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SULFUR POLYMER CEMENT FOR MACROENCAPSULATION
OF MIXED WASTE DEBRIS

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ABSTRACT

In FY 1997, the U.S. DOE Mixed Waste Focus Area (MWFA) sponsored a demonstration of the macroencapsulation of mixed waste debris using sulfur polymer cement (SPC). Two mixed wastes were tested – a D006 waste comprised of sheets of cadmium and a D008/D009 waste comprised of lead pipes and joints contaminated with mercury. The demonstration¹ was successful in rendering these wastes compliant with Land Disposal Restrictions (LDR), thereby eliminating one Mixed Waste Inventory Report (MWIR) waste stream from the national inventory.

I. INTRODUCTION

The MWFA has a need for developing treatment technologies for mixed wastes. One class, mixed waste debris, presents a challenge because of its diversity. The Environmental Protection Agency (EPA) LDR under the Resource Conservation and Recovery Act (RCRA) require macroencapsulation for this class. The process used for macroencapsulation must result in a surface coating or jacket of inert inorganic materials to substantially reduce surface exposure to potential leaching media (40 CFR 268.40, Table 1). Other Department of Energy (DOE) sites have tested the use of various matrices such as epoxy² or polymer^{3,4} for encapsulation of mixed waste debris.

Sulfur polymer cement (SPC) is a relatively new material in the waste immobilization field, although it was developed in the late 1970s by the U.S. Bureau of Mines. Its chemical and physical properties are interesting (e.g., development of high mechanical strength in a short time and high resistance to many corrosive environments). Because of its very low permeability and porosity, SPC

has been considered for the immobilization of hazardous or radioactive waste.⁵ The ability of this material to form very insoluble products with many metals renders the matrix even more attractive than others, because a chemical reaction occurs during the encapsulation.⁶ Based on the results of previous work performed at Oak Ridge,^{7,8} the idea of using SPC for this purpose was submitted to, and accepted by, the MWFA.

II. WORK DESCRIPTION

Before selecting the equipment necessary for the experimental work, it was necessary to determine the size and shape of the final waste form that would be cast. Three major parameters were taken into consideration for the selection: U.S. Department of Transportation (DOT) requirements, final disposal requirements, and handling requirements.

The location for the final disposal of the treated waste was not firmly determined when the study started; therefore, Envirocare's (Utah) – one of the two places accepting the storage for final disposal of Mixed Low Level Wastes (MLLW) – waste acceptance criteria were selected as a guide for the selection process.

For final acceptance of macroencapsulated waste forms, Envirocare required the following steps:

- Provide a sample of the actual waste to be macroencapsulated as well as a statement indicating that the sample is representative.
- Surround the waste with a barrier of at least 2 in. of the encapsulating material, and ensure that the barrier is in intimate contact with the waste. Encapsulate the waste during a continuous pour. The presence of

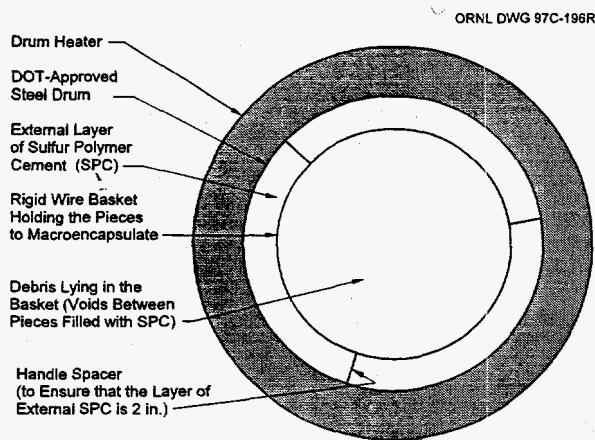
space holders or any device that could provide a pathway to the outside is forbidden.

- Provide a copy of the treatment plan, showing that the methodology meets the definition of macroencapsulation.

There were some concerns about the possibility of thermal shrinkage of the material after cooling, especially for large monoliths. Even though this potential problem could probably have been remediated by adding some fibers to the molten SPC, the time frame for the demonstration did not allow research in this area. After consideration of all the issues involved, a DOT-approved, 5-gal metal pail (1A2/Y1.8/100) was selected for the container in which to cast the waste form.

The debris was introduced into a wire basket that was contained within the 5-gal metal pail with the help of a device that supported the weight, centered the basket, and maintained the basket securely to retain a 5-cm surrounding layer of SPC (Fig. 1). The space between the drum and the wire was filled by SPC to ensure that no pathway existed between the debris and the outside of the waste form. Molten SPC was poured into the drum to concomitantly provide the outer layer of SPC and fill the voids between the pieces of debris. The pour of sulfur was continuous until it reached 5 cm from the top of the drum, at which level it was stopped. After the bottom part had hardened, a "cap layer" of molten SPC was added to the drum as a final barrier following removal of the holding device. Upon cooling and hardening of the SPC, the drum was sealed in a form acceptable for land disposal.

