γ

CONF-9008119--2

BNL-45163

Comparison of Modified Sulfur Cement and Hydraulic Cement for Encapsulation of Radioactive and Mixed Wastes*

BNL--45163

DE91 001130

P.D. Kalb, J.H. Heiser III, and P. Colombo
Waste Management R & D Group
Department of Nuclear Energy
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

The majority of solidification/stabilization systems for low-level radioactive waste (LLW) and mixed waste, both in the commercial sector and at Department of Energy (DOE) facilities, utilize hydraulic cement (such as portland cement) to encapsulate waste materials and yield a monolithic solid waste form for disposal. Because hydraulic cement requires a chemical hydration reaction for setting and hardening, it is subject to potential interactions between elements in the waste and binder that can retard or prevent solidification. A new and innovative process utilizing modified sulfur cement developed by the U.S. Bureau of Mines has been applied at Brookhaven National Laboratory (BNL) for the encapsulation of many of these "problem" wastes. Modified sulfur cement is a thermoplastic material, and as such, it can be heated above its's melting point (120 °C), combined with dry waste products to form a homogeneous mixture, and cooled to form a monolithic solid product.

Under sponsorship of the DOE, research and development efforts at BNL have successfully applied the modified sulfur cement process for treatment of a range of LLWs including sodium sulfate salts, boric acid salts, and incinerator bottom ash and for mixed waste contaminated incinerator fly ash. Process development studies were conducted to determine optimal waste loadings for each waste type. Property evaluation studies were conducted to test waste form behavior under disposal conditions by applying relevant performance testing criteria established by the Nuclear Regulatory Commission (for LLW) and the Environmental Protection Agency (for hazardous wastes). Based on both processing and performance considerations, significantly greater waste loadings were achieved using modified sulfur cement when compared with hydraulic cement. After normalizing for differences in product densities, 6.0 times more sodium sulfate, 2.6 times more boric acid, 1.4 times more bottom ash and 2.7 times more incinerator fly ash can be incorporated per drum using modified sulfur cement, compared with hydraulic cement. Technology demonstration of the modified sulfur cement encapsulation system using production-scale equipment is scheduled for FY 1991.

INTRODUCTION

Although hydraulic cement has been used extensively over the years to solidify and stabilize LLW, constituents present in many radioactive, hazardous, and mixed waste streams can interfere with solidification chemistry and/or degrade the integrity of waste forms over time. Large volumes of waste generated at DOE facilities encompassing diverse physical and chemical properties have been identified as "problem" wastes because they are either difficult to encapsulate using conventional materials such as hydraulic cement, or result in waste forms that do not adequately immobilize contaminants. As a result, the Waste Management Research and Development Group at BNL, under the sponsorship of 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.

---

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

One such material is modified sulfur cement which has been shown to provide improved waste loadings and waste form performance in comparison with conventional binders. This paper presents an overview of research and development work performed at BNL for both hydraulic cement and modified sulfur cement encapsulation of radioactive, hazardous, and mixed waste streams.

COMPARISON OF MATERIALS

The majority of solidification/stabilization systems for LLW and mixed waste, both in the commercial sector and at DOE facilities, utilize hydraulic cement (such as portland cement) to encapsulate waste materials and yield a monolithic solid waste form for disposal. Hydraulic cement can be defined as the general class of cementitious materials that require addition of water and solidify as a result of various hydration reactions. During the atomic weapons development program known as the Manhattan Project some 50 years ago, hydraulic cement was the first material used to solidify LLW. It continues to be widely used in the waste treatment field today, primarily because it is relatively inexpensive (on the order of $0.10/lb or less), readily available, fairly easy to process, and highly alkaline (an advantage for immobilizing soluble toxic metals).

Many types of hydraulic cement are available, depending on specific end-use requirements. Portland cement is, by far, the most commonly used hydraulic cement. It is made by heating mixtures of limestone and clay and grinding the resultant clinker with gypsum into a fine powder. As shown in Table 1, the ASTM classifies eight types of portland cement depending on particular needs such as high early strength, low heat of hydration, and resistance to sulfates.[1] Constituent proportions differ among the types, but in general, portland cement consists of varying proportions of tricalcium and dicalcium silicates with smaller amounts of tricalcium aluminate, calcium aluminoferrite, and several other oxide compounds. In addition to selecting among the varieties of hydraulic cement, various admixtures are available to modify its properties. For example, plasticizers can be used to improve fluidity and facilitate mixing, air-entraining agents are used to improve frost resistance, other types of admixtures are available to retard or accelerate setting, reduce permeability, increase/decrease shrinking, or improve mechanical properties.

