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Encapsulation of Mixed Radioactive and Hazardous Waste Contaminated Incinerator Ash in Modified Sulfur Cement

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ABSTRACT

Some of the process waste streams incinerated at various Department of Energy (DOE) facilities contain traces of both low-level radioactive (LLW) and hazardous constituents, thus yielding ash residues that are classified as mixed waste. Work is currently being performed at Brookhaven National Laboratory (BNL) to develop new and innovative materials for encapsulation of DOE mixed wastes including incinerator ash. One such material under investigation is modified sulfur cement, a thermoplastic developed by the U.S. Bureau of Mines. Monolithic waste forms containing as much as 55 wt% incinerator fly ash from Idaho National Engineering Laboratory (INEL) have been formulated with modified sulfur cement, whereas maximum waste loading for this waste in hydraulic cement is 16 wt%. Compressive strength of these waste forms exceeded 27.6 MPa (4000 psi). Wet chemical and solid phase waste characterization analyses performed on this fly ash revealed high concentrations of soluble metal salts including Pb and Cd, identified by the Environmental Protection Agency (EPA) as toxic metals. Leach testing of the ash according to the EPA Toxicity Characteristic Leaching Procedure (TCLP) resulted in concentrations of Pb and Cd above allowable limits. Encapsulation of INEL fly ash (at waste loadings up to 43 wt%) in modified sulfur cement with a small quantity of sodium sulfide added to enhance retention of soluble metal salts reduced TCLP leachate concentrations of Pb and Cd well below EPA concentration criteria for delisting as a toxic hazardous waste.

INTRODUCTION

As a result of its defense and research activities, the DOE is a major generator of both hazardous and mixed (hazardous/radioactive) waste. The Waste Management Research and Development Group at BNL, funded by DOE's Hazardous Waste Remedial Action Program (HAZWRAP), is investigating new and innovative techniques for encapsulation of these waste streams generated at various DOE sites. Hazardous and mixed wastes at DOE facilities include a broad range of waste types (such as evaporator concentrate salts, sludges, filter materials, ion exchange resins, and incinerator ash) that encompass diverse physical and chemical properties. Many of these wastes have been identified as "problem" wastes because they are difficult to encapsulate using conventional technologies, and/or produce waste forms of poor quality that do not successfully retain hazardous constituents in the disposal environment. These phenomena are usually related to the chemical and physical properties of the wastes and their interactions with the binder materials. Thus the objective of this program is to develop materials and processes that: (i) have the potential to encapsulate "problem" mixed wastes where current practices are inadequate; (ii) minimize the potential for release of toxic materials to the environment; (iii) result in durable waste forms that can withstand anticipated conditions during storage, transportation, and disposal; and (iv) are simple to operate, easy to maintain and economical.

WASTE CHARACTERIZATION

Because of the large volume reduction resulting from incineration of contaminated combustibles materials, remaining ash residues may contain sufficient quantities of hazardous elements, i.e., heavy metals, that they meet EPA definitions for hazardous waste as well as DOE definitions for low-level radioactive waste. Such "mixed wastes" must first be treated to immobilize hazardous constituents according to EPA's guidelines for delisting before disposal at approved LLW disposal sites. One of the DOE mixed waste streams currently under investigation at BNL is incinerator fly ash generated at the Waste Experimental Reduction Facility (WERF) at INEL.