Fig. 1. Top view of the experimental setup.



II. RESULTS

D. Determination of the Operational Conditions — Bench-Scale Testing

The process optimization was conducted using smaller metal 1-gal pails. Scrap metal pieces were placed in wire-mesh baskets. After a series of tests, the resulting waste forms were observed after being cut transversely. The resulting observations made in the bench-scale experiments are discussed in the paragraphs that follow.

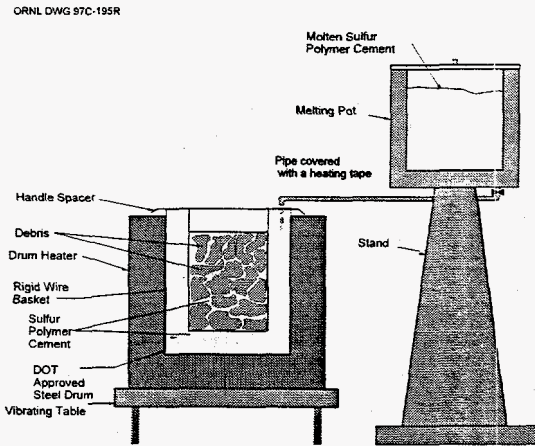
- As recommended in the literature, heating the debris to a temperature of 140-150°C helped to ensure that no fast cooling of SPC occurred on the cold surfaces. This procedure consequently reduced the formation of air pockets.
- Vibrating the container that holds the basket of debris proved to give better results in general. The vibration was found to be sufficient when vibration was applied throughout the pouring sequence and maintained for 2 min or so after the end of the pour.
- Samples obtained from a continuous pour were compared with those made in three successive additions of SPC. Transverse cuts of the samples showed no obvious discontinuity for multiple pours.
- Without a cooling treatment step, the formation of air bubbles was observed at the top surface of the SPC, regardless of whether the cooling was slow or rapid. The hardening of the top layer probably prevented the bubbles generated by the still-molten SPC underneath from escaping. To remediate this problem, the top portion of the container was heated while the rest of it was cooling down. The top heating was maintained for about 8 h. After the sample had been cut, it was confirmed that no air pockets were present.

B. Determination of the Operational Conditions — Full-Scale Testing

Two 5-gal pails were used for testing the equipment and the experimental parameters at larger scale (Fig. 2). During the first test, the pail and its contents were heated in the drum heater at 130°C for 5 h. Two 2-in.-wide heating tapes were placed at the top of the pail to maintain the SPC in a molten state while the bottom part was cooling. Next, SPC was continuously poured into the top of the pail. The vibrating table was activated during the pour and left on for about 3 min thereafter. The two

heating tapes were left on for 6 h, while the drum heater was turned off. When the pail of cooled SPC was cut, some air bubbles were observed at about 2 to 3 cm from the top surface.

Fig. 2. Experimental setup used for the demonstration.



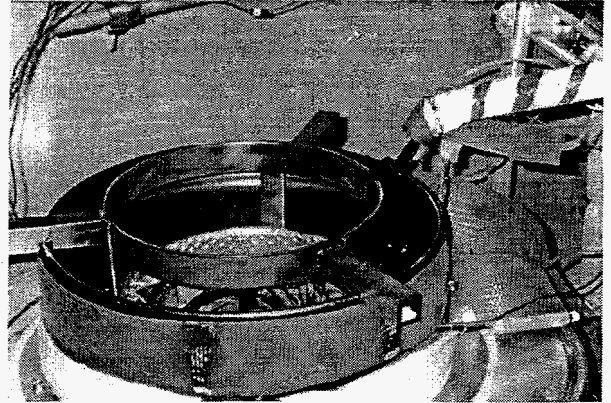
A second test was performed in which the operating temperature was increased, because it was suspected that the lower temperature in the previous test had caused the formation of bubbles.

The drum heater containing the debris in the basket was set up for a temperature fluctuating between 140 and 150°C, as measured by a thermocouple placed at about 1 in. from the wall of the pail. Two tapes placed on top of the pail heated the top portion of the pail and the waste, helping to eliminate any moisture present at the surface of the debris. The temperature of these two tapes was set at 160°C.

