US Army Corps
of Engineers
Engineer Research and
Development Center

ERDC/CERL TR-00-6
February 2000

Sol-Gel Stabilization of Heavy Metal Waste

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The Army is continually faced with the disposal or treatment of media contaminated with heavy metals such as lead, chromium, and cadmium. The types of media are varied and include soils, ashes, and sludges. Waste having a leachable metal concentration above the Toxicity Characteristic Leaching Procedure limit established by the U.S. Environmental Protection Agency can be treated to render it non-hazardous.

Several stabilization/solidification (S/S) processes are used for the treatment of hazardous wastes. Vitrification, for example, incorporates hazardous waste into glass, but the high temperatures needed to make the glass are undesirable. Sol-gel chemistry is a means to make glass at low temperatures. Also, the heavy metals can be chemically incorporated in the glass matrix rather than merely encapsulated. This work examines the ability of sol-gel chemistry to replace vitrification as an S/S technique. A recipe was formulated for immobilizing lead in glass by the sol-gel process. The merits of the process are discussed.

Results showed that sol-gel processing stabilized some lead from solutions and encapsulated some metals in a glass matrix. However, sol-gel was found to be too sensitive to chemistry, too limited in application, and too expensive to compete with current S/S processes.

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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 40162720D048, "Industrial Operations Pollution Control Technology (6.2 Exploratory Development)"; Work Unit U79, "Sol-Gel Stabilization of Heavy Metal Waste." The technical reviewer was Chris Vercautren, Industrial Operations Command, Rock Island Arsenal, IL.

The work was performed by the Environmental Processes (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. Donald M. Cropek. Dr. Ilker R. Adiguzel is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The technical editor was Linda L. Wheatley, Information Technology Laboratory. Dr. Alan W. Moore is the CERL Acting Director.

CERL is an element of the Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Acting Director of ERDC is Dr. Lewis E. Link, Jr., and the Commander is COL Robin R. Cababa, EN.

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1 Introduction

Background

The Army is continually faced with the disposal or treatment of media contaminated with heavy metals such as lead, chromium, and cadmium. The types of media include soils, ashes, and sludges. For example, firing range soils are high in lead content because the ammunition used contains lead. Soil surrounding and underlying some structures and playgrounds on Army installations become contaminated by lead leaching from lead-based paints used on the structures and equipment. Incineration of items containing heavy metals (e.g., metal catalysts in propellant formulations) eliminates much of the matrix but concentrates the metal in the baghouse ash. Other examples are sludges from industrial processes (e.g., electroplating) that have very high levels of chromium, and painting/de-painting operations that generate sludges and blast media high in metal content.

The key parameter in examples such as these is the amount of heavy metal that can leach out of the waste to become bioavailable. If an organism (e.g., a human) ingests the waste, only the heavy metal that can leach from the waste will have toxic effects on the organism. In addition, only the leachable heavy metal fraction can move through the environment, carried along by groundwater into other sensitive areas.

The U.S. Environmental Protection Agency (EPA) developed the Toxicity Characteristic Leaching Procedure (TCLP) to determine the leachable contaminant content of samples, including different organic and metallic species. Depending on whether the waste has a leachable metal concentration below or above the TCLP limit, the waste is said to either “pass” or “fail” TCLP, respectively. The cost of treatment and disposal for a waste can be high if it fails TCLP. Such a waste can be treated to lower the leachable metal to a level below the TCLP value, thus rendering the waste non-hazardous.

According to EPA literature (Barth et al. 1990), stabilization/solidification (S/S) of hazardous wastes involves three steps:

1. Improve the handling and physical characteristics of the waste.
2. Decrease the surface area of the waste to limit leachability of contaminants.
3. Decrease the solubility of the hazardous constituents of the waste.

In the case of heavy metals, an S/S process makes a solid monolithic structure that prevents leaching of the metal by either a physical encapsulation mechanism or a chemical reaction. Generally, the use of a chemical reaction to convert a metal from a soluble form to an insoluble form is preferred over encapsulation, which can fail upon fracture or weathering of the monolith.

Several S/S processes have been used for the treatment of hazardous wastes (Barth et al. 1990; Jackman and Powell 1991). Cement-based S/S is a physical/chemical process that incorporates the metals into Portland cement during the curing step. Pozzolanic S/S is a similar process that combines the waste with silica or aluminosilicate material, which is then added to a cementitious product. It tends to use primarily a physical encapsulation mechanism. Organic S/S uses either a thermoplastic material or a polymer matrix to physically encapsulate the hazardous waste. The S/S technique of particular interest to this research is vitrification (or glassification), which involves melting a waste alone or mixing it with glass-forming ingredients under high temperatures. The high temperatures are required to create a fluid melt into which the waste can be stirred. Upon cooling, the mix forms a glasslike monolith in which the waste is now physically encapsulated (Jackman and Powell 1991; Conner 1990).