In spite of its many attributes however, because hydraulic cement requires a chemical hydration reaction for setting and hardening, it is subject to potential interactions between elements in the waste and binder that can retard or prevent solidification. Elements and compounds common in many LLW and mixed waste streams (e.g., inorganic salts and metal compounds) can thus, severely reduce allowable waste loadings or preclude use of hydraulic cement entirely. Table 2 lists some of the inorganic constituents present in many waste streams that can inhibit cement hydration or degrade mechanical strength. Reduction of the amount of waste that can be encapsulated (i.e., decreased loading efficiency), offsets potential cost savings from low material costs. Furthermore, small variations in waste composition can adversely impact hydraulic cement solidification formulations, creating the need for frequent recipe development, process modifications, and quality assurance testing. Thus, what is generally thought to be a simple process can, in fact, be quite sophisticated and labor intensive.

A new and innovative process utilizing modified sulfur cement developed by the U.S. Bureau of Mines (USBM) has been applied at Brookhaven National Laboratory (BNL) for the encapsulation of LLW, hazardous and mixed waste streams. Modified sulfur cement is a thermoplastic material, and as such, it can be heated above its's melting point, combined with dry waste products to form a homogeneous mixture, and cooled to form a monolithic solid product. Since no chemical reaction is required for setting, solidification is assured and modified sulfur cement is compatible with a wide range of wastes, encompassing diverse physical and chemical compositions.

Since its initial development about 20 years ago, use of modified sulfur cement in construction applications has grown steadily. It is made by reacting elemental sulfur with a total of 5 wt% hydrocarbon modifiers consisting of equal parts of dicyclopentadiene and oligomers of cyclopentadiene. These modifiers suppress a solid phase transformation that occurs during cooling of elemental sulfur and leads to an unstable material. The supply of raw materials for modified sulfur cement is plentiful. Increasingly stringent sulfur dioxide air emission controls and the recovery of sulfur from petroleum refining operations has led to large supplies of by-product or waste sulfur. It is estimated that by the year 2000, up to 90% of all sulfur production will result from these clean-up operations, yielding over 5.0×10^6 tons per year. Modified sulfur cement is commercially available under license to the USBM and currently costs about $0.17/lb for quantities up to one ton.[2]

In addition to the fact that solidification is not susceptible to chemical interferences, modified sulfur cement has several other advantages compared to hydraulic cement. For example, sulfur concrete compressive and tensile strengths twice those of comparable portland concretes have been achieved and full strength is reached in a matter of hours rather than weeks.[3] Sulfur concretes are highly impervious and resistant to attack in aggressive acid and salt environments.[4] Figure 1 compares portland cement concrete and modified sulfur cement concrete samples after exposure to a 30% solution of hydrochloric acid for 6 days.[5] Its low melting point (119 °C) and melt viscosity (~25 cp at 135 °C) make processing of modified sulfur cement relatively easy.

WASTE CHARACTERIZATION

As a result of research and development efforts at BNL, the modified sulfur cement process has successfully been applied for treatment of a range of waste streams that are generated at commercial and DOE facilities. These include LLWs (such as sodium sulfate salts, boric acid salts, and incinerator bottom ash) and mixed waste contaminated incinerator fly ash. Some waste streams such as ion exchange resins and sodium nitrate salt waste are not recommended for stabilization with modified sulfur cement. Ion exchange resins shrink during thermal processing as water is driven off and then undergo expansion upon exposure of the waste form to moisture, causing severe cracking and degradation.[6] Sodium nitrate can form a potentially reactive mixture when combined with sulfur compounds and thus is not applicable for this process.