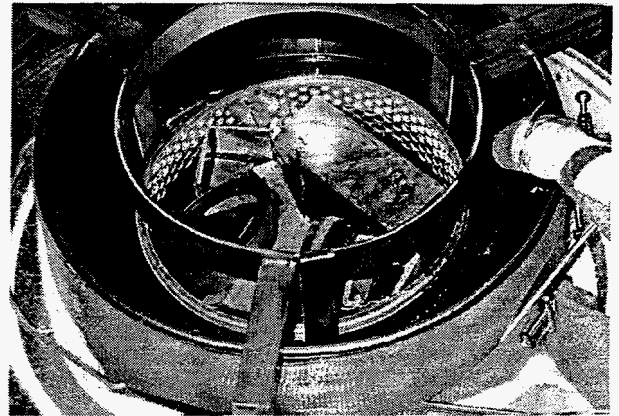
After the debris had been heated for about 6 h, the molten SPC was poured into the pail while the vibrating table underneath the pail was helping entrapped air bubbles to escape (Fig. 3). The molten SPC, which was very fluid, was able to fill the voids between the pieces. The pour was stopped when the level of SPC reached the holding device, situated 2 in. from the top of the pail, which served to keep the basket in place. The vibrating table was left on for an additional period of 3 to 5 min.

The drum heater was turned off, but the heating tapes were maintained at temperature for an additional 10 h. The purpose of this operation was to keep the upper portion of the SPC molten to allow air bubbles generated during the cooling of the lower part to escape.

Fig. 3. Filling the pail with molten SPC.

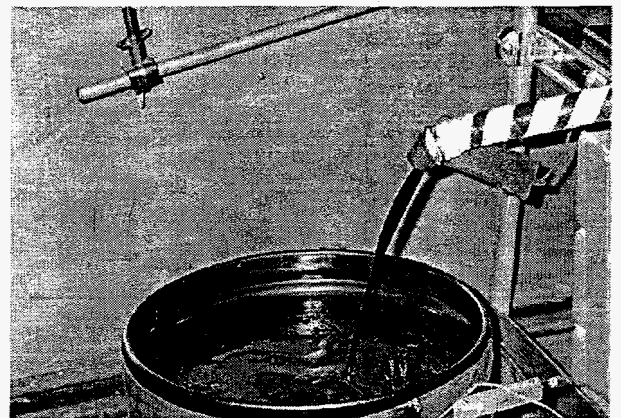


4. Top view of the debris in the basket after hardening of the first layer of SPC.



The holding device was removed on the following day, when the SPC had solidified (Fig. 4). The two heating tapes were turned on and allowed to melt the upper portion of the solidified monolith. This operation

Fig. 5. Preparation of the cap layer of SPC after the upper solidified part had melted.



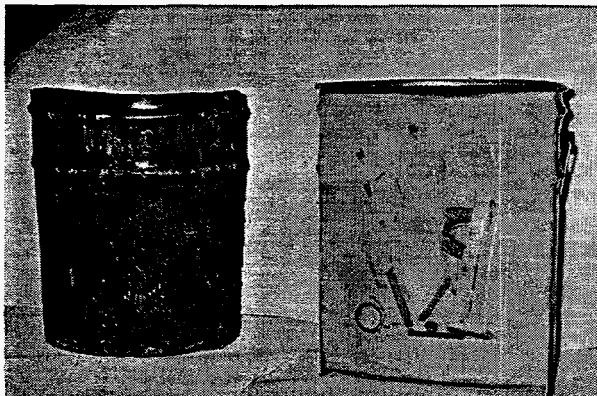
required several hours. When the upper part of the SPC was liquid, molten SPC was added to complete the remaining 2 in. (Fig. 5). The cap layer, which was prepared by contact of molten SPC with molten SPC, prevented the formation of any possible pathways from the waste to the outside.

After solidification, the surface of the waste form was found to be defect free (Fig. 6). When the drum was cut transversally, it was not possible to locate the interface between the two layers. Further examination showed good contact between the debris pieces and the SPC; no voids were present (Figs. 7, 8, and 9). These results indicated that the process was valid and all requirements had been fulfilled; therefore, it was possible to start processing actual waste where cutting of the waste form could not be done.

Fig. 6. View of the hardened waste form.



Fig. 7. Transverse cut of the pail after hardening.



During the demonstration, personnel from Industrial Hygiene made measurements to determine if the process was generating any gases. They placed the probe of their

instrument just above the molten SPC and were not able to detect any H_2S or SO_2 .

Fig. 8. Examination of solidified waste form, showing intimate contact between the waste and the SPC, as well as no pores.