The WERF incinerator is a dual chamber, controlled air design. Currently operating about 2000 hours per year, average annual throughput is 60,000 ft^3 of solid waste burned, resulting in a volume reduction ratio on the order of 300:1. Waste is fed dynamically at an average rate of about 181 kg/hr (400 lbs/hr) and the incinerator is generally operated in cycles of a feed/initial burn for 4 hours followed by a final burn for 4 hours. The flue gas cleanup and fly ash collection system consists of a bag house and HEPA filtration. Data for the feed composition of the ash used in this study were unavailable, but a typical feed for the WERF incinerator contains 50 wt% rags and paper, 35 wt% polyethylene, 10 wt% wood, and 5 wt% rubber.[1]

The INEL fly ash contains a total of about 1.5 Bq/g (40 pCi/g) of activity consisting of mixed fission products (primarily Cs-137) and activation products (primarily Co-57 and Sb-125). Elemental analyses of the ash were performed for 12 elements by acid digest and flame emission atomic absorption spectrophotometry (AA). Results of these analyses expressed as wt% of ash are summarized in Table 16. Hazardous constituents include significant concentrations of 2 of the 8 metals (i.e., Pb and Cd) identified by EPA as toxic metals in the recently published final rule on Identification and Listing of Hazardous Waste.[2] Encapsulation and disposal of this ash is further complicated by the presence of highly soluble metal chloride salts (primarily zinc chloride) that create an acidic environment in the presence of moisture (pH of the ash slurry is about 3.8) - a condition that can interfere with the solidification reaction of conventional encapsulation materials and greatly increase mobility of contaminants. Solid phase analysis of the ash was performed using a scanning electron microscope (SEM) and energy dispersive x-ray spectrophotometry. Figure 1 is an SEM photo and associated x-ray spectrum of INEL fly ash magnified 15,000 times, depicting a typical zinc chloride crystal.

Table 1. Elemental Composition of INEL Incinerator Fly Ash

Element	Weight Percentage
Zinc	36.0
Lead	7.5
Sodium	5.5
Potassium	2.8
Calcium	0.8
Copper	0.7
Iron	0.5
Cadmium	0.2
Chromium	BDL[a]
Barium	BDL
Silver	BDL
Nickel	BDL

(a) Below detection limits (<0.05 wt%)

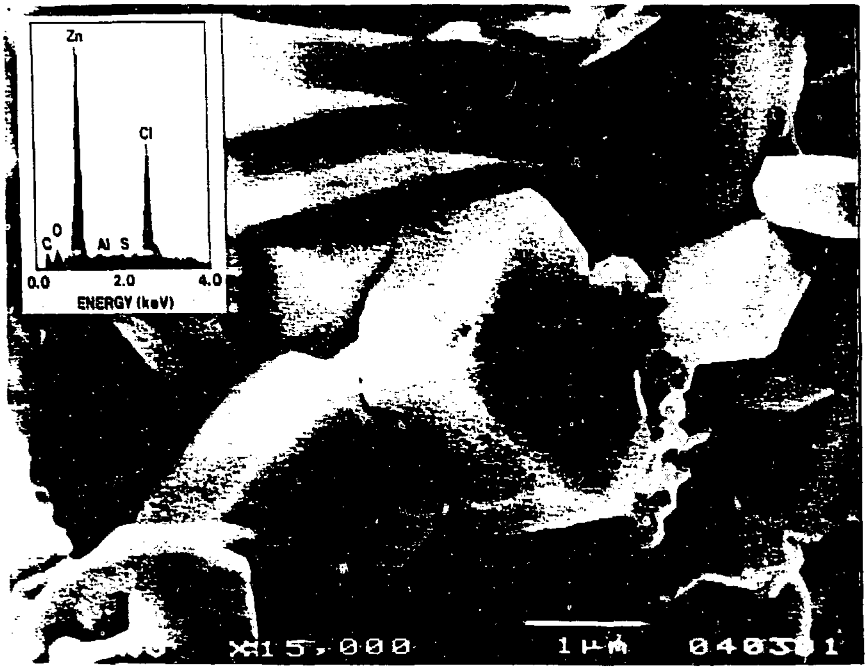

Fig. 1 Zinc chloride crystal present in INEL incinerator fly ash magnified 15,000 times by scanning electron microscope and associated energy dispervise x-ray spectrum.

