SOLIDIFICATION/STABILIZATION OF ELEMENTAL MERCURY WASTE BY AMALGAMATION

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ABSTRACT

Experiments on solidification of elemental mercury waste were conducted by amalgamation with several metal powders such as copper, zinc, tin, brass and bronze. Unlike the previous studies which showed a dispersible nature after solidification, the waste forms were found to possess quite large compressive strengths in both copper and bronze amalgam forms. The durability was also confirmed by showing very minor changes of strength after 90 days of water immersion. Leachability from the amalgam forms is also shown to be low: measured mercury concentration in the leachate by the Toxicity Characteristic Leaching Procedure (TCLP) was well below the Environmental Protection Agency (EPA) limit. Long term leaching behavior by Accelerated Leach Test (ALT) has shown that the leaching process was dominated by diffusion and the effective diffusion coefficient was quite low (around 10^{-19} cm^2/sec). The mercury vapor concentration from the amalgam forms were reduced to a 20% level of that for elemental mercury and to one-hundredth after 3 months.

INTRODUCTION

Elemental mercury wastes are generated commonly from industry, laboratories and hospitals in Korea. Most of the collected wastes are usually purified by distillation and reused. Often, from an economic point of view, elemental mercury wastes are not recycled due to high cost of collection and purification. Some special elemental mercury waste, e.g., elemental mercury contaminated by radionuclide is not considered for reuse. Elemental mercury wastes not recycled are usually stored in containers such as cans or bottles filled with water without any treatment. Because of its dispersible and toxic nature, as is well known, elemental mercury waste should also be very carefully controlled during its storage and disposal (1).

Solidification technology is currently being applied to immobilize liquid elemental mercury waste into a stable solid form (2,3), Amalgamation, the formation of a mercury alloy with zinc or sulfur, has been studied at first as solidification/stabilization technology for elemental mercury waste. It was known however, that the products of amalgamation were pastes or powder, which require further treatment to convert them into a non-dispersible form. To make matters worse, it was observed that amalgamation didn't provide reduction in vapor concentrations as compared with elemental mercury (4).

In this study, we have re-attempted amalgamation with various metals such as zinc, tin, copper, bronze, and brass to solidify elemental mercury waste in a form that would be non-dispersible, to meet EPA leaching criteria, and to have low mercury vapor pressure after amalgamation.

EXPERIMENTS

Materials

Elemental mercury waste used in the experiments was obtained from the Nuclear Fuel Fabrication Facility at the Korea Atomic Energy Research Institute (K.A.E.R.I). It was slightly contaminated by a small quantity of uranium powder and unknown impurities. Mercury content of the elemental mercury waste was 99.4±0.2%. As a reference material for the elemental mercury waste, pure elemental mercury of 99.999% (C & S International Co.) was also used.

Metal powders(zinc, tin, copper, brass, and bronze) for amalgamation were first grade reagents having a purity of 99% and they were used in the experiment as received. The brass was an alloy composed of copper and zinc (copper 65%, zinc 35%). The bronze was an alloy composed of copper and tin(copper 90%, tin 10%).

Sample Preparation

Amalgam samples were prepared using a mechanical amalgamator which is used in dental clinics to make Ag-amalgam. Elemental mercury waste (or mercury) and metal powder were dispensed with a pestle in a capsule. The ratio of waste to metal powder was varied in the range of 3:1 ~ 1:3 (waste:metal powder). The mixing called trituration was done to produce amalgam by vibrating the capsule. The produced amalgam was then transferred into a mold and lightly pressed to form a cylindrical shape measuring 1 cm in diameter and 2 cm in height. After being pushed out from the mold the amalgam was left in a chamber for 18 ~ 24 hours for solidification without any treatment. These samples were subjected to several performance tests to evaluate mechanical stability, durability by water immersion, leaching properties and the release rate of mercury vapor. The microstructure observation and X-ray diffraction analysis have also been conducted on the samples. Larger amalgam samples were fabricated by using a shatter box which is commonly used in milling. The large sample preparation was conducted in the same manner as a small sample preparation. Two molds with diameters of 2.5 cm and 5 cm were used to fabricate waste forms measuring 2.5 cm in diameter and 2.5 cm in height and another form 5 cm in diameter and 5 cm in height, respectively.

