Conf-910559--2

BNL-45292

**Durability of Incinerator Ash Waste Encapsulated in Modified Sulfur Cement***

BNL--45292

DE91 011730

P.D. Kalb, J.H. Heiser III, R. Pietrzak, and P. Colombo

Brookhaven National Laboratory
Upton, NY 11973

MAY 13 1991

**ABSTRACT**

Waste form stability under anticipated disposal conditions is an important consideration for ensuring continued isolation of contaminants from the accessible environment. Modified sulfur cement is a relatively new material and has only recently been applied as a binder for encapsulation of mixed wastes. Little data are available concerning its long-term durability. Therefore, a series of property evaluation tests for both binder and waste-binder combinations have been conducted to examine potential waste form performance under storage and disposal conditions. These tests include compressive strength, biodegradation, radiation stability, water immersion, thermal cycling, and leaching.

Waste form compressive strength increased with ash waste loadings to 30.5 MPa (4,430 psi) at a maximum incinerator ash loading of 43 wt%. Biodegradation testing resulted in no visible microbial growth of either bacteria or fungi. Initial radiation stability testing did not reveal statistically significant deterioration in structural integrity. Additional testing is being conducted for confirmation. Results of 90 day water immersion tests were dependent on the type of ash tested. Waste forms containing a mixture of incinerator fly ash and bottom ash from a rotary kiln incinerator at Rocky Flats Plant (RFP) were not significantly affected by water immersion testing. Waste forms containing Idaho National Engineering Laboratory (INEL) incinerator fly ash with high concentrations of soluble salts tended to swell and crack as a result of immersion testing. In response, an admixture formulation was developed that improved mechanical integrity and eliminated waste form cracking under saturated conditions. There were no statistically significant changes in compressive strength detected after completion of thermal cycle testing. Radionuclides from ash waste encapsulated in modified sulfur cement leached between 5 and 8 orders of magnitude slower than the leach index criterion established by the Nuclear Regulatory Commission (NRC) for low-level radioactive waste. Modified sulfur cement waste forms containing up to 43 wt% INEL incinerator fly ash passed EPA Toxicity Characteristic Leaching Procedure (TCLP) criteria for lead and cadmium leachability.

* **This work was sponsored by the U.S. Department of Energy under contract No. DE-AC02-76CH00016.**

**MASTER**

## INTRODUCTION

Incineration of combustible radioactive waste at Department of Energy (DOE) facilities results in ash residues contaminated with both radioactive species and toxic heavy metals. This ash meets Environmental Protection Agency (EPA) criteria for RCRA characteristic hazardous wastes, as well as DOE definitions for low-level radioactive waste. Previous research efforts at Brookhaven National Laboratory (BNL) focused on the development of an improved encapsulation system using modified sulfur cement to immobilize hazardous constituents in incinerator ash, such as fly ash generated at the Waste Experimental Reduction Facility at Idaho National Engineering Laboratory (INEL). [1]

Modified sulfur cement is a thermoplastic material (melt temperature 119 ° C) that can be heated to a molten state, combined with dry waste solids to form a homogeneous mixture, and cooled to form a monolithic solid waste form. It was developed for use in the construction industry by the U.S. Bureau of Mines as a means of utilizing waste sulfur by-products. Modified sulfur cement consists of elemental sulfur reacted with a small percentage (~5 %) of polymer modifier to improve physical properties. [2] There are no chemical reactions required for solidification (in contrast to hydraulic cement processes), so waste-binder interactions are minimized. This allows a broader range of waste types to be encapsulated and results in better waste loading efficiencies (i.e., more waste per drum). Formulations were developed that contain as much as 43 wt% incinerator fly ash, while still maintaining leachability of toxic metals below allowable EPA criteria. Maximum waste loadings using conventional portland cement are limited to about 16 wt% ash. A comparison of maximum waste loadings per 55 gallon drum using modified sulfur cement vs. hydraulic cement to encapsulate incinerator bottom ash and fly ash is presented in Figure 1.

