50.6 wt % mercury, in contrast to 73 wt % for the Cu_7Hg_6 and 86 wt % for the HgS . Table 3 summarizes these results.

Table 3. Analysis results from four batches of Hg-Zn prepared by the method described in this report

Batch number	TCLP Hg (mg/L)	Headspace Hg (mg/m ³)
Z1	6.30	14
Z2	0.09	12
Z3	4.90	14
Z4	0.03	8
Average	2.80	12

Because the LESAT extraction method does not separate metallic amalgams such as those of zinc and copper from elemental mercury, a different analytical technique had to be used to determine the free-mercury concentrations in the copper and zinc amalgams. The determination of the free-mercury concentrations in these two amalgams is not a straightforward problem. Quantitative X-ray diffraction (XRD) could work only if the temperature could be kept below the melting point of mercury (-38.9°C) so that the mercury would retain a definite crystal structure, and, as has been mentioned, extractive separation of the amalgam phases from the elemental mercury is not that well studied.

The analytical method chosen as an experimental attempt to characterize the copper and zinc amalgams by free mercury was X-ray microfluorescence (XRMF) imaging. This method involves the use of an X-ray beam as a probe to excite X-ray fluorescence (XRF) in a specimen and produce a spatially resolved image of the element distribution.⁸ Elemental mercury appears to fluoresce with higher intensity than either the Cu_7Hg_6 or the HgZn_3 , which gives rise to a quantitative technique based on XRF. The technique involves first running a scan on a sample of elemental mercury to determine the minimum intensity observed. Then, a scan should be run on the amalgam sample(s) to generate a histogram (number of pixels vs intensities). If the area under the histogram corresponding to the intensity range of the free mercury is compared with the overall area, one should obtain a reasonable estimate of the areal concentration of the free mercury in the amalgam sample(s). If the sample is homogeneous in three dimensions, the areal concentration should translate well to a volume concentration. Figure 1 gives XRMF images of the copper and zinc amalgams. The brightest areas correspond to the unreacted/partially-reacted mercury present

in the waste forms. At the time this report was written, the quantitative scheme had not been sufficiently refined to allow free mercury percentages (and thus reaction yields) to be calculated for the zinc and copper amalgams.

Hg XRMF Images of Metal Amalgams

Cu/Hg

Zn/Hg

Fig. 1. X-ray microfluorescence images of copper and zinc amalgams.

SUMMARY OF AMALGAM ANALYTICAL RESULTS

To make a direct comparison of the performances of the various amalgams, the results for each are summarized in Table 4. As can be seen in the table, the mercury-sulfur material has a significantly lower TCLP value for mercury and a lower mercury headspace value than either the mercury-copper or mercury-zinc amalgams. Additionally, the mercury loading of the mercury-sulfur material is somewhat higher than that of the other amalgams.

Table 4. Comparison of analyses of prepared amalgams

Amalgam	Composition (% Hg)	TCLP Hg (mg/L)	Elemental Hg (mg/L)	Reaction yield (%)	Headspace Hg (mg/m ³)
Hg-S	83	<0.0008	299	99.97	0.008
Hg-Cu	62	0.0700	-	-	11.0000
Hg-Zn	45	2.8000	-	-	12.0000

THERMAL DECOMPOSITION OF MERCURIC SULFIDE

Another important property of mercury amalgams is their thermal stability in the environment. As can be seen from the headspace results and as is verified by thermodynamic calculations, both the mercury-copper and the mercury-zinc compounds oxidize at ambient temperature to form elemental mercury and metal oxides. The thermal decomposition behavior of mercuric sulfide was studied to provide analogous information on its stability. Figure 2 shows the decomposition behavior of reagent grade HgS (cinnabar) in air as it is heated at a rate of 100°C/h. An ultraviolet detector was used to monitor the vapor-phase mercury at 253.7 nm as the HgS decomposed. As can be seen in Fig. 2, the decomposition rate became significant at about 250°C and increased with increasing temperature.

Fig. 2. Thermal decomposition profile for mercuric sulfide.

Figure 3 shows the time dependence of the decomposition of HgS at a constant temperature of 307°C. The near linearity of the logarithm of the rate versus time curve (shown in red on the graph) indicates the reaction kinetics is consistent with a first order rate process.

While the crystalline phase of HgS produced by the method described in this report is somewhat different from the cinnabar used for the thermal decomposition studies, the decomposition rates of the two phases are likely to be similar. It is clear that for most considerations, the decomposition rate of HgS is very slow below 250°C and insignificant below 200°C.