Test methods

Compressive strength testing was performed on small samples by using a Zwick/Roell Model 1445 universal tester. Water immersion testing was performed on three replicate small samples of amalgam forms containing mercury waste and pure mercury (two copper amalgam forms with pure mercury and mercury waste, and one bronze amalgam with mercury waste). Each sample was immersed completely in demineralized water at an ambient temperature (25°C) and was examined periodically. Upon completion of immersing in water for 90 days, they were removed from the water and checked for variations in weight and dimension. Then, their compressive strengths were measured. Leach testing was conducted in accordance with the Toxicity Characteristic Leaching Procedure (TCLP) of the U.S. Environmental Protection Agency (5). Long-term leaching behavior was evaluated with Accelerated Leach Test (ALT), ASTM C-1308(6). Initial release rate of mercury vapor was determined by measuring the vapor concentration in the bottle periodically which contained the sample of amalgam waste form. Microstructure of amalgam waste form was observed by using an optical microscope. X-ray diffraction analysis was carried out using Cu Kα radiation (scanning range: 20 to 100°, step: 0.02°, scanning speed: 4°/min.).

RESULTS AND DISCUSSION

Preparation of amalgam waste form

The zinc amalgam waste could not be made in a monolithic form in this experiment but in the form of granule. The brass amagam waste formwere produced when equal amounts of the elemental mercury waste and the brass powder were mixed. However, the waste form was soft and sweated mercury droplets within a few days after preparation. The tin amalgam waste form didn't sweat mercury droplets but it was too soft to handle. All other amalgam forms (brass, tin, copper, and bronze) except the zinc amalgam could be obtained in a rigid form. The maximum loadings of mercury in these two amalgam waste forms reached about 70 wt%, respectively. However, when the loading of mercury was less than 45 wt% the amalgams couldn't be made in a monolithic form. Accordingly, it was found that when the loading of mercury is in the range of 50 ~ 70 wt%, the copper amalgam and the bronze amalgam can be fabricated in rigid waste forms.

Compressive Strength

The results of compressive strength testing on some amalgam waste forms are summarized in Table I. The testing was performed on the waste forms when 7 days had passed after preparation.

Table I. Compressive Strengths of Amalgam Waste Forms

Sample Description	Compressive Strength*, kg_f/cm^2 (Mpa)
Copper amalgam (50 wt% Pure Mercury)	1,065 ± 218 (104 ± 21)
Copper amalgam (53 wt% Pure Mercury)	789 ± 152 (77 ± 15)
Copper amalgam (67 wt% Pure Mercury)	382 ± 102 (37 ± 10)
Copper amalgam (50 wt% Mercury Waste)	968 ± 189 (95 ± 18)
Copper amalgam (53 wt% Mercury Waste)	797 ± 132 (78 ± 13)
Copper amalgam (67 wt% Mercury Waste)	412 ± 121 (40 ± 12)
Bronze amalgam (53 wt% Pure Mercury)	632 ± 154 (62 ± 15)
Bronze amalgam (53 wt% Mercury Waste)	612 ± 121 (60 ± 12)

The compressive strengths of copper amalgam forms containing pure mercury were very similar to those of copper amalgam forms containing elemental mercury waste. The small amount of impurities in mercury waste didn't affect the compressive strength of the amalgam waste form. The compressive strengths of the copper amalgam form decreased as mercury loading increased. They were higher than those of the bronze amalgam form. The compressive strengths of the copper and the bronze amalgam waste forms were very high compared to those of the usual cement waste form or the usual plastic waste form. This means that the copper and the bronze amalgam waste forms possessed excellent mechanical integrity. Although the copper amalgam form containing 50wt% mercury had the highest compressive strength, workability for molding was very poor when preparing the waste forms. And the copper amalgam waste form and bronze amalgam waste form containing 53 wt% mercury, respectively, were subjected to other performance tests to evaluate durability by water immersion, leaching properties and the release of mercury vapor.

Durability by Water Immersion

Water immersion testing was performed on three replicate samples for copper amalgam waste forms containing 53wt% mercury waste and 53wt% pure mercury, respectively, and bronze amalgam waste form containing 53wt% mercury waste. All samples had negligible changes in weight and dimensions after 90 day water immersion. Their compressive strengths were also retained after water immersion. Results are summarized in Table II. Improvement of compressive strength after 90 days may be considered by the fact that the amalgam forms are seasoned and its structure reaches a more stable state.