MODIFIED SULFUR CEMENT

Modified sulfur cement is a thermoplastic material that can be easily melted, combined with waste components in a homogenous mixture, and cooled to form a solid monolithic waste form. Compared with hydraulic cements, sulfur cement has several advantages. For example, no chemical reactions are required for solidification, eliminating the possibility that elements in the waste can interfere with setting and thereby limit the range of waste materials that can successfully be encapsulated. Sulfur concrete compressive and tensile strengths twice those of comparable portland concretes have been achieved, and full strength is attained in several hours rather than weeks.[3] Sulfur concretes are resistant to attack by most acids and salts, e.g., sulfates that can severely degrade hydraulic cement have little or no effect on the integrity of sulfur cement.[4]

Modified sulfur cement was developed by the U.S. Bureau of Mines in 1972 as a means of utilizing waste sulfur from flue gas and petroleum distillation processes. Previous attempts to use elemental sulfur as a construction material in the chemical industry [5] failed due to internal stresses set up by changes in crystalline structure during cooling. By reacting elemental sulfur with hydrocarbon polymers, the Bureau of Mines developed a product that successfully suppresses the solid phase transformation, and thus dramatically improves stability of the material. A Bureau of Mines formulation that is licensed commercially was used for this work. The formulation contains a total of 5 wt% modifiers consisting of equal amounts dicyclopentadiene (DCPD) and cyclopentadiene (CPD).[6] It has a melting point of 119°C and a viscosity of ~25 cp at 135°C.

PROCESSING AND FORMULATION DEVELOPMENT

Since modified sulfur cement is a thermoplastic material, thermal input is required for processing. Because of its low viscosity in the molten state, modified sulfur cement flows readily but when mixed with dry waste materials it tends to form a thick paste. The primary requirements for processing, therefore, are suitable thermal input to supply latent heat of fusion and maintain a molten condition, and ability to thoroughly mix waste and binder under viscous conditions to form a homogeneous mixture. Additional considerations include: (i) the ability to operate under vacuum to vent entrained air and residual moisture that may be present in the waste, (ii) precise monitoring and control of process temperatures, and (iii) the ability to transfer waste-binder mixtures into sample molds for cooling. Several mixing systems were investigated for encapsulating hazardous ash mixtures in modified sulfur cement including high-shear stirrers, emulsifiers, blenders, kneaders, and single and double planetary orbital mixers.

Based on the processing requirements of modified sulfur cement/waste combinations, a double planetary orbital mixer equipped with a heat-jacketed container and vacuum capability was chosen as the most appropriate method of mixing. This type of mixer contains two rectangularly shaped stirrer blades that revolve around the mixing container on a central axis. At the same time, each blade revolves on its own axis at approximately the same speed as the central rotation. The combined effect of the dual rotational action results in the blades quickly covering the entire area within the mixing container, insuring complete homogeneity of the ingredients in several minutes. An auxiliary direct discharge system is used to extrude mixtures through a 1 inch ball valve at the bottom of the container. The laboratory-scale processing system is shown in Figure 2.