Many of the waste streams examined contain one or more of the constituents listed in Table 2 that inhibit cement hydration or degrade mechanical integrity of the waste form, and thus are difficult to encapsulate using hydraulic cement. For example, incinerator fly ash generated at the Waste Experimental Reduction Facility (WERF) at Idaho National Engineering Laboratory (INEL) and analyzed by atomic absorption spectrophotometry was found to contain over 50 wt% heavy metal salts. As seen in Figure 2, these include significant concentrations of zinc (36 wt%), lead (7.5 wt%), sodium (5.5 wt%), and copper (0.7 wt%), all of which can inhibit hydration. Scanning electron microscopy and energy dispersive analysis of the ash revealed that many of these elements are present in the chloride form, further exacerbating cement hydration.[7]

FORMULATION AND PROCESS DEVELOPMENT

Formulation and process development studies were performed to determine maximum waste loadings for each binder, while still maintaining adequate waste form performance as defined by existing regulatory criteria. With the addition of the necessary water for hydration, hydraulic cement is a three component system (i.e., waste, cement and water), so that ternary compositional phase diagrams were generated to define regions of acceptable formulations. Formulation data and descriptions of process equipment requirements/procedures have been previously reported for both hydraulic cement [8,9] and modified sulfur cement [6,7] waste forms.

WASTE FORM PERFORMANCE TESTING

Examination of waste form properties and performance is an essential part of the overall disposal system performance assessment methodology. Prediction of potential long-term behavior of waste forms in storage and disposal is a difficult task, however. Waste form performance can be affected by various interactions between the waste, binder, waste form and the environment, as well as by natural or man-made changes to the environment. In spite of these difficulties, testing of laboratory-scale waste forms can provide valuable information on potential waste form performance and can provide a basis for comparison of various waste-binder formulations. To this end, a series of standardized property evaluation tests were conducted including compressive strength (ASTM C-39), water immersion (90 days), thermal cycling (ASTM B-553), and leachability (ANS 16.1) for LLW waste forms and toxic leachability (EPA TCLP) for mixed waste forms containing toxic metals. Tests performed for radioactive waste forms are included in those recommended by the Nuclear Regulatory Commission (NRC) in support of 10 CFR 61. [10] The Toxicity Characteristic Leaching Procedure (TCLP) was recently issued by Environmental Protection Agency (EPA) in support of 40 CFR 261. [11] Specific data from these tests are available in the previously cited references [6,7,8,9], but some of the results for modified sulfur cement waste form performance testing are summarized in the following figures.

Figure 3 compares average compressive strength for various waste loadings of sodium sulfate, boric acid, incinerator bottom ash, and incinerator fly ash encapsulated in modified sulfur cement. In most cases, the dry waste solids acted as an aggregate and increased compressive strength above that of the control sample containing no waste. By comparison, all samples tested were well above the 0.4 Mpa (60 psi) minimum waste form strength specified by the NRC.

The effects of water immersion and thermal cycling on modified sulfur cement waste form compressive strength are presented in Figures 4 and 5, respectively. In both of these tests waste form strength increased for some samples and decreased for others. Differences were relatively small, however, and not considered significant. In any case, compressive strength of all immersion and thermally conditioned samples was considerably higher than the NRC minimum standard.

Radionuclide leachability from modified sulfur cement waste forms is summarized in Figure 6. Waste forms containing 25 and 40 wt% sodium sulfate and 20 and 40 wt% incinerator bottom ash, each containing the isotopes Co-60 and Cs-137, were leached for 90 days according to procedures outlined in ANS 16.1.[12] Results are presented in terms of the leachability index, a figure of merit inversely proportional to the log of the effective diffusivity. Thus, each incremental increase in leach index represents an order of magnitude reduction in leachability. As expected, leachability for the highly soluble sulfate salts was greater than that of the incinerator bottom ash. In general, radionuclides leached very slowly. Leach indices ranged between 9.7 and 14.6, representing leach rates of about 4 to almost 8 orders of magnitude less than those expressed by the minimum NRC leach index of 6.0.

Incinerator fly ash waste contained significant concentrations of cadmium (Cd) and lead (Pb). These metals (along with arsenic, barium, chromium, mercury, selenium, and silver) have been identified by EPA as toxic metals, which if present in leachates above allowable concentrations, define a waste stream as hazardous. EPA's recently published TCLP test is used to implement its criteria for determining hazardous toxicity of wastes and waste forms. As seen in Table 3, leachates from INEL incinerator fly ash alone and when encapsulated in modified sulfur cement at 40 and 55 wt% loading, yielded concentrations of Cd and Pb above allowable limits. To further reduce the mobility of these toxic metals and comply with EPA regulatory limits, potential additives were examined including precipitation, sorption, and ion exchange agents. Sodium sulfide (Na_2S) was selected for use as an additive because it reacts preferentially with these metals to form highly insoluble metal sulfides. Addition of small quantities (about 7 wt%) of Na_2S resulted in lowering TCLP leachate concentrations well below EPA concentration limits of 1.0 and 5.0 ppm, for Cd and Pb, respectively. A maximum waste loading of 43 wt% incinerator fly ash was encapsulated while still meeting criteria for delisting as a hazardous waste.