Vitrification is best for wastes that are stable at high temperature. Organic wastes tend to volatilize or pyrolyze at these temperatures. In the field, a high electrical current has been used to glassify contaminated soils in-situ (Conner 1990). The primary application for vitrification, however, has been for the S/S of low-level radioactive waste (Wicks and Ross 1984). The final glass products are not leachable and have a high degree of waste containment even though the stabilization mechanism is not chemical in nature. Unfortunately, the high temperatures needed require expensive equipment and incur a large energy cost, which precludes using vitrification as an S/S technique for common heavy metal wastes. The high temperature may also contribute to the undesirable escape of volatile metals. A desirable technique would overcome these problems while still providing the benefits of glass as an S/S matrix. This report documents studies done using sol-gel chemistry as an S/S technique.

Sol-gel chemistry is the preparation of ceramic material (e.g., glasses) by preparation of a sol, gelation of the sol, and subsequent removal of the solvent

(Brinker and Scherer 1990; Hench and West 1990; Hua 1991). Sol-gel chemistry originated in the mid-1800s with several studies on the creation of silicon dioxide (SiO_2) glass from the tetraethoxysilane (TEOS) precursor (Ebelman 1846; Graham 1864). Starting with the glass precursor chemicals (metal alkoxides), sol-gel chemistry can create the metal oxide glass with a two-step process. Equation 1 shows the first hydrolysis step for formation of SiO_2 glass from TEOS:

$$Si(OR)_4 + nH_2O \text{ --- } Si(OR)_{4-n}(OH)_n + nROH \qquad \text{(Eq 1)}$$

where R is a $-CH_2CH_3$ group. This step replaces the alkoxide groups with hydroxyl groups. The second step is a condensation process that initiates the silicate glass structure:

$$=Si(OH) + RO\text{-}Si= \text{ --- } =Si - O - Si= + ROH \qquad \text{(Eq 2)}$$

or

$$=Si(OH) + HO\text{-}Si= \text{ --- } =Si - O - Si= + H_2O \qquad \text{(Eq 3)}$$

The condensation process continues to make an extended three-dimensional silicate glass matrix.

This process has made sol-gel chemistry a powerful tool for making films and coatings, optics, fibers, powders, and membranes with desired characteristics (Brinker and Scherer 1990). Sol-gel processing has two main benefits over vitrification. First, sol-gel glasses can be made at lower temperatures than those required for traditional glass melts (>1100 °C) (Brinker and Scherer 1990). Lower temperatures save energy, reduce volatility problems, and eliminate the need for specialized S/S equipment. Second, by beginning with the precursor materials, metals can be chemically incorporated into the glass matrix rather than merely encapsulated. The presence of metal cations at the condensation step (Equations 2 or 3) may allow covalent bonding in the silicate structure. This bond increases the immobility of the metal thus resulting in a better-defined S/S product. The research reported here examined the ability of sol-gel chemistry to replace vitrification as a S/S technique.

Objective

The objective of this work was to investigate sol-gel chemistry as an S/S method for heavy metal contaminated waste. The goal was to assess the value of this technology and identify a simple recipe for metal treatment. Initial work focused

on solutions that contain soluble forms of heavy metals rather than contaminated solids. Solutions containing known concentrations of heavy metal will provide a controlled system with the highest chance of stabilization success.

Approach

The literature was surveyed to select a starting point for experimentation of the various sol-gel parameters: metal salt, catalysis condition and concentration, ratios of precursor materials, and heat treatment of the glass. Glasses were created using tetramethoxysilane (TMOS) and TEOS mixed with lead cations employing different sol-gel parameters. The final products were tested using TCLP. Success of encapsulation was determined by atomic absorption (AA) analysis of the TCLP extract and calculation of the percent lead immobilized. The discussion section evaluates the behavior of sol-gel chemistry to stabilize heavy metal contaminated liquid.

Mode of Technology Transfer

It is anticipated that the results of this study will provide information and direction for any further use of sol-gel chemistry to treat heavy metal-contaminated waste.

