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OF RCRA
TOXIC METALS AND METAL OXIDES

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SULFUR POLYMER CEMENT ENCAPSULATION OF RCRA TOXIC METALS AND METAL OXIDES

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ABSTRACT

A study was conducted to determine the suitability of Sulfur Polymer Cement (SPC) encapsulation technology for the stabilization of RCRA toxic metal and metal oxide wastes. In a series of bench-scale experiments, the effects of sodium sulfide additions to the waste mixture, residence time, and temperature profile were evaluated. In addition, an effort was made to ascertain the degree to which SPC affords chemical stabilization as opposed to physical encapsulation.

Experimental results have demonstrated that at the 25 wt % loading level, SPC can effectively immobilize Cr, Cr₂O₃, Hg, Pb, and Se to levels below regulatory limits. SPC encapsulation also has been shown to significantly reduce the leachability of other toxic compounds including PbO, PbO₂, As₂O₃, BaO, and CdO. In addition, data has confirmed sulfide conversion of Hg, Pb, PbO, PbO₂, and BaO as the product of their reaction with SPC.

INTRODUCTION

Heavy metal contamination is endemic of a significant portion of hazardous wastes at DOE facilities, much of which exists in an oxidized state. SPC is currently being investigated as a possible alternative final waste form for that segment of these wastes which does not readily lend itself to vitrification and/or grout stabilization. Previous work has demonstrated that SPC effectively immobilizes some RCRA toxic metal and metal salt species [1]. However, the use SPC as an encapsulant is relatively new, and the scope of tested waste streams has been limited.

Accordingly, it has been the intent of the authors to identify and ascertain the effects of process variables on final waste form properties with respect to individual metal and metal oxide waste constituents. A series of bench-scale experiments was conducted to study the effects of sodium sulfide additions to the waste mixture, residence time, and temperature profile.

BACKGROUND

SPC, also known as modified sulfur cement, was originally developed as a corrosion resistant structural material in the late seventies by the Bureau of Mines. However, it has only been recently considered for the immobilization of mixed waste by Idaho National Engineering Laboratory (INEL), Brookhaven National Laboratory (BNL), and others [2]. SPC is a thermoplastic material and is typically composed of 95 percent elemental sulfur and 5 percent cyclopentadiene modifier. Accordingly, several of its chemical and physical properties resemble sulfur itself including solidification temperature, viscosity behavior, and manner of attack by strong alkalies, strong oxidants and organic solvents [3].

SPC affords several advantages as a final waste form including high mechanical strength, low permeability, high waste loading, and resistance to attack by bacteria, mineral acids and high salt environments. Laboratory specimens have successfully passed all Nuclear Regulatory Commission requirements for radioactive waste forms, and irradiated samples have demonstrated little or no gas evolution for standard tests. Also, as a thermoplastic material, SPC does not rely on interaction with waste constituents for setting and thereby accommodates a variety of waste compositions.

To date, there have been only a limited number of experimental studies pertaining to SPC encapsulation, many of which have focused on four predominant waste streams: incinerator ash, sodium sulfate salt, boric acid, and ion exchange resins [2].

DISCUSSION OF EXPERIMENTAL METHODS

Materials

The sulfur polymer cement used for these experiments was purchased from Martin Resources, Inc., and is typically 94 to 96 wt % sulfur and 4 to 6 wt % equal parts of oligomeric and polymeric cyclopentadiene. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was purchased from Johnson Matthey Catalog Company and $\text{Na}_2\text{S} \cdot 1\text{H}_2\text{O}$ was obtained from EM Science, a division of EM Industries, Inc. Metals and metal oxides were bought from Aldrich Chemical Company, Inc. and were typically less than 100 mesh and 99.9% pure.

Experimental Setup and Processing

Bench-scale experiments are conducted in a permitted laboratory hood using the setup in Figure 1. For a typical run, the batch ingredients are weighed, then SPC is added to the stainless steel reaction beaker. The beaker is heated to approximately 140 C, and held until the temperature of the molten SPC equilibrates. Temperature is measured at the bottom outside edge of the beaker and in the center of the molten mixture. Next, Na_2S , at room temperature, may be added over the top of the molten SPC and intimately stirred by hand. Stirring then occurs intermittently throughout the run at 5 to 10 minute intervals. After the temperature stabilizes for 15 minutes, the pure waste constituent, at room temperature, is added over the top of the SPC mixture and intimately stirred. The SPC

waste mixture is then held for the appropriate process time. After being held for the appropriate time, the mixture is either removed from heat for a "quick cool" or allowed to cool on the hot plate for a "slow cool" profile. These correspond to average cooling rates of approximately 5 °C/min and 1 °C/min respectively.