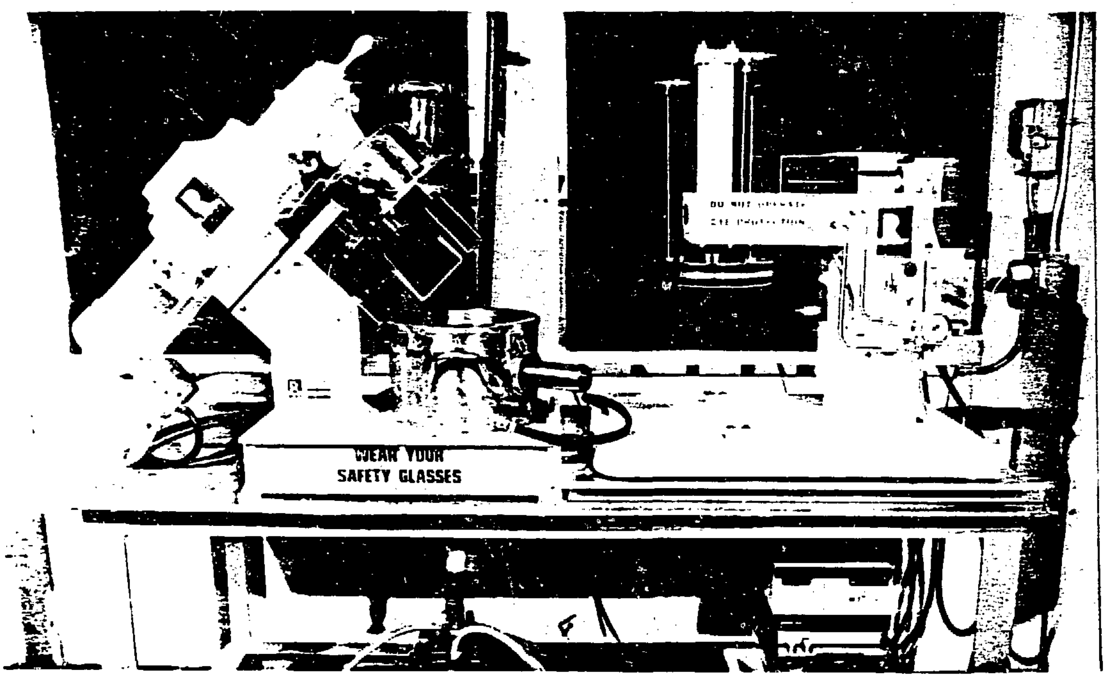

Fig 2. Double planetary mixer and direct discharge system for processing ash with modified sulfur cement.

Formulation and process development work was conducted to determine the limits and ease of processibility, while at the same time producing waste forms that conform to regulatory criteria. Maximum waste loadings were determined by first processing at waste loadings above the limits of workability (i.e., extremely dry mixtures that yielded friable products with little structural integrity) and then adding additional increments of modified sulfur cement until acceptable workability and product integrity were achieved.

Reported waste loadings represent weight percent of dry ash, after all residual moisture has been removed. Using this procedure, a maximum waste loading of 55 wt% INEL incinerator fly ash was determined. Due its low pH and high chlorides content, the maximum waste loading using portland cement achieved at INEL is 16 wt%.

WASTE FORM PERFORMANCE

Waste form property evaluation tests including compressive strength, water immersion, freeze-thaw resistance, and leachability were conducted on laboratory scale specimens to provide information on structural integrity and potential waste form behavior in a disposal environment. The EPA has established criteria for delisting of hazardous wastes defined in the Resource Conservation and Recovery Act and published test procedures for their implementation. These tests, the Extraction Procedure Toxicity Test (EP Tox) [7] and the recently finalized revised method, the TCLP [8] were conducted on selected formulations to assess mobility of contained EPA characteristic contaminants and results are reported. Water immersion testing is in progress and additional testing to demonstrate compliance with Nuclear Regulatory Commission (NRC) criteria for LLW, including freeze-thaw testing and radionuclide leachability have been reported previously.[9]

Measurement of compressive strength is a general indication of a waste form's mechanical integrity and it's ability to withstand loading pressures associated with overburden soil at a disposal site. Modified sulfur cement is a relatively brittle material and tends to fail by a shattering fracture under an axial compressive load. Thus, compressive strength testing was conducted in accordance with the standard method developed for hydraulic cements, ASTM C-39, "Compressive Strength of Cylindrical Concrete Specimens".[10]

Results from compressive strength testing of waste form specimens containing 40 and 55 wt% INEL fly ash encapsulated in modified sulfur cement are presented graphically in Figure 3 and are compared with compressive strength data for modified sulfur cement specimens containing no waste. Mean values for compressive strength were not highly dependent on waste loading - 27.9 MPa (4,053 psi) for 40 wt% ash; 28.4 MPa (4,118 psi) for 55 wt% ash - but both waste loadings displayed more than 2 times greater strength than the binder material alone - 12.4 MPa (1800 psi).