COMPARISON OF WASTE LOADINGS

Maximum waste loadings using hydraulic cement and modified sulfur cement are compared in Figure 7. Because of differences in the product densities (which vary based on specific formulations) these data are also presented in terms of maximum waste loadings per 55 gallon drum in Figure 8. Data are based on research and development efforts at BNL and consider both processing and waste form performance criteria. As demonstrated in Figures 7 and 8, dramatic improvements in waste loading potential are possible for most waste types tested using modified sulfur cement in place of hydraulic cement. In the case of incinerator bottom ash, modified sulfur cement encapsulation resulted in somewhat smaller increases in potential waste loading.

CONCLUSIONS

Modified sulfur cement can be used effectively for many waste types that are difficult to encapsulate using conventional hydraulic cement. It's properties make it applicable to a wide range of wastes, reduce the need for frequent testing and process modification, and result in waste forms that are durable in the face of harsh environments. Based on both processing and performance criteria, 6.0 times more sodium sulfate, 2.6 times more boric acid, 1.4 times more incinerator bottom ash, and 2.7 times more incinerator fly ash waste can be encapsulated per drum using modified sulfur cement than with hydraulic cement. A production-scale technology demonstration for the modified sulfur cement encapsulation process is being planned in conjunction with INEL for FY 1991.

Table 1. Some types of hydraulic cement that have been used for waste stabilization[a]

Type	Description
ASTM Type I[b]	General-purpose portland cement; least expensive; most common type used for waste stabilization
ASTM Type II[b]	For use where moderate sulfate attack is anticipated or moderate heat of hydration is required
ASTM Type III[b]	High early strength; cold climates
ASTM Type IV[b]	Low heat of hydration; used in massive structures where exotherm is a concern
ASTM Type V	For use where exposure to high sulfate soils and groundwater is expected; develops strength slowly
ASTM Type IS[b]	Portland/blast furnace slag cements; low early strength but slowly cures to same ultimate strength as Type I; more common in Europe than U.S.
ASTM Type IP[b]	Pozzolan-containing cements; made by intergrinding suitable pozzolans with cement clinker
Masonry cements	Usually contains hydrated lime, limestone, chalk, shell, talc, slag, or clay; good workability, plasticity, and water retention; has been used to solidify LLW boric acid concentrates
Natural cements	Made from same materials as portland, but processed at lower temperatures
High-alumina	Not a portland cement; sets slowly but develops very high strength quickly; may have long-term durability problems

a) Adapted from Reference 1.
b) Available with air-entraining agents for improving resistance to freeze-thaw and scaling.

Table 2. Inorganic constituents present in waste streams that can inhibit hydraulic cement hydration or degrade waste form integrity

Borates
Chlorides
Copper compounds
Heavy metal salts
Lead compounds
Magnesium compounds
Phosphates
Sodium compounds
Sulfates and sulfides
Tin compounds
Zinc compounds

Table 3. Results from EPA Toxicity Characteristic Leaching Procedure (TCLP) for INEL Ash Encapsulated in Modified Sulfur Cement(MSC)

	Concentrations of Criteria Metals, ppm [(a)]	
Sample Tested:	Cd	Pb
INEL Fly Ash	85.0	46.0
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[(b)]	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) Na_2S = sodium sulfide