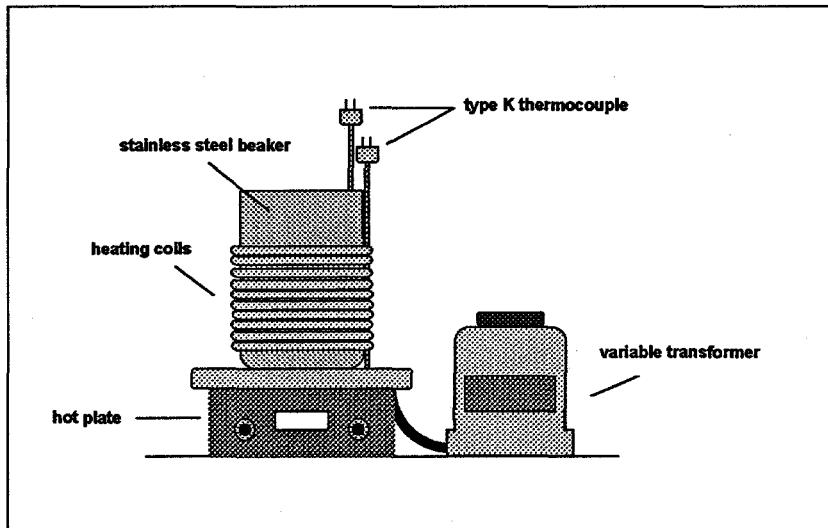


Figure 1: Experimental setup for bench-scale experiments.

The cooled SPC waste monolith is consequently removed from the stainless steel beaker and crushed for consequent modified Toxicity Characteristic Leaching Procedure (MTCLP) analysis.

MTCLP and Standard Distribution

The Toxicity Characteristic Leaching Procedure (TCLP) as described in SW846 [4], generates a considerable degree of waste. Consequently the sample size for analysis was reduced while keeping the leachate:sample ratio the same as that in the standard. Approximately 50 g of waste material passing through a 4.75 mm sieve was collected, and a sub-sample of approximately 10 g was subjected to the TCLP test. The extract collected from the TCLP test was homogenized, transferred to an appropriate container, and preserved, as required, for the subsequent constituent analysis [5].

An effort was made by the authors to assess any possible effects that the particle size distribution of the crushed monolith might have on the MTCLP results. Consequently, several samples were divided into coarse (-4+6 mesh) and fine (-80 mesh) fractions and subjected to the MTCLP. Results from preliminary tests indicated considerable variability in the MTCLP between coarse and fine fractions of the same sample with differences ranging up to an order of magnitude.

As a result of these tests, a MTCLP sample standard distribution was developed. A representative sample of SPC runs was screened through a graded sieve set, and the weight percent of material retained on each sieve was recorded. The average particle size distribution was then simplified by the combination of screen fractions to obtain the MTCLP standard.

DISCUSSION OF RESULTS

No Additive Encapsulation

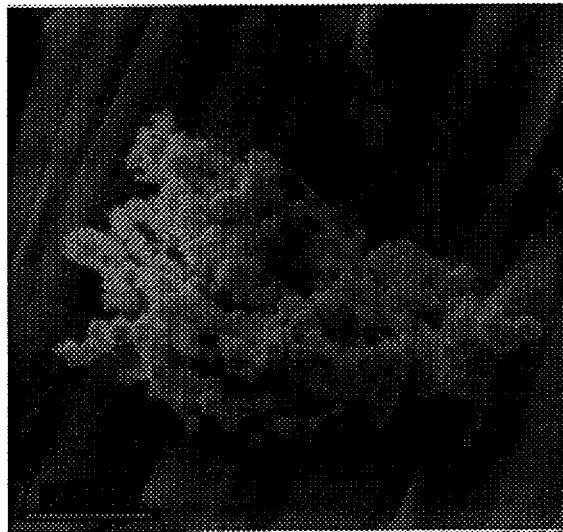
Initially, experimental trials were conducted with SPC and hazardous constituents only in order to determine the extent of chemical reaction and to also establish a baseline for MTCLP extract metal concentrations. MTCLP data from these trials indicate that even with 25 wt % hazardous constituent loading, SPC immobilization was sufficient to render Cr, Cr₂O₃, Hg, and Se well below their regulatory limits. This is to be expected if one examines the solubility of these materials with respect to water and ascetic acid. While the other materials failed to pass MTCLP with no additives to the SPC waste mixture, PbO₂ and As exhibited significantly low concentration values at the 25 wt % loading level. The results suggest that for many waste streams with small quantities of these materials, SPC may be a sufficient encapsulant for waste immobilization.