2 Experimental Parameters

Chemicals

Glassy samples were made by the sol-gel method using the alkoxide TMOS (Aldrich, 98%) or TEOS (Aldrich, 99%). The solvents were water and HPLC grade methanol (Aldrich, Milwaukee, WI) or HPLC grade ethanol (Aldrich). Researchers prepared a 0.1 M acid solution from trace metal grade nitric acid (Aldrich, 70%), and a 0.2 M caustic solution from trace metal grade ammonium hydroxide (Fisher, 20.9%). Lead (II) acetate trihydrate (Aldrich, 99%) was used to make three stock solutions of different Pb^{+2} concentration: 10,991 ppm, 109.91 ppm, and 54.96 ppm. Complete solubility of lead acetate required slight acidification, which was achieved by adding 0.5 mL concentrated nitric acid to 100 mL lead acetate solution. ACS grade lead nitrate (Fisher Scientific, Pittsburgh, PA) was also used as a second form of lead. All water was distilled and deionized with a Milli-Q Plus system (Millipore Systems, Bedford, MA). All chemicals were used as received.

TCLP requires an acidic solution of 4.93 +/- 0.05 pH. This extraction solution was prepared from trace metal grade glacial acetic acid (Fisher) and sodium hydroxide (Aldrich, 97%) as instructed in the EPA's SW846 Method 1311 (EPA 1986).

Sol-Gel Procedure

Four different methods were used to apply the sol-gel process. Method 1 sequentially added 15 to 50 mL of water, 0.04 to 0.1 mL of concentrated nitric acid, and 1.5 to 15.5 mL of TEOS to a specific amount of solid lead nitrate. After stirring, the lead nitrate was completely dissolved. The gels were dried at 70 °C for 3 days followed by curing at 500 °C for 12 minutes. Method 2 dissolved the lead acetate before adding it to the other ingredients. The general recipe for the second method was the sequential addition of 5 to 20 mL of 1.0 M TMOS in methanol, 5 to 20 mL water, 10 mL of 0.1 M nitric acid and/or 10 mL of 0.2 M ammonium hydroxide, and 10 mL of 0.05 M lead acetate (109.92 mg added Pb^{+2}). These gels were aged for 4 days at room temperature and dried in a two-stage process; 2 hr at 65 °C and overnight at 100 °C. Method 3 combined a methanol mixture and

an aqueous mixture. The general recipe for the third method was to mix equal amounts (10.0 mL) of neat TMOS and methanol in a beaker. In a second beaker, 10.0 mL of a lead acetate solution was combined with 10.0 mL water and 3.0 mL of 0.1 M nitric acid. The lead acetate solutions were either 11,000 ppm, 110 ppm, or 55 ppm Pb^{+2}. The aqueous mixture was added to the TMOS/methanol mixture with gentle agitation. Solidification occurred in 2 to 3 days at room temperature. The heat treatment conditions varied with experiment. Method 4 was prepared similarly to Method 3 except for the heating conditions. An aqueous mixture was prepared from 10 mL of 0.1 M nitric acid, 5 mL of water, and 5 mL of one of two lead acetate solutions: 11,000 ppm Pb^{+2} or 55 ppm Pb^{+2}. This aqueous mixture was then added to 20 mL of 1.0 M TMOS in methanol. Five days of continuous stirring at room temperature resulted in solidification. The gels were dried at 70 °C for 5 days. The gels were further dried at 110 °C for either 19 or 44 days.

Immobilization Test Procedure

The EPA established the TCLP as the method to determine the amount of leachable metal in a sample. For lead, a leachable concentration less than 5.0 ppm passes the TCLP. The immobilization of lead in glass by the sol-gel process was tested in two steps. Preliminary results were obtained in the first step by extracting with water (pH = 7.0) in a modified TCLP method. Samples were also subjected to an extraction with the 4.93 pH extraction fluid of the TCLP method in the second step.

Samples for TCLP must have particles less than ¼ in. in diameter. The sol-gel glasses met the particle size requirements as they broke into small pieces during the drying stage of the sol-gel process. After the sol-gels are transferred to an extraction vessel (plastic bottles), the appropriate extraction fluid is added at a ratio of 20 mL solution per gram of sample. Extraction of lead from the sol-gels proceeds for 18 hr with agitation. The sample is decanted, and the solution is analyzed by AA (Perkin-Elmer [Norwalk, CT] Model 3030B).

3 Test Results

Method 1

The first method added solid $Pb(NO_3)_2$ directly to the sol-gel ingredients without prior dissolution and omitted the addition of alcohol. Many different ratios of the added ingredients were tried. The amount of the lead in the final product ranged from approximately 430 mg to 1080 mg. The behavior of the final glass products had varying results, but all greatly exceeded the TCLP limit of 5 ppm. The calculated percent of immobilized lead ranged from 67 to 0 percent with most samples falling between 15 and 30 percent. Thus, the majority of the introduced lead leached out from all the samples. Visual inspection of the final glass products revealed a white or yellow precipitate coated on and around the surface of the SiO_2 particles. This indicates that the $Pb(NO_3)_2$ recrystallized out of solution without incorporation into the glassy matrix.