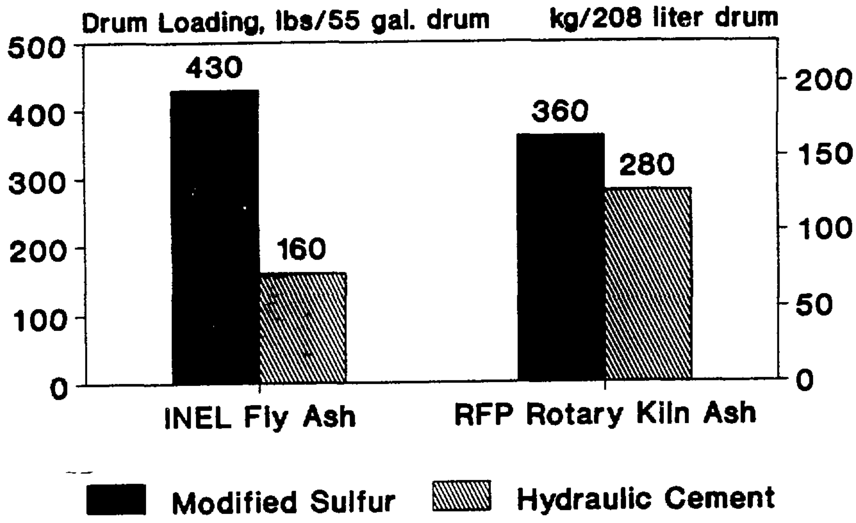


Figure 1. Comparison of maximum waste loadings per 55 gallon drum using modified sulfur cement vs. hydraulic cement to encapsulate incinerator bottom ash and fly ash.

## WASTE FORM STABILITY

Encapsulation of contaminants within a waste form is the first of several barriers used to isolate radioactive, hazardous and mixed wastes from the accessible environment. The durability of waste forms over long periods of time can therefore play an important role in ensuring continued isolation of contaminants. Little data are available, however, concerning the long-term durability of modified sulfur cement. Examining the effects of accelerated aging conditions on material properties is a difficult task. Currently, no reliable test methods exist for this purpose. The approach used for this study to provide reasonable assurance that waste forms will be structurally stable over time involves application of short-term conditioning and property tests that reflect anticipated conditions of disposal. The Nuclear Regulatory Commission (NRC) uses a similar approach for the licensing of commercial low-level radioactive (LLW) waste forms, as published in the Technical Position on Waste Form [3] in support of regulations contained in 10 CFR 61. [4] The focus of this work was on encapsulated incinerator ash wastes, but test data on modified sulfur cement binder and combinations with other wastes are included, where applicable. Waste form performance testing included compressive strength, water immersion, thermal cycling, biodegradation, the effects of gamma irradiation, and leaching of radioactive constituents. Leaching of hazardous constituents contained in the fly ash (i.e., toxic metals) was performed according to Environmental Protection Agency (EPA) protocol contained in 40 CFR 261. [5]

## WASTE FORM TESTING

Compressive strength is an overall indication of waste form structural integrity. Thus, it can be used to measure potential changes that may result from other test conditions such as biodegradation, radiation stability, and thermal cycling. Compressive strength testing was conducted in accordance with ASTM C-39, "Compressive Strength of Cylindrical Concrete Specimens," since modified sulfur cement fails by brittle fracture under compressive loads. Average compressive strength data for plain modified sulfur cement and waste forms containing rotary kiln ash and incinerator fly ash are presented in Table I.

Table I Representative Compressive Strength Data for Modified Sulfur Cement Waste Forms

| Sample | Compressive Strength, psi | Compressive Strength, MPa |
|---|---|---|
| Modified Sulfur Cement (MSC)[a] | 2,460 ± 530 | 17.0 ± 3.7 |
| Rotary Kiln Ash: 20 wt%[b] | 4,320 ± 300 | 29.8 ± 2.1 |
| 43 wt%[b] | 4,430 ± 260 | 30.5 ± 1.8 |
| Incinerator Fly Ash: 40 wt%[b] | 4,050 ± 650 | 27.9 ± 4.5 |
| 55 wt%[c] | 4,120 ± 330 | 28.4 ± 2.3 |

a) Error expressed at the 95% confidence limit for 10 replicate samples.
b) Error expressed as ± 1 standard deviation for 3 replicate samples.
c) Error expressed as ± 1 standard deviation for 5 replicate samples.