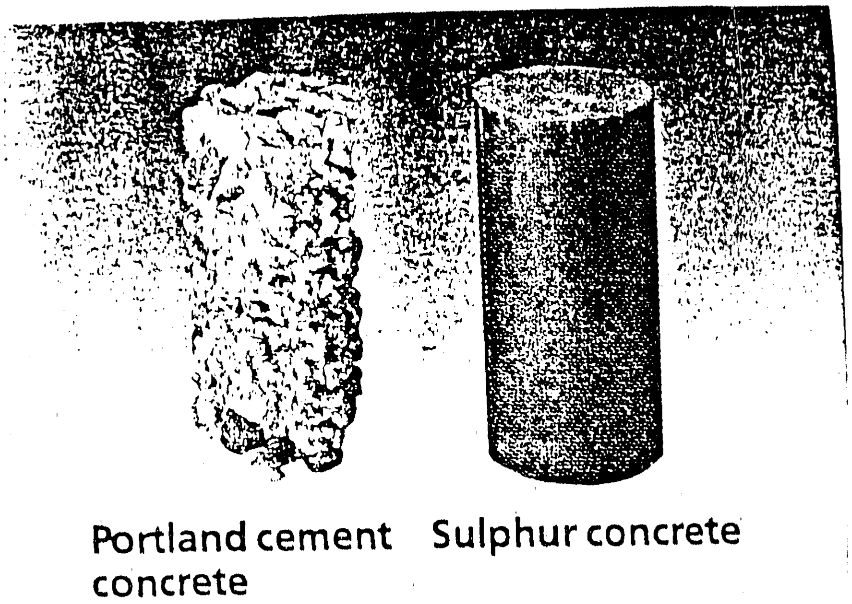

Figure 1. Portland cement concrete and modified sulfur cement concrete samples after exposure to a 30% solution of hydrochloric acid for 6 days. [5]

Element	Weight Percent
Zinc	38.0
Lead	7.6
Sodium	6.6
Potassium	2.8
Calcium	0.8
Copper	0.7
Iron	0.6
Cadmium	0.2
Chromium	BDL
Barium	BDL
Silver	BDL
Nickel	BDL

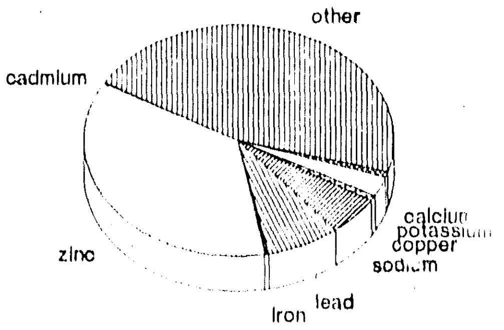

Figure 2. Elemental composition of fly ash generated at the Waste Experimental Reduction Facility at Idaho National Engineering Laboratory.

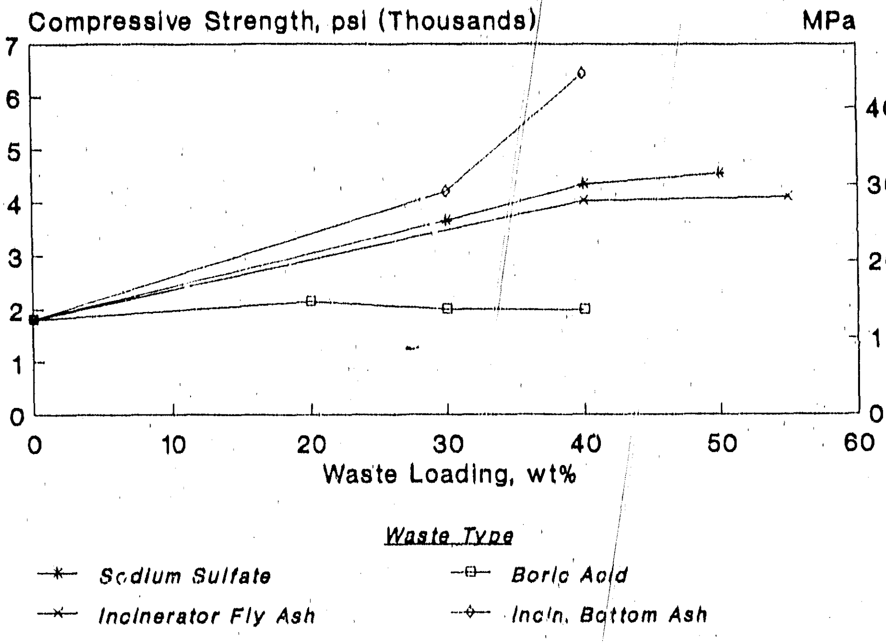

Figure 3. Average compressive strength for modified sulfur cement waste forms tested in accordance with ASTM C-39.