Sulfides of silver, arsenic, cadmium, lead, mercury and selenium were also encapsulated with SPC, and the MTCLP data for these were compared to that for the metals and metal oxides. The metal sulfide concentrations were all well below their respective regulatory limits with values typically less than 0.5 mg/L. With the exception of mercury, these sulfide values suggest that little or no chemical reaction takes place for the base mixture of SPC and the individual hazardous metal and metal oxide constituents. This is confirmed by the X-ray diffraction data.

Encapsulation with Sodium Sulfide Additive

Previous work by BNL, INEL and others has indicated that sodium sulfide can facilitate the formation of RCRA toxic metal sulfides from the reaction of toxic metals and/or metal salts with SPC [1,2]. Accordingly, bench-scale SPC tests were conducted with sodium sulfide added for several hazardous constituents. These included As, As₂O₃, BaO, CdO, Cr, Cr₂O₃, Pb, PbO, PbO₂, PbS, and Se. MTCLP data indicated that in addition to Cr, Cr₂O₃, Hg, and Se, the addition of sodium sulfide to the waste mixture yielded metal concentrations below regulatory values only for lead samples. However, a significant improvement in leaching performance was observed for As₂O₃, BaO, CdO, and PbO₂ samples. No additional improvements in performance were observed for Cr, Cr₂O₃, or Se. In contrast, a decrease in leaching performance was observed for arsenic samples. The reason for the poorer performance of arsenic has not been definitively determined. However, it is the authors opinion that this may be attributed to the solubility sensitivity of arsenic with respect to changes in pH.

Figure 2 is a comparison of two similarly processed Pb samples. Photo (a) is of a waste form processed without Na_2S , and photo (b) was processed with the Na_2S additive. The nodular morphology of the first photo contrasts significantly with that of the angular particles of the second suggesting chemical reaction.



(a)



(b)

Figure 2: comparison of microstructure of encapsulated lead waste samples (a) without Na_2S and (b) with Na_2S additive.

X-ray Analysis

For a mixtures of SPC and waste only, sulfide formation was confirmed by X-ray diffraction for Hg, Pb, and BaO trials. However, in the case of Pb and BaO, the sulfide phases were minor constituents only. The reaction of these materials with SPC was dominated by sulfate and hydroxide/sulfate phases for Pb and BaO respectively.

With the addition of Na₂S to the SPC waste mixture, sulfide formation was also observed for PbO and PbO₂ as a tertiary phases. The reaction of Pb metal with SPC to form PbS was determined to be favored over that of the sulfate phase. In addition, all of the tested metals and compounds formed unidentified minor phases when processed with added Na₂S. At this time, it cannot be determined if this unidentified phase is responsible for some of the improved leaching behavior of the final waste form as observed with the addition of Na₂S.

Process Observations

Testing of other variable effects was also done on a limited basis which yielded two interesting observations. For SPC runs without additives, increasing the process time improved leaching performance. However, for runs with Na₂S, varying the process time between 0.5 to 4.0 hrs resulted in no apparent changes in leaching performance. Also, no observable difference in leaching performance was observed for "slow" and "quick cooled" samples.

CONCLUSIONS

Bench-scale tests have demonstrated that SPC has considerable potential as stabilization/solidification technology. SPC can effectively immobilize 25 wt % of high purity Cr, Cr₂O₃, Hg, Pb, and Se to levels below regulatory limits. It has also been shown to significantly reduce the MTCLP metals concentration for PbO, PbO₂, As₂O₃, BaO, and CdO encapsulated wastes. In addition, sulfide conversion was confirmed for the reaction of SPC with Hg, Pb, PbO, PbO₂, and BaO, and an unidentified minor phase was detected for runs processed with sodium sulfide. The extent to which process variables effect final waste form leachability was investigated and was determined to be highly dependent on waste mixture composition.

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