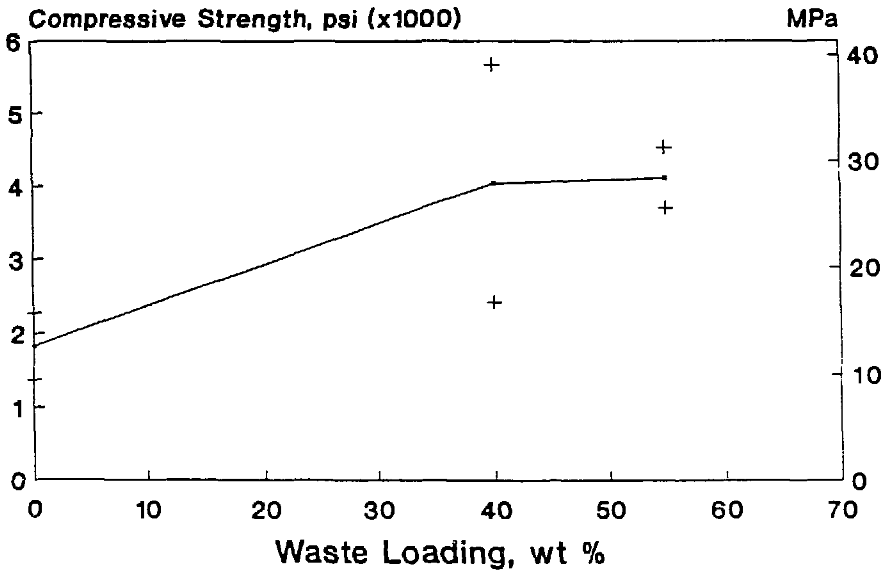

Fig. 3 Compressive strength data for INEL incinerator fly ash encapsulated in modified sulfur cement. (Data shown are mean values for 3 replicates (5 for 55% samples); with error bars at 95% confidence interval.)

When testing was initiated, the EPA test for toxic contaminants currently in place was the EP Toxicity Test. The TCLP test which incorporates several modifications to the EP Tox procedures has since been issued as a final rule. One of the primary differences between the two procedures is that TCLP no longer allows testing of monolithic waste forms. Hazardous waste that is encapsulated in a solid matrix must be "prepared for extraction by crushing, cutting, or grinding the solid material" so that it "is capable of passing through a 9.5 mm (0.375 inch) standard sieve." [11] In addition, TCLP requires a more vigorous method of agitation (end-over-end rotary tumbler).[12]

INEL ash and samples of encapsulated ash at several waste loadings were tested using both the EP Tox and the TCLP. Both procedures specify maximum allowable concentrations of eight metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and a number of organic compounds. Leachate analyses were performed by AA and results presented in Table 2 show that Pb and Cd are present in TCLP leachates well above EPA allowable limits. These elements are also evident above allowable limits in TCLP leachates from waste encapsulated in plain modified sulfur cement, albeit at lower concentrations. (Leachate concentrations for encapsulated waste samples tested by the EP Tox method are considerably lower, demonstrating the conservative nature of the TCLP test).

Thus, to further reduce the mobility of toxic heavy metals in the fly ash and comply with EPA TCLP hazardous waste concentration limits, potential additives were examined, including precipitation agents, adsorption agents, and ion exchange resins. Based on the results of scoping experiments and other considerations (e.g., ease of processing, cost, availability) sodium sulfide was selected for use as an additive. Sodium sulfide reacts with the toxic metal salts to form metal sulfides of extremely low solubility. It has been used extensively in the related field of waste water treatment, and as such, it has been identified by EPA as a "Best Demonstrated Available Technology" (BDAT). A ratio of sodium sulfide/fly ash of 0.175 was used based on the results of an experiment to determine the effectiveness of this additive on Cd mobility under EPA leaching conditions. As seen in Table 2, TCLP leachates from waste forms containing 40 wt% ash, 53 wt% modified sulfur cement, and 7 wt% sodium sulfide were well within allowable concentration limits for Cd and Pb. Optimization of INEL incinerator fly ash waste loading with added sodium sulfide (while maintaining additive/ash ratio constant) yielded a maximum waste loading of 43 wt% fly ash, 49.5 wt% modified sulfur cement, and 7.5 wt% sodium sulfide. As seen in Figure 4, this represents about 2.7 times more incinerator fly ash per 55 gallon drum than is currently possible using portland cement, while still meeting EPA criteria for delisting as a hazardous waste.