Modified sulfur cement specimens containing no waste were tested for resistance to microbial degradation in accordance with ASTM G-21, "Determining Resistance of Synthetic Polymeric Material to Fungi," and ASTM G-22, "Determining Resistance of Plastics to Bacteria." These tests were designed for use with polymers, but have been adopted by the NRC as generic tests for microbial degradation of waste forms. They are conducted under conservative test conditions, i.e., specimens are exposed to active biological cultures under ideal growth conditions including:

- incubation at 35 - 37°C
- moist atmosphere (relative humidity of $\geq$ 85%)
- presence of a nutrient agar to sustain growth.

The specimens are examined for evidence of microbial growth following 21 days of incubation. Results for ASTM G-21 are reported on a scale of 0 (no observed growth) to 4 (heavy growth, $\geq$ 60% of surface covered). Results for ASTM G-22, are expressed simply as growth/no growth. If growth is observed, it is an indication that the microbes were able to metabolize carbon contained in the test specimen. Modified sulfur cement contains approximately 5 wt% carbon. Additional biodegradation testing is being conducted using several thiobacillus strains that have the potential for metabolizing sulfur materials. [6]

Six replicate specimens were tested for each procedure. All samples exposed to the fungi (ASTM G-21) were given a growth rating of 0. All samples exposed to the bacteria (ASTM G-22) exhibited no growth. Biodegradation specimens were then tested for compressive strength and results are presented in Table II. Average compressive strength was 18.1 ± 5.1 MPa (2,620 ± 740 psi), compared with untreated modified sulfur cement control samples, which had an average compressive strength of 17.0 ± 3.7 MPa (2,460 ± 530 psi). Thus, there were no statistically significant changes in strength observed as a result of biodegradation testing.

Table II Compressive Strength of Modified Sulfur Cement Waste Forms Following Biodegradation and Radiation Stability Testing[a]

| | Modified Sulfur Cement | Modified Sulfur Cement with 39 wt% Sludge |
|---|---|---|
| Biodegradation: | | |
| Compressive Strength psi | 2,620 ± 740[b] | 2,960 ± 1,040[d] |
| Compressive Strength, MPa | 18.1 ± 5.1 | 20.4 ± 7.2 |
| Radiation Stability: | | |
| Compressive Strength, psi | 1,950 ± 940[c] | 3,150 ± 1,000[e] |
| Compressive Strength, MPa | 13.4 ± 6.5 | 21.7 ± 6.9 |

a) Error expressed at 95% confidence limit.
b) Eleven replicate samples tested.
c) Nine replicate samples tested.
d) Eleven replicate samples tested.
e) Five replicate samples tested.

The effects of gamma irradiation on radioactive and mixed waste forms can have an important influence on long-term durability. Absorbed radiation dose is a cumulative phenomenon. Therefore, significant doses can be accumulated over time, depending on the activity level contained within the waste form and the radiation field from other waste forms in the immediate disposal environment. Waste form specimens were exposed to total doses of $\geq 10^6$ Grays ($10^8$ rads) at the BNL $^{60}$Cobalt Gamma Irradiation Facility to examine potential effects of gamma irradiation. Irradiation test specimens included modified sulfur cement containing no waste and modified sulfur cement waste forms containing 39 dry wt% sludge from the Oak Ridge National Laboratory Y-12 facility. Dose rates ranged between $1.2 \times 10^4$ and $2.6 \times 10^4$ Grays/hr ($1.2 \times 10^6$ and $2.6 \times 10^6$ rad/hr), depending on location with respect to the gamma sources. Exposure estimates are based on time within the facility and do not account for self-shielding effects of the material, which are expected to be relatively insignificant.