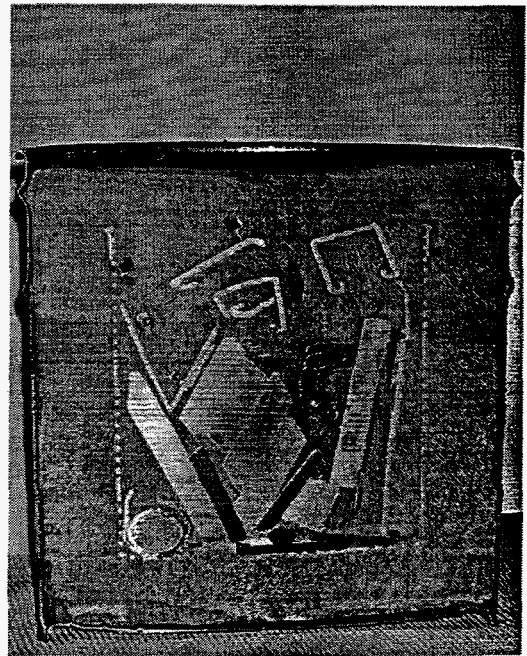
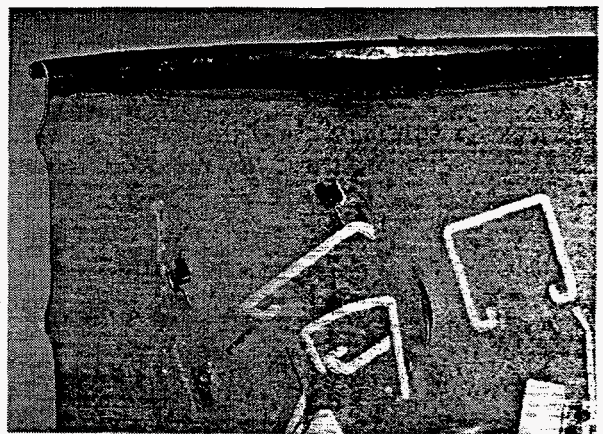


Fig. 9. Details of the upper surface of the monolith.

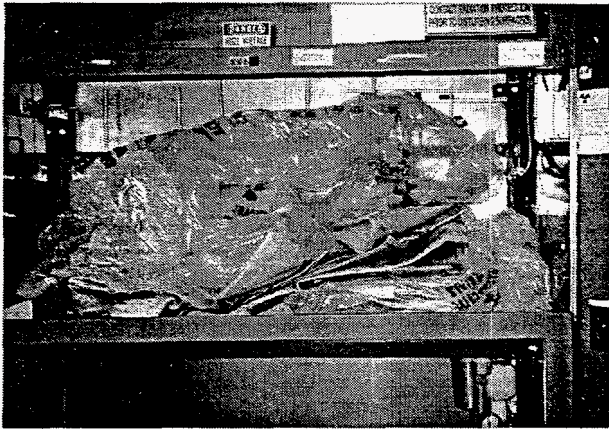


C. Macroencapsulation of Mixed Waste Debris

The ORNL Waste Management database was surveyed as a mean of finding actual wastes that would be good candidates for the demonstration. Two legacy mixed wastes were selected:

- 152 kg of cadmium sheets (Fig. 10), EPA waste code D006 (TS22), and

Fig. 10. View of the cadmium sheets before size reduction.



- 165 kg of lead pipes contaminated with some mercury (Fig. 11), EPA codes D008 and D009 (TS24).

Fig. 11. View of the lead joints before size reduction.



The first drum of waste contained folded sheets of cadmium with sizes ranging from 10 cm to about 1 m in one dimension; different thicknesses of metal were present. Size reduction was necessary for this waste.

Some of the thickest pieces could not be rendered flat enough to allow maximum compaction in the basket (Fig. 12) so as to increase the waste loading, thus resulting in the generation of 12 pails of 5 gal each.

The next waste stream was composed of lead pipes and joints; little size reduction was necessary because of the easy pliability of the lead pieces (Fig. 13). Eight 5-

gal pails were generated for the treatment of this waste.

Fig. 12. View of the cadmium waste in the basket.

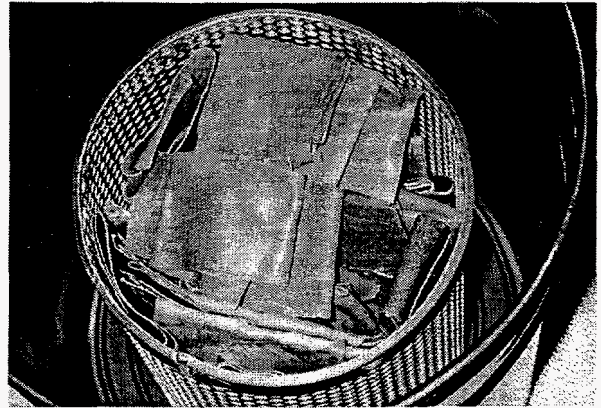


Fig. 13. View of the lead waste in the basket.