Method 2

The second method used a different form of the lead, dissolved this lead salt before addition into the mixture, and subjected the gel to a lower final temperature than Method 1 (100 °C versus 500 °C). Specifically, lead nitrate was replaced by a solution of lead acetate. Dissolution of the salt before addition was done to maximize the participation of lead ions in the condensation process. The alkoxide was TMOS instead of TEOS and methanol was used in the mixture. Experiments were performed varying the ingredients in content and relative amounts among the sol-gels. Two sol-gels were made with an acid catalyst (0.1 M HNO_3) to compare to two sol-gels made with a base catalytic (0.2 M NH_4OH). Also, a set of sol-gels was prepared by a two-step catalyst process; sequential addition of the acid followed by base. For all three sets, TMOS and water were adjusted to provide a high and a low water condition for the formation of sol-gels. A gentler extraction of the final glasses was performed using water because of the considerable lack of success in Method 1. Demonstration of immobilization under a gentler extraction would indicate improvement over Method 1, but a harsher extraction would be required to determine the extent of success.

Table 1 shows the results of leaching these sol-gel samples with water. Samples 1 and 2 used an acid catalyst, samples 3 and 4 used the base catalyst, and the remaining samples were prepared with both catalysts. All samples failed this modified TCLP test. A crackling sound was heard with several samples with the addition of the aqueous extraction fluid suggesting incomplete formation of the matrix. Calculations showed that over 50 percent of the lead usually leached from the sol-gels regardless of the formulation conditions. The base catalyst performed slightly better than the acid catalyst and the two step catalyst process had widely varying results. Only slight improvements over Method 1 results are noted in Table 1.

Table 1. Analysis of leachable lead from samples made from Method 2.

Sample ID	Initial Pb (mg)	AA Results (ppm)	Leached Pb (mg)	Immobilized Pb (%)
1	109.9	2220	71.0	35.4
2	109.9	6000	66.0	39.9
3	109.9	1434	41.6	62.1
4	109.9	6000	60.0	45.4
5	109.9	2820	53.6	51.3
6	109.9	6000	108.0	1.8
7	55.0	1709	29.0	47.1
8	109.9	5700	62.7	43.0

Method 3

The third method differed from Method 2 in the final temperature used to treat the gel. Three different final temperatures were used, including one temperature substantially higher than any other gel treatment. Three sets of acid catalyzed sol-gels were made under different heat treatment conditions to identify critical parameters for immobilization of lead. The ingredients and ratios were the same for all the sol-gels, except for the lead content. For each set, either 110 mg, 1 mg, or 0.5 mg of Pb^{+2} was introduced into each sol-gel. Processing temperatures are based on the boiling point of methanol (65 °C) and water (100 °C). The drying condition for the glassy products of Set A was 70 °C for 24 hr immediately following gelation to remove any remaining methanol. These glasses were then kept at room temperature until TCLP. The glasses of Set B aged 2 days at room temperature and then were dried at 100 °C for 24 hr and at 120 °C for 12 hr. At these temperatures, any remaining water and methanol were removed. These products were also kept at room temperature until TCLP. In contrast, the final products of set C were dried at 70 °C for 24 hr and then 100 °C for 2 hr to remove methanol and water. These glasses were then heated from 100 to

700 °C at a rate of 2 °C per minute and held at this elevated temperature for 5 days. These glasses cooled and were stored at room temperature until leachability testing.

All nine samples from Sets A, B, and C were extracted with water instead of acidic extraction fluid in the TCLP method. Table 2 shows the AA analysis results from this modified TCLP test. Included in the table is the calculated percent of lead immobilized. The samples in Sets A and B all have low levels of immobilized lead for the three lead loadings. Increasing the treatment temperature from 70 to 120 °C had little if any beneficial effect on lead stabilization. Three of the samples showed no stabilization of lead cations. Only the highest lead loading (110 mg) indicated any real involvement of lead in the sol-gel matrix.

In contrast to the behavior of Sets A and B, lead was almost completely trapped in the sol-gels of Set C, and all samples passed this modified TCLP test. The maximum loss of lead from the sol-gels of Set C was approximately 2 percent, and its optimal performance occurs with the maximum lead loading.

The sol-gels of Set C were formed again in triplicate for each initial lead