The arbitrary absorbed dose limit of $10^6$ Grays ($10^8$ rads) is conservative and represents an upper bound of anticipated dose for LLW waste forms generated at commercial power reactors. For example, one study estimates that waste forms from boiling water reactors (BWRs) containing as much as $1.1 \times 10^{11}$ Bq/m$^3$ (10 Ci/ft$^3$) would experience a total dose of about $2 \times 10^5$ Grays ($2 \times 10^7$ rads) during 1000 years in disposal. Waste forms generated at pressurized water reactors (PWRs) with a similar activity content but different radionuclide ratios would receive about $9 \times 10^5$ Grays ($9 \times 10^7$ rads) over a period of 1000 years. [7] INEL incinerator ash has a relatively low specific activity (about 260 Bq/g or $7.0 \times 10^{-9}$ Ci/g). A modified sulfur cement waste form containing 43 wt% INEL incinerator fly ash would have an activity concentration of about $2.1 \times 10^5$ Bq/m$^3$ (2.0 x $10^{-4}$ Ci/ft$^3$), or roughly 5 orders of magnitude lower than the conservative estimates for commercial reactor waste forms cited above.

Specimens were tested for compressive strength following removal from the irradiation source. Results are given in Table II. The average compressive strength for 9 replicate modified sulfur cement samples irradiated to $10^6$ Grays ($10^8$ rads) was 13.4 ± 6.5 MPa (1,950 ± 940 psi), compared with the untreated control samples (17.0 ± 3.7 MPa or 2,460 ± 530 psi). While there was a reduction in average compressive strength of about 20%, the large degree of scatter in these data make it difficult to attribute loss of strength to the effects of irradiation. Mean compressive strength for the 6 replicate waste forms containing sludge irradiated to $10^6$ Grays ($10^8$ rads) was 21.7 ± 6.9 MPa (3,150 ± 1000 psi). There was no statistically significant change in strength for these samples detected, compared with compressive strength data for similar samples that were not irradiated (20.4 ± 7.2 MPa or 2,960 ± 1,040 psi). Confirmatory testing by means of differential scanning calorimetry (DSC) on irradiated modified sulfur cement is currently being performed to determine if changes in material structure can be detected. Additional irradiation testing of modified sulfur cement waste forms containing incinerator fly ash is planned.

Water immersion testing is performed to simulate conditions in a saturated disposal environment. It has been shown that catastrophic failures of waste form structural integrity can occur upon immersion in water for some types of waste. [8] Previous water immersion testing for modified sulfur cement waste forms containing incinerator ash from a rotary kiln incinerator resulted in no significant changes in dimensions or compressive strength. This test was repeated for waste forms containing INEL incinerator fly ash because of the extremely high concentrations of soluble metal salts (e.g., 36 wt% zinc, 7.5 wt% lead, 5.5 wt% sodium, 2.8 wt% potassium). Large expansive forces can result causing cracking of the waste form when these metal salts (primarily in the chloride form) come into contact with water. Results of 90 day water immersion testing for modified sulfur cement waste forms containing 40, 35, and 30, wt% INEL incinerator fly ash are shown in the photographs in Figure 2. Each of these waste forms experienced cracking as a result of water immersion. The severity of the cracking is directly related to the waste loading of INEL incinerator fly ash.

Several approaches were taken to alleviate cracking failures of INEL incinerator fly ash waste forms in water immersion. Additional additives were tried to reduce the solubility of metal chloride salts and, thereby, reduce cracking of the waste forms by swelling. A scoping experiment was devised using $Ca(OH)_2$ and MgO as potential additives. $Ca(OH)_2$ was added to the formulation at additive/ash ratios of 0.08, 0.15, and 0.22. MgO was added at ratios of 0.06 and 0.08. The additives were mixed with INEL incinerator fly ash, the mixtures were leached in water and the leachates were analyzed for Zn, Ca, and Mg. Concentration of zinc in the leachate without additives was high (6050 mg/l) as shown in Table III. $Ca(OH)_2$ was able to reduce Zn solubility (0.1 mg/l at 0.15 additive/ash ratio), but at the expense of introducing soluble Ca (2850 mg/l). The MgO was less effective reducing Zn concentrations (lowered to 260 mg/l at an additive/ash ratio of 0.08), but the total concentrations of Zn, Ca, and Mg combined was about 12 times less than with no additives, and about 6 times less than with $Ca(OH)_2$. Waste forms containing 38 wt% fly ash, 53 wt% modified sulfur cement, 6 wt% $Na_2S$, and 3 wt% MgO were formulated based on these results. However, these waste forms also cracked when subjected to water immersion testing.