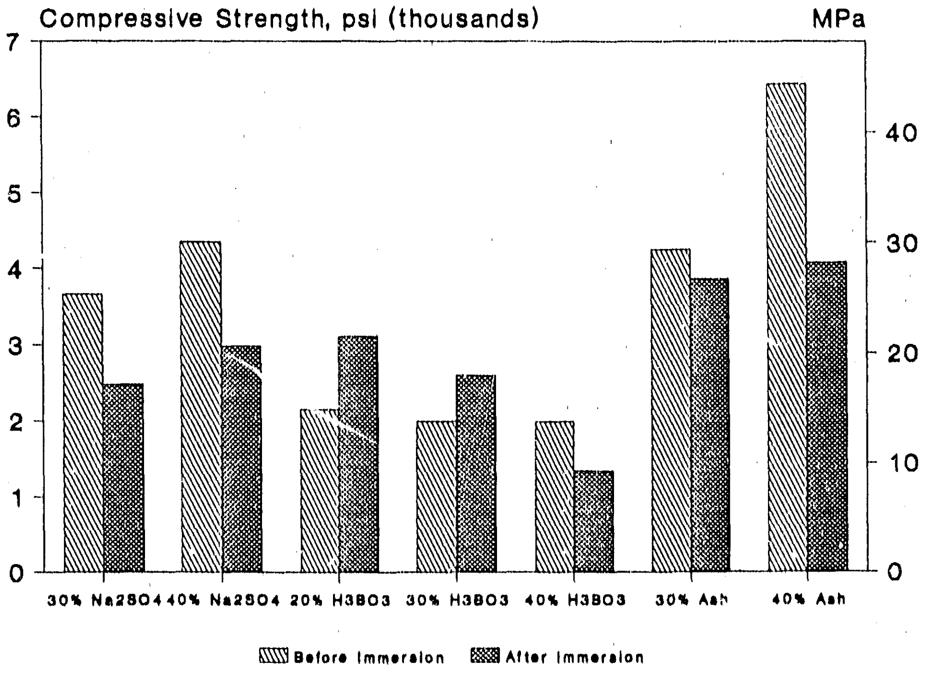

Figure 4. Effects of 90 day water immersion testing on compressive strength for modified sulfur cement waste forms containing sodium sulfate (Na_2SO_4), boric acid (H_3BO_3) and incinerator bottom ash.

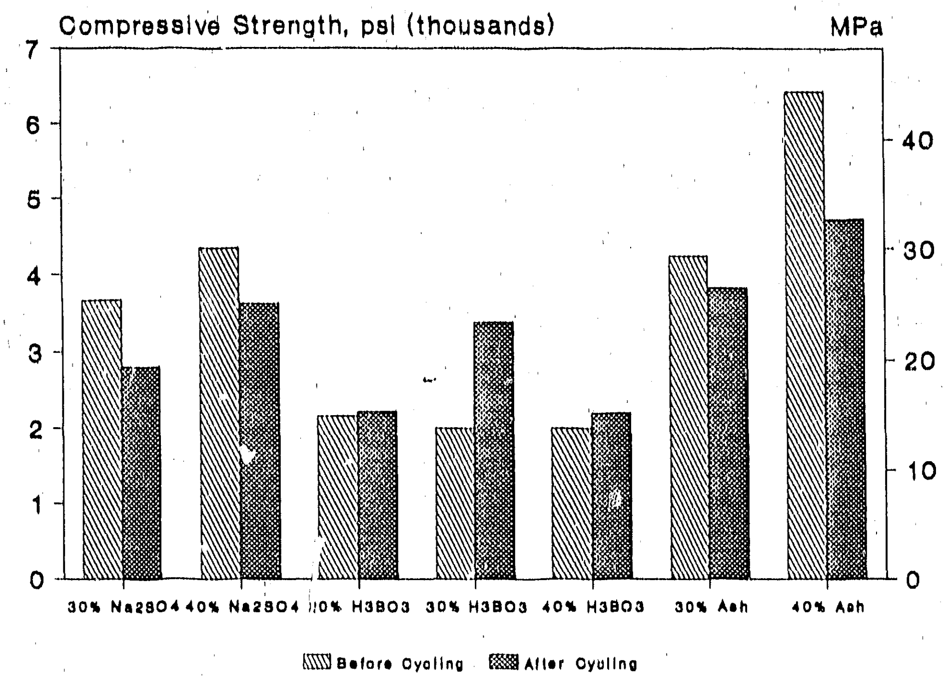

Figure 5. Effects of thermal cycling on compressive strength of modified sulfur cement waste forms containing sodium sulfate (Na_2SO_4), boric acid (H_3BO_3) and incinerator bottom ash (based on modified ASTM B-553).