Fig. 3. Thermal decomposition of HgS at 307°C.

SOLIDIFICATION WITH MODIFIED SULFUR CEMENT

Modified sulfur cement (MSC) is being widely considered for the immobilization of all eight of the RCRA heavy metals and their leachable compounds. The cement that was used in this investigation was bought from Martin Resources, Inc., and is typically 94 to 96 wt % sulfur and 4 to 6 wt % oligomer/polymer of cyclopentadiene used as a structural modifier. Experiments were conducted to determine if the material behaved similarly to elemental sulfur. Mercury was combined directly with molten MSC and allowed to mix for 12, 40, 70 and 130 min. The samples were leached according to the LESAT method (given earlier in this report) to determine free mercury amounts, sent for X-ray diffraction to determine the predominant phase(s) that were present, and sent for TCLP and subsequent cold cathode atomic absorption analysis for mercury in the leachate. The results are presented in Table 5. All 4 samples had a composition by weight of 2/3 mercury and 1/3 MSC. The batches were made in metal cans on a hot plate in a hood permitted for mercury experimentation. Mixing was done manually, and the temperature was held between 125° and 150° C.

Table 5. Summary of MSC experiments

Sample	Residence time (min)	TCLP Hg (mg/L)	Elemental Hg (ppm)	Predominant phase
MSC1	10	2.0	182,000	HgS
MSC2	40	1.4	175,000	HgS
MSC3	70	0.4	160,000	HgS
MSC4	130	0.2	45,000	HgS

From these data, direct reaction with the mercury the MSC is an inferior choice to the elemental sulfur for several reasons. The cement comes in flat, plate-like chips that are (from a visual estimate) about 2 in. by 2 in. by 1/4 in. Also, because of the polymeric modifier in the cement composition, the MSC is less active than elemental sulfur in its reaction with elemental mercury (i.e., the reaction between elemental mercury and MSC proceeds slower than the reaction between elemental mercury and sulfur). These two facts almost rule out reaction at room temperature between the MSC and the elemental mercury because the chips would have to be ground to produce a fine, particle-size dust, and the processing times per batch in the paint shaker would be longer than those done with elemental sulfur. So, the MSC process is done at 125° to 150° C, which is not as desirable as a room-temperature operation. The TCLP concentrations are higher than are expected for even a batch of 100% elemental mercury, indicating that one detrimental result of the elevated processing temperature in air may be the formation of the rather soluble HgO phase (making amalgams of MSC and elemental mercury likely to wind up in a Subtitle C rather than a Subtitle D disposal facility). Also, when elemental mercury is processed at elevated temperature, an additional concern about worker safety always exists because of the possibility of accidents that result in acute doses of mercury vapors. Finally, the engineering costs (to avoid release of mercury vapors into the air) and the energy costs associated with a molten MSC process would be greater than those associated with the room-temperature process with elemental sulfur.

The only sample that passed the TCLP test was MSC4, which had a residence time of just over 2 h. One can see that even this sample contains about 4.5% elemental mercury (45,000 ppm) compared with an average of about 0.03% for the samples made at room temperature with elemental sulfur. Evident from just these scoping experiments is the fact that to get the same quality (quality being confirmed by TCLP results, headspace results, and free mercury remaining in the product) final waste form that is produced by the room temperature elemental sulfur method would necessitate the following conditions:

1. much longer batch residence times would be required,
2. additional engineering would be required to mitigate concern for worker safety,
3. inert atmosphere might be required over the melt so that significant amounts of HgO are not formed (if the end objective is to dispose of the waste in a Subtitle D facility) and
4. additional energy costs would be associated with the molten MSC process.

MSC, although not the best candidate for direct stabilization of elemental mercury, is a good candidate for a micro- or macroencapsulant for HgS. If the HgS powder is not compacted (i.e., remains granular), the MSC would be a microencapsulant (surrounding individual granules of waste); if, however, the HgS has been compacted, the MSC would act as a macroencapsulant. In either case, an encapsulant such as MSC would be desired either for an additional barrier to the migration of mercury from the HgS into the environment or as a way to provide a monolithic waste form having structure integrity that meets the waste acceptance criteria (WAC) of a particular disposal site.