Table 1 provides information on the waste volume and weight loading obtained in both the inner basket and the entire pail. The 5-cm barrier requested by Envirocare negatively affects the results obtained for the pail since the available volume for the waste itself is only about one-third that of the pail (i.e., pail volume ~21.1 L; waste volume ~ 6.2 L).

The treatment of the two wastes went smoothly over a 1-month period. Typically on each day, one pail was filled with the first layer; and both the drum heater containing the pail with the waste and the melting pot containing the chunks of SPC were turned on early in the morning. Heating tapes that were installed on the top portion of the drum provided heat to keep the SPC molten after the drum heater had been turned off to allow the air bubbles to escape. The waste was heated to reach a temperature of ~140-150°C to prevent the cooling of the liquid SPC on cold surfaces. This treatment also helped

to remove any moisture present on the surface of the pieces. After about 6 h of heating, the heating tape around the pipe connecting the melting pot to the pail and the valve that allowed delivery of the molten SPC was turned on for at least 30 min. The pail was then filled with SPC following activation of the vibrating table on top of which the pail was resting.

Table 1. Results Obtained Using Mixed Waste Debris

	Vol load. in basket ^a (%)	Wt load. in basket ^b (%)	Vol. load. in pail ^c (%)	Wt load. in pail ^d (%)
TS 22 - A	26.4	54.7	7.8	21.3
TS 22 - B	21.0	50.6	6.2	19.5
TS 22 - C	36.7	63.0	10.8	25.3
TS 22 - D	19.4	43.9	5.7	15.8
TS 22 - E	28.6	54.4	8.4	20.6
TS 22 - F	42.5	68.1	12.5	28.1
TS 22 - G	34.6	65.1	10.1	27.6
TS 22 - H	35.2	59.6	10.3	22.9
TS 22 - I	28.8	63.4	8.5	27.3
TS 22 - J	33.2	61.6	9.8	24.9
TS 22 - K	28.9	64.9	8.5	28.6
TS 22 - L	22.2	53.4	6.5	21.1
TS 24 -M	27.5	67.4	8.1	31.3
TS 24 - N	35.7	70.7	10.5	32.7
TS 24 - O	52.3	80.1	15.4	38.8
TS 24 - P	46.0	76.0	13.5	35.5
TS 24 - Q	33.3	71.6	9.8	34.2
TS 24 - R	40.2	75	11.8	36.3
TS 24 - S	34.1	70.3	10.0	32.7
TS 24 - T	41.4	75.5	12.2	36.5

^a Volume loading obtained in the inner basket (D = 19.1 cm, H = 23.5 cm) containing the waste.

^b Weight loading achieved in the basket.

^c Volume loading obtained in the 5-gal pail (D = 29.2 cm, H = 34.8 cm).

^d Weight loading achieved in the pail.

Next to the setup used for the formation of the first layer, a pail containing the solidified first layer of SPC, prepared on a previous day, was heated on the top 10 cm for preparation of the pour of the cap layer. Such heating served to melt the top portion of the solidified SPC, thus allowing a good contact with the molten SPC poured to complete the filling of the pail. This method ensures that voids in the cap layer do not form, and provide pathways to the outside.

D. Disposal of the Waste Form Generated

After a review by personnel from the Site Environmental Compliance Office, the waste forms generated were declared LDR compliant. A request for

disposal was made to ORNL Waste Management, and the pails were subsequently disposed of as solid low-level waste on the ORNL site.

IV. CONCLUSIONS

The use of SPC as a macroencapsulation matrix for mixed waste debris was demonstrated successfully during this project. One waste stream from the national MWIR was treated for the known mixed wastes it contained (more than 300 kg), that were suitable for this technology. The waste was rendered LDR compliant and, therefore, sent for final disposal.

The treatment process was simple to implement and very well suited for the solid, dry wastes treated during this demonstration. Preheating of the debris was performed only to bring the individual pieces to a temperature slightly above the melting point of SPC. One of the advantages of using SPC is that there is no need for characterization of the waste to be encapsulated, thus reducing the associated cost. Also, SPC has a significant advantage over some other macroencapsulating matrices (e.g., resins and polyethylene) because it actually forms some very insoluble sulfide compounds with many metals such as mercury, lead, or cadmium, providing at least minimal chemical stabilization during the encapsulation process.

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