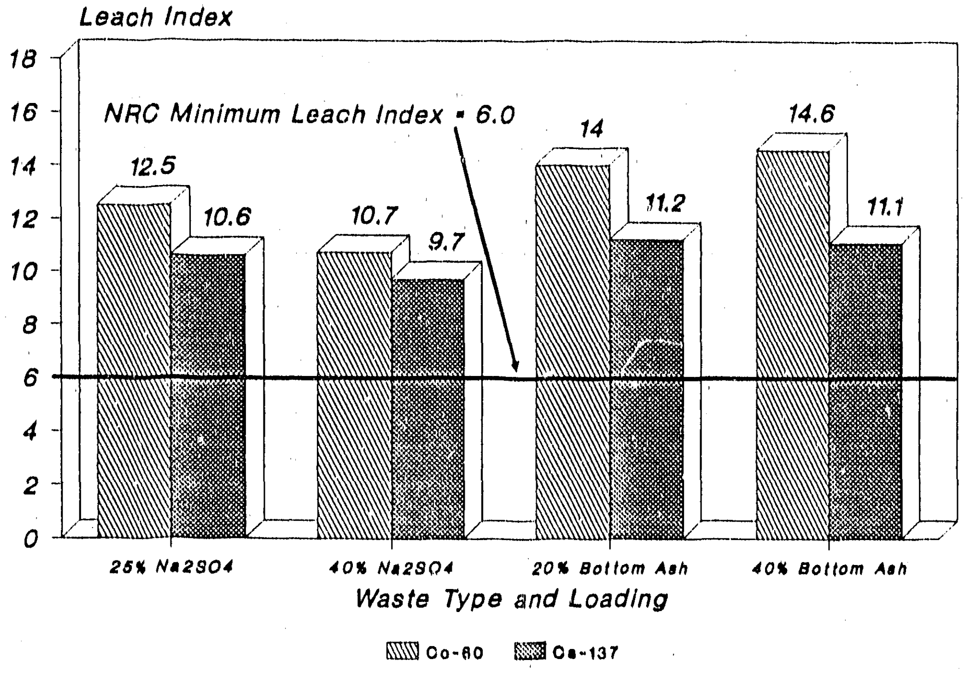

Figure 6. Radionuclide leachability for Co-60 and Cs-137 from modified sulfur cement waste forms containing sodium sulfate (Na_2SO_4) and incinerator bottom ash waste.

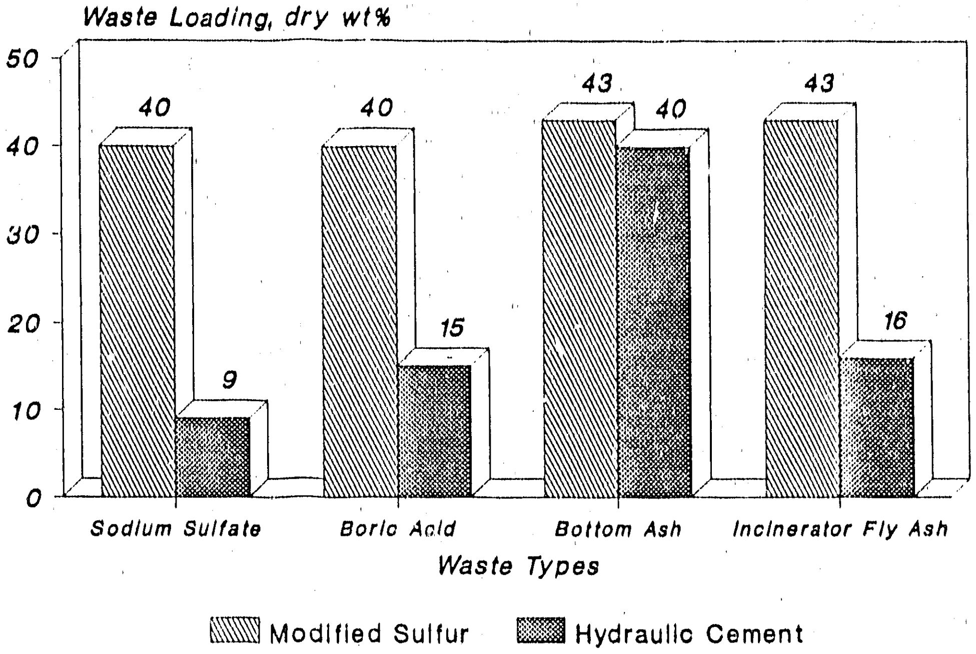

Figure 7. Comparison of maximum waste loadings using modified sulfur cement and hydraulic cement based on processing and waste form performance considerations.