A second approach was aimed at improving the ability of the waste forms to withstand expansive forces by addition of glass fibers. Use of these additives to improve the structural integrity of sulfur polymer concrete in the construction industry has been reported. [9] A small quantity (0.5 wt%) of glass fibers manufactured by Owens Corning (0.5 in. length) was added to the incinerator fly ash waste forms. Larger quantities tended to clump and make the mixture unworkable. Waste forms containing 40 wt% ash, 52.5 wt% modified sulfur cement, 7 wt% $Na_2S$, and 0.5 wt% glass fibers were formulated and subjected to water immersion testing. The addition of 0.5 wt% glass fibers provided sufficient tensile and flexural strength to maintain structural integrity during the 90 day water immersion test, as shown in Figure 2.

Table III Leaching Results to Determine Effectiveness of Additives in Reducing Metal Salt Solubility for INEL Fly Ash

| Additive | Additive/Ash Ratio, g/g | Leachate Concentrations, mg/l | | |
|---|---|---|---|---|
| | | Zn | Ca | Mg |
| None (plain ash) | 0 | 6,050 | 159 | 6.2 |
| $Ca(OH)_2$ | 0.08 | 770 | 1,690 | 34 |
| $Ca(OH)_2$ | 0.15 | 0.1 | 2,850 | 13 |
| $Ca(OH)_2$ | 0.22 | 0.4 | 3,030 | 18 |
| MgO | 0.06 | 810 | 111 | 153 |
| MgO | 0.08 | 260 | 108 | 129 |

Waste forms may be subjected to severe changes in temperature during storage and transport. Thermal cycling of waste forms is conducted to determine if such changes in temperature lead to degradation in structural integrity. Thermal cycle conditioning was performed in accordance with the procedures outlined in ASTM B-553 "Thermal Cycling of Electroplated Plastics," with modifications suggested by NRC. [3] Temperatures were cycled between -40 and +60 °C over a five hour period for a total of 30 cycles. Potential changes in material properties were measured by changes in compressive strength. Test samples included 20 wt% and 43 wt% rotary kiln ash encapsulated in modified sulfur cement. Results presented in Table IV indicate that no significant changes in strength were detected as a result of thermal cycling.