Table II. Compressive Strengths of Amalgam Waste Form After Water Immersion Test

Sample Description	Compressive Strength after 90 days without Water Immersion, kg_f/cm^2 (Mpa)	Compressive Strength after 90 day Water Immersion kg_f/cm^2 (Mpa)
Copper amalgam (53 wt% Pure Mercury)	1,150 ± 132 (112 ± 13)	1,075 ± 125 (105 ± 12)
Copper amalgam (53 wt% Mercury Waste)	1,076 ± 92 (105 ± 9)	1,225 ± 162 (120 ± 16)
Bronze amalgam (53 wt% Mercury Waste)	1,123 ± 125 (110 ± 12)	1,023 ± 134 (100 ± 13)

Leachability of the Amalgam Waste Form

Following TCLP of U.S. EPA, the leach testing was performed on elemental mercury waste, pure elemental mercury, copper amalgam waste forms containing 53 wt% mercury waste and bronze amalgam waste forms containing 53 wt% when 7 days had passed after preparation. The results are summarized in Table III.

The mercury concentrations in leachates of the copper amalgam form and the bronze amalgam form were 55 μg/L and 27 μg/L respectively, well below the EPA's current allowable limit of 200 μg/L while those of the elemental mercury and pure mercury were very high as expected and exceeded more than 10 and 500 times the limit, respectively. Copper and tin, the components of bronze, are not classified as toxic characteristic contaminant and have no EPA's limit. However, the concentrations of copper and zinc in leachates were measured and the results on copper are listed in Table III. For the bronze amalgam waste form, the concentration of zinc in leachate was less than 0.1 mg/L.

Table III. Concentrations of Mercury and Copper in TCLP leachate

Sample Description	Mercury Concentration, μg/L	Copper Concentration, μg/L
Elemental mercury waste	11,400	-
Pure mercury	2,610	-
Copper amalgam (53 wt% Mercury Waste)	55	5.9
Bronze amalgam (53 wt% Mercury Waste)	27	5.1

Long-term Leaching Behavior

The ALT was applied on some amalgam waste forms to evaluate the long-term leaching behavior of the amalgam waste forms. The results are shown in Fig. 1, in which the experimental data are indicated with symbols and the modeling results by diffusion are shown in continuous curves for each data set.

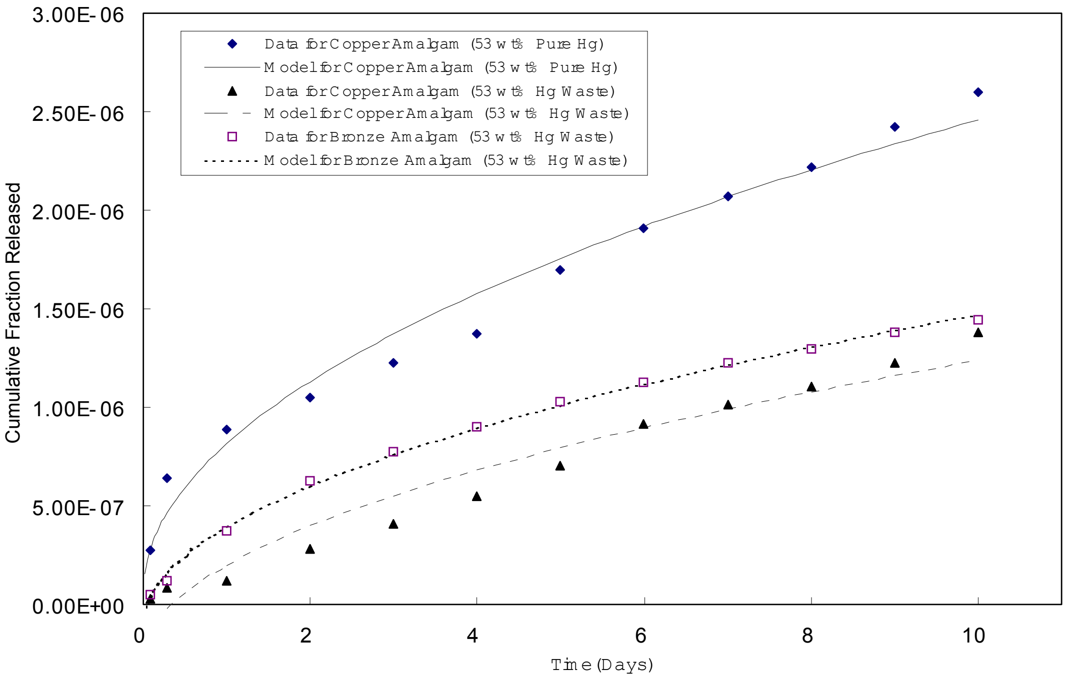

Fig. 1. Leaching Data Points of Mercury and Diffusion Model Curves of Hg for Amalgam Forms