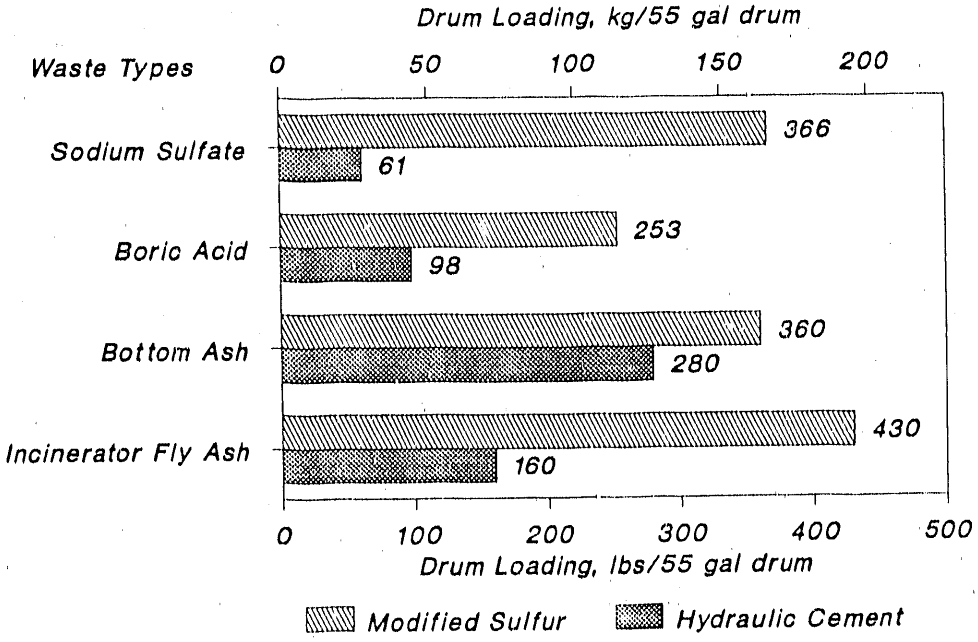

Figure 8. Comparison of maximum waste loadings per 55 gallon drum for modified sulfur cement and hydraulic cement.

REFERENCES

1. Conner, J.R., "Chemical Fixation and Solidification of Hazardous Wastes", Van Nostrand Reinhold, New York, 1990.

2. Personal communication, Hugh Harbour, Martin Chemicals, Odessa, TX, Feb. 5, 1990.

3. "Sulphur Concrete...A New Construction Material Comes of Age", Sulphur Research and Development, Vol. 2, 1979.

4. "SCRETE Sulfur Concrete", Manufacturer's Data Sheet, Chevron Chemical Co., San Francisco, CA.

5. "Acid-Proof, Salt Resistant Chempruf Sulphur Concrete", 4K A/S, Copenhagen, available through The Sulfur Institute, Washington DC.

6. Kalb, P.D., and P. Colombo, Modified Sulfur Cement Solidification of Low-Level Wastes, BNL-51923, Brookhaven National Laboratory, Upton NY, Oct. 1985.

7. Kalb, P.D., J.H. Heiser III, and P. Colombo, Modified Sulfur Cement Encapsulation of Mixed Waste Contaminated Incinerator Fly Ash, *Waste Management* "Incineration '90" issue, in press.

8. Neilson, R.M. Jr., and P. Colombo, Waste Form Development Program Annual Progress Report, BNL-51614, Brookhaven National Laboratory, Upton NY September 1982.

9. Zhou, H., and P. Colombo, Solidification of Low-Level Radioactive Wastes in Masonry Cement, BNL-52074, Brookhaven National Laboratory, Upton NY, March 1987.

10. USNRC, "Branch Technical Position on Waste Form", US Nuclear Regulatory Commission, Low-Level Waste Licensing Branch, Washington, DC, May 1983.

11. USEPA, "Toxicity Characteristic Leaching Procedure (TCLP)", 40 CFR 261, Appendix II, 55 FR 11863, U.S. Environmental Protection Agency, Washington DC, March 29,1990.

12. ANS Standards Committee, Working Group 16.1, Measurement of the Leachability of Solidified Low-Level Wastes, American Nuclear Society, June 1984.

END

DATE FILMED

11 / 06 / 90