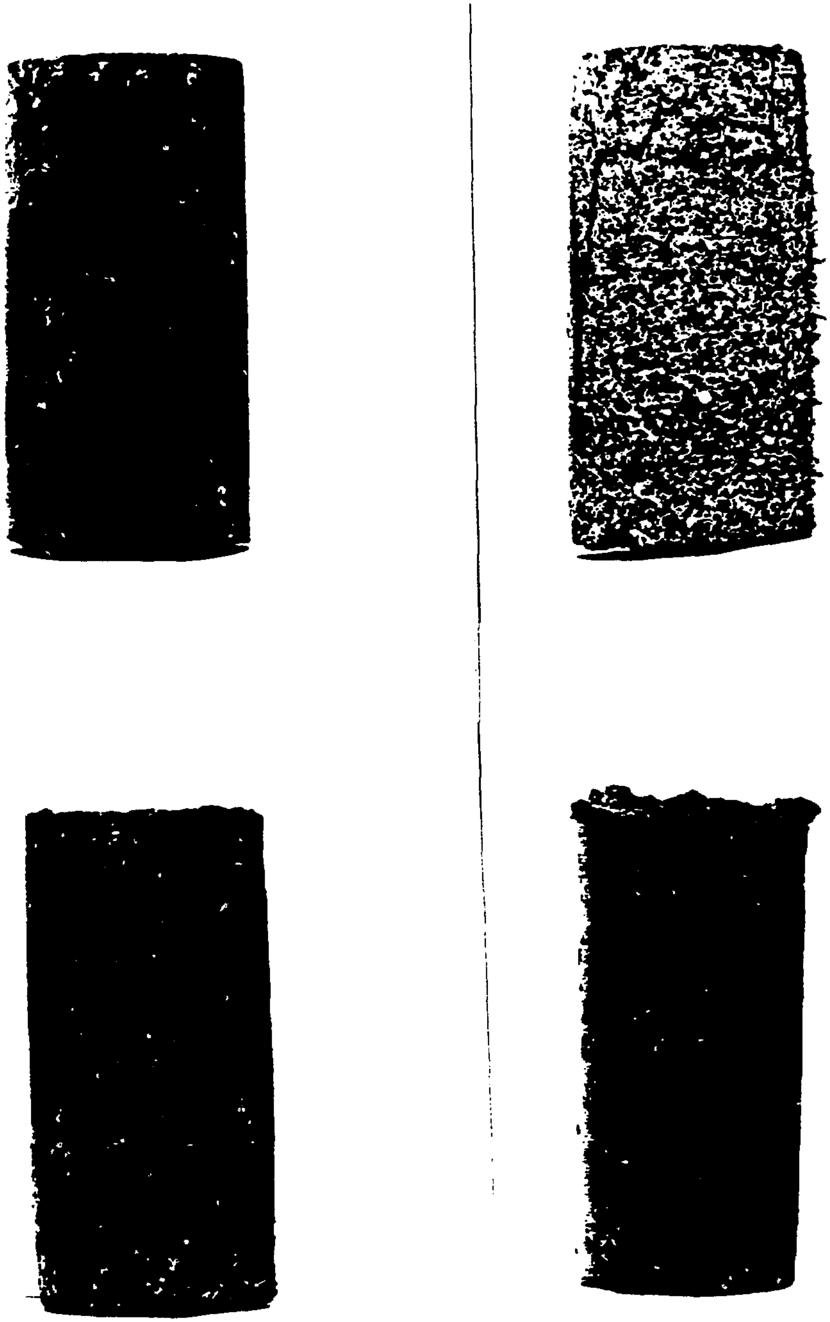

Figure 2. Modified sulfur cement waste form specimens containing INEL incinerator fly ash following 90 day water immersion test. Upper left = 30 wt% fly ash; upper right = 35 wt% fly ash; lower left = 40 wt% fly ash; lower right = 40 wt% ash with addition of 0.5 wt% glass fibers. Precipitation of insoluble metal salts seen in upper right photo was removed from other samples to examine surface for cracking.

| Table IV Effects of Thermal Cycling on Compressive Strength of Rotary Kiln Ash Encapsulated in Modified Sulfur Cement[a] | | |
|---|---|---|
| Waste Loading | Compressive Strength, psi | Compressive Strength,MPa |
| 20 wt% | 4,370 ± 930 | 30.1 ± 6.4 |
| 43 wt% | 4,340 ± 2,870 | 29.9 ± 19.8 |

(a) Results reflect mean values for 3 replicate specimens. Error represents ± 1 standard deviation.

Leaching is a primary mechanism for dispersal of contaminants under humid disposal conditions. Although laboratory leaching conditions do not reflect those found in actual disposal sites, standardized leaching tests can provide useful information on the leaching behavior of waste forms.

Leaching of radioactive constituents was performed for 90 days using distilled water leachant, in accordance with the ANS 16.1 Standard, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes." Modified sulfur cement waste forms containing 20 and 40 wt% rotary kiln ash treated with a tracer solution of $^{137}Cs$ and $^{60}Co$ were leached. [10] Leaching results are presented in Table V in terms of the leachability index, a figure of merit inversely proportional to the logarithm of the effective diffusivity constant. Leachability index values between 11.1 and 14.6 represent imprcvements over the minimum NRC leachability index criterion of 6.0 by more than 5 and 8 orders of magnitude, respectively.

| Table V Average Leachability Index Values for Modified Sulfur Cement Waste Forms Containing Rotary Kiln Incinerator Ash [a,b] | | |
|---|---|---|
| Waste Loading, wt% | $^{60}Co$ Leachability Index | $^{137}Cs$ Leachability Index |
| 20 | 14.0 | 11.2 |
| 40 | 14.6 | 11.1 |

a) As per procedures outlined in ANS 16.1 Standard Leach Test Method.
b) Average of two replicate samples.