RECOMMENDATIONS

In addition to the radioactively contaminated elemental mercury likely to be generated during future decontamination and decommissioning activities on ORR, a significant amount of this waste is already in inventory. All of this waste in storage is in Appendix B of both the FFC Agreement and the FFC Act, meaning that no on-site treatment method exists for this waste. Information on the inventoried radioactively contaminated elemental mercury waste on ORR is given in Table 6. This inventory totaled 8263.5 kg on December 31, 1993, all of which have AMLGM as the treatment method specified in 40 CFR Part 268.42, Table 3.

Table 6. Inventory of radioactively contaminated mercury on ORR as of December 31, 1993

MWIR stream	Amount (kg)	Location
1078 B	4430.0	K-25
1113 B	3067.0	K-25
2006 B	675.0	ORNL
3094 B	59.0	Y-12
3096 B	0.5	Y-12
3097 B	32.0	Y-12

The authors recommend that an application be submitted to both EPA and TDEC asking for approval of the use of black mercuric sulfide as a final waste form for any radioactively contaminated elemental mercury waste on ORR. The process for making the sulfide that has been presented in this topical report produces a final waste form that

1. uses a reagent (sulfur) given in the definition of AMLGM that is given in 40 CFR Part 268.42, Table 1;
2. reduces emissions of elemental mercury vapors to the air by a factor of 1750;
3. has leachable mercury concentrations at least a factor of 250 times below the regulatory limit of 0.2 mg/L;
4. carries out its fabrication in an enclosed system at room temperature;
5. is produced with no secondary waste streams; and
6. is consistently the same.

The process is easily scalable with just the addition of paint shakers (at a cost of ~\$1500/shaker), and Y-12 Plant Development Organization personnel will be happy to assist Waste Operations in any scale-up plans.

If the disposal site WAC require a monolithic structure with a given compressive strength, the process should include encapsulation with either molten sulfur or modified sulfur cement. This encapsulation step would follow the conversion of the elemental mercury to the HgS (which is done in a paint shaker at room temperature).

Additionally, issues and ideas that arose from this project and may warrant further attention in the form of sponsored research and development are as follows:

1. *In Situ* immobilization of elemental mercury found in inaccessible places in the ground (i.e., underneath building foundations) that exists as a source for groundwater contamination. A technique such as this could be a viable substitute for a commitment to continuous groundwater treatment around these mercury sources far into the future.

2. Long-term leach modeling of HgS in environments having a full range of pH. This would help determine where to dispose of the HgS and how long the HgS would likely last in the chosen disposal environment. The issue here is really one of conscience rather than regulatory necessity. It is realized that the HgS waste form derived from the developed process presented here contains a significant amount of excess sulfur. In neutral and acidic environments (the only environments addressed by the regulations are a subset of these), the solubility of the product has been demonstrated (through the literature and TCLP tests done during this study) to be extremely low; in alkaline environments, it is anticipated that the solubility of the mercury in the product would increase to some extent. It seems that a study which includes the measurement of this anticipated increase in mercury solubility in alkaline environments would provide information that further completes the characterization of the HgS product as a final waste form.

CONCLUSIONS

Although all three of the preceding materials processes produce final waste forms that render elemental mercury nonhazardous according to RCRA law, concerns about longevity clearly make the HgS the preferred disposal form. Both the zinc and the copper in the amalgam form seem to oxidize readily in an open-air environment, with the oxidation of the zinc proceeding more rapidly than that of the copper. This oxidation results in a final waste form that relinquishes elemental mercury into the disposal environment over time. The longevity of the HgS is well known because the red form occurs as a natural mineral in deposits in the earth's crust.

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ACRONYMS

AMLGM	amalgamation
CCWE	constituent concentrations in waste extract
CFR	Code of Federal Regulations
D&D	decontamination and decommissioning
DOE-ORO	U. S. Department of Energy-Oak Ridge Operations
EPA	Environmental Protection Agency
FFCAct	Federal Facilities Compliance Act
FCCAgreement	Federal Facilities Compliance Agreement
IDLH	immediately dangerous to life and health
LDR	land disposal restrictions
LESAT	Lockheed Environmental Systems and Technologies Company
MSC	modified sulfur cement
ORR	Oak Ridge Reservation
RCRA	Resource Conservation and Recovery Act
TCLP	toxicity characteristic leaching procedure
TDEC	Tennessee Department of Environment and Conservation
TLV	threshold limit value
WAC	waste acceptance criteria
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRMF	X-ray microfluorescence

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