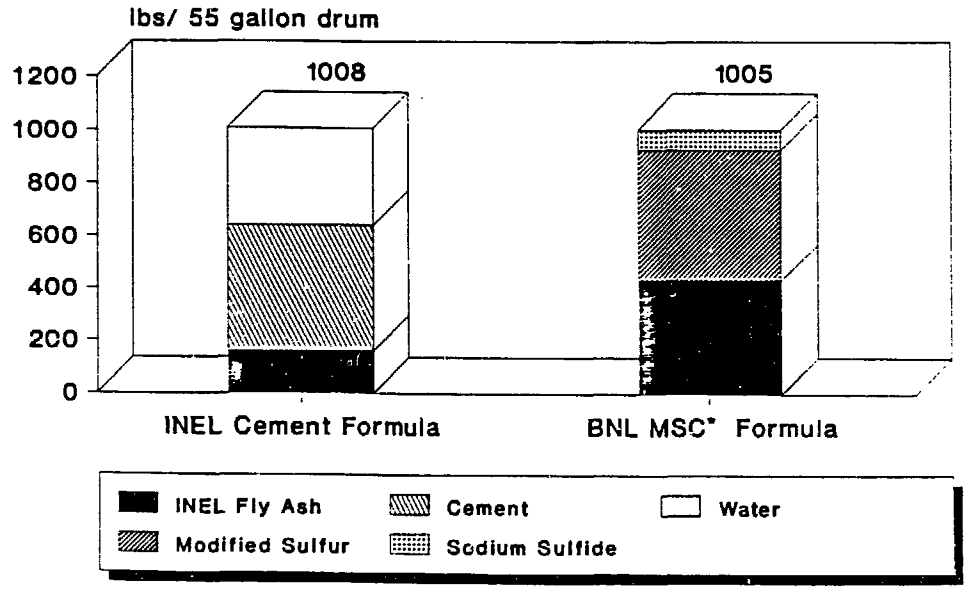

Fig. 4 **Comparison of waste loadings for encapsulation of INEL incinerator fly ash in modified sulfur cement and portland cement. (*MSC = Modified Sulfur Cement.)**

Table 2. Results from EPA Extraction Procedure Toxicity Test and Toxicity Characterization Leaching Procedure for INEL Ash Encapsulated in Modified Sulfur Cement

	Concentrations of Criteria Metals, ppm [a,b,]	
Sample Tested:	Cd	Pb
INEL Fly Ash	85.0	46.0
55 wt% Ash 45 wt % MSC[c] (EP Tox)	1.5 (2.7)	2.4 (4.4)
55 wt% Ash 45 wt% MSC	27.5 (50.0)	17.6 (32.0)
40 wt% Ash 60 wt% MSC	13.6 (34.0)	12.0 (30.0)
40 wt% Ash 53 wt% MSC 7 wt% Na_2S	0.1 (0.3)	1.0 (2.5)
43 wt% Ash 50 wt% MSC 7 wt% Na_2S	0.2 (0.5)	1.5 (3.5)
EPA Allowable Limit	1.0	5.0

a) Data in parentheses represent concentrations normalized to account for reduced mass of fly ash in tested sample.
b) Data represent TCLP results except where noted.
c) MSC = modified sulfur cement

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