The experimental data were in close agreement with those predicted by the diffusion model. Measured diffusion coefficients were 2.87×10^{-19} cm^2/sec for copper amalgam waste forms containing 53 wt% pure mercury, 1.00×10^{-19} cm^2/sec for copper amalgam waste forms containing 53 wt% mercury wasteand 9.42×10^{-20} cm^2/sec for bronze amalgam waste forms containing 53 wt% mercury waste. These values are lower than those for the sulfur polymer waste form containing elemental mercury which averaged 7.6×10^{-18} cm^2/sec. The experimental data were in close agreement with those predicted by the diffusion model. However, the leaching curves of amalgam waste forms containing 53 wt% pure mercury forms and bronze amalgam waste forms containing 53 wt% mercury waste, after 3 days, appear to be linear unlike the expected behavior under leaching which is strictly controlled by diffusion. Fuhrmann and his co-workers (2) have already observed similar tendencies for sulfur polymer waste forms containing elemental mercury. They attributed the behavior to the surface dissolution of mercury, at a very low rate, which contributes to the diffusion-dominated leaching process. This process is often observed for materials with very low leach rate.

Initial Release Rate of Mercury Vapor

Previous studies on amalgamation for solidification/stabilization of elemental mercury waste indicated that amalgamation with zinc provides no reduction in vapor concentrations as compared to that of elemental mercury. However, in this study, it has been found that the initial release rate of mercury vapor on amalgam forms aged 7 days after preparation, were reduced approximately to 20 % of that of elemental mercury and, furthermore, those of amalgams aged 3 months were remarkably reduced by about one-hundredth of that of elemental mercury. The results are summarized in Table IV.

Table IV. Initial Release Rate of Mercury Vapor

Sample Description	Initial Release Rate of Mercury Vapor, mg/(cm^2·hr)	
	After 7 days	After 90 days
Pure Mercury	2.91 x 10^{-3}	2.87 x 10^{-3}
Copper amalgam (53 wt% Mercury Waste)	6.84 x 10^{-4}	4.53 x 10^{-5}
Bronze amalgam (53 wt% Mercury Waste)	5.31 x 10^{-5}	2.81 x 10^{-5}

Microstructure and X-ray Diffraction Analysis

Microstructure of the copper amalgam waste form containing 53wt% mercury waste is shown in Fig. 2. The copper amalgam phase and the copper phase were clearly observed in the waste form. The amalgam exists in continuous phase while the copper uniformly disperses in the amalgam phase. The bronze amalgam waste form also has a similar microstructure and its picture is omitted.

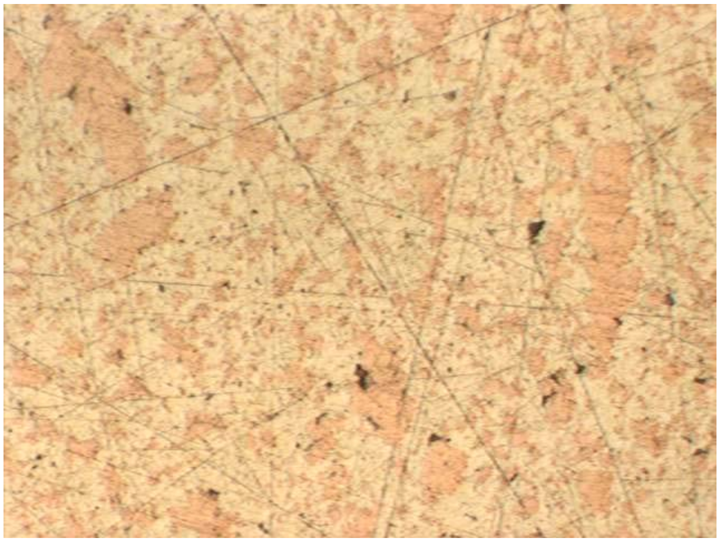

Fig. 2. Microstructure of Amalgam Forms Containing 53 wt% Mercury (×500)

As the results of X-ray diffraction analysis for the copper amalgam waste form and the bronze amalgam waste form, it was found that the main constituents of the copper amalgam and the bronze amalgam are Cu_7Hg_8. The copper amalgam waste form is distinctly composed of Cu_7Hg_8 and Cu, while the bronze amalgam waste form may be considered to be composed of Cu_7Hg_8, $Cu_{16\sim17}Sn$(bronze), and $Cu_{(16\sim17)-x}Sn_{1-y}$.