Leaching of the hazardous constituents (toxic metals) contained in the INEL incinerator fly ash was performed in accordance with Environmental Protection Agency (EPA) protocol specified in the Toxicity Characteristic Leaching Procedure (TCLP). [11] The TCLP is an 18 hour extraction procedure using a buffered acetic acid leachant (to simulate conditions at a sanitary landfill), small particles (must pass through a 9.5 mm sieve), and vigorous end-over-end rotary tumbling. Results presented previously [1] indicated that concentrations of toxic metals leached from the plain INEL incinerator fly ash (85.0 mg/l, Cd and 46.0 mg/l, Pb) were reduced below EPA TCLP concentration criteria (1.0 mg/l, Cd and 5.0 mg/l, Pb) by means of encapsulation using the modified sulfur cement process. Samples containing 43 wt% INEL incinerator fly ash, 49.5 wt% modified sulfur cement, and 7.5 wt% sodium sulfide yielded leachate concentrations of 0.2 mg/l Cd and 1.5 mg/l Pb.

## CONCLUSIONS

Modified sulfur cement is a relatively new material that has only recently been applied for encapsulation of mixed wastes. Short-term testing of material properties under anticipated disposal conditions was performed to demonstrate long-term durability of waste forms, in lieu of reliable accelerated aging test methods. Results presented in this paper indicate that modified sulfur cement can maintain stability under most anticipated disposal conditions. Additional work is either underway or planned in those areas needed to fully confirm long-term stability.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the efforts of Sandra G. Lane for providing editorial assistance and Patricia Durcan for help in preparation of this manuscript.

## DISCLAIMER

## REFERENCES


1. Kalb, P.D., J.H. Heiser, III, and P. Colombo, "Modified Sulfur Cement Encapsulation of Mixed Waste Contaminated Incinerator Fly Ash," *Waste Management*, Vol. 11, No. 1, pp. 1-7, (1991).

2. Sullivan, T.A., and W.C. McBee, "Development and Testing of Superior Sulfur Concretes," RI-8160, Bureau of Mines, U.S. Department of Interior, Washington, DC, (1976).

3. U.S. Nuclear Regulatory Commission, "Technical Position on Waste Form," Rev. 0, Washington D.C., May 1983.

4. U.S. Code of Federal Regulations, Title 10, Energy, "Part 61 -- Licensing Requirements for Land Disposal of Radioactive Waste," U.S. Government Printing Office, 1990.

5. U.S. Environmental Protection Agency, Identification and Listing of Hazardous Waste (40 CFR 261), *Fed. Reg.*, 45: 3319, May 19 (1980).

6. Meyer, B., *Sulfur, Energy, and Environment*, Elsevier Scientific Publishing Co., New York, (1977).

7. Neilson, R.M. Jr., and P. Colombo, "Properties of Radioactive Wastes and Waste Containers, First Topical Report," BNL-NUREG-50957, Brookhaven National Laboratory, Upton, NY, January 1979.

8. Neilson, R.M., Jr., P.D. Kalb, M. Fuhrmann, and P. Colombo, "Solidification of Ion Exchange Resin Waste in Hydraulic Cement," *The Treatment and Handling of Radioactive Wastes*, A.G. Blasewitz, et al., eds., Springer-Verlag, NY, (1983).

9. Jong, B.W., W.C. McBee, K.L. Rasmussen, and T.A. Sullivan, "Fiber Reinforcement of Sulfur Concrete to Enhance Flexural Properties," RI-8956, Bureau of Mines, U.S. Dept. of the Interior, Washington, DC, (1985).

10. Kalb, P.D., and P. Colombo, "Modified Sulfur Cement Solidification of Low-Level Wastes, Topical Report," BNL-51923, Brookhaven National Laboratory, Upton, NY, October 1985.

11. U.S. Environmental Protection Agency, Toxicity Characteristic Leaching Procedure (TCLP), (40 CFR 261, Appendix II), *Fed. Reg.*, 55: 11863, March 29 (1990).