Larger Amalgam Waste Form

The copper amalgam waste forms, one with 2.5 cm in diameter and 2.5 cm in height and another one with 5 cm in diameter and 5 cm in height, respectively, were successfully fabricated by using a shatter box for the mixing of elemental mercury waste and copper powder. These copper amalgam forms are shown in Fig. 3.

(a)

(b)

Fig. 3. Larger Cu-Amalgam Forms Containing 53 wt% Spent Mercury

(a) 2.5 cm Diameter ×2.5 cm Height

(b) 5 cm Diameter ×5 cm Height

Through this fabrication experiment, it was found that larger amalgam waste forms could be fabricated if larger mixing apparatus with increased capability to mix (trituration) enough quantity of the elemental mercury waste and the copper or the bronze powder is used in amalgamation.

SUMMARY AND CONCLUSIONS

In this study, we have attempted amalgamation with various metals such as zinc, tin, copper, bronze, and brass to solidify elemental mercury waste in a form that would be non-dispersible, to meet EPA leaching criteria, and to have a low mercury vapor pressure. Of these metal powders, copper and bronze have the capability to build a rigid monolithic form by amalgamation with mercury. The copper amalgam form and bronze amalgam form, each containing 53 wt% mercury, were subjected to selected performance tests to evaluate mechanical integrity, durability, leaching properties, and the release of mercury vapor. Compressive strengths of the copper amalgam form and the bronze amalgam form were respectively around 80 Mpa and 60 Mpa when 7days had passed after preparation. It indicates that these amalgam forms possessed excellent mechanical integrity. The mercury concentrations in leachates of the copper amalgam form and the bronze amalgam form assessed by the TCLP were 55 μg/L and 27 μg/L respectively, well below the EPA limit of 200 μg/L. The ALT were also conducted to evaluate long term leaching behavior of amalgam forms. The comparison of the measured data with the prediction by a diffusion model for each amalgam form was fairly good. Both effective diffusion coefficients of mercury in the copper amalgam form and the bronze amalgam form averaged around 10^{-19} cm^2/sec. Initial release rates of mercury vapor of amalgam forms that aged 7 days after preparation were reduced to 20% of that of elemental mercury. And those of amalgams after 3 months were remarkably reduced to about one-hundredth of that of elemental mercury. The amalgam forms were characterized by X-ray diffraction analysis and it was found that the main constituents of the copper amalgam and the bronze amalgam are Cu_7Hg_8.

From these results, we conclude that elemental mercury waste could be successfully solidified and stabilized by amalgamation using copper or bronze.

REFERENCES

1. S.P. YIM, J.S. SHON, B.G. AHN, H.J. LEE, J.W. LEE, C.G. JI, S.H. KIM, J.H. YOON, "Conditioning of Spent Mercury by Amalgamation," KAERI/RR-2188/2001, Korea Atomic Energy Research Institute (2001).
2. M. FUHRMANN, D. MELAMED, P.D. KALB, J.W. ADAMS, and L.W. MILIAN, "Sulfur Polymer Solidification/Stabilization of Elemental Mercury Waste," BNL-67697, Brookhaven National Laboratory (1999).
3. W.P. HAMILTON, A.R. BOWERS, "Determination of Acute Hg Emissions from Solidification/Stabilized Cement Waste Forms," Waste Management, 17:25 (1997).

4. C.H. MATTUS, "Measurement of Mercury Released from Amalgams and Sulfide Compounds," ORNL/TM-13728, Oak Ridge National Laboratory (1999).
5. U.S. EPA, "Toxicity Characteristic Leaching Procedure (TCLP), 40 CFR 261, Appendix II, U.S. Environmental Protection Agency (1994).
6. American Society for Testing and Material, "Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms, ASTM C-1308-95, American Society of Testing and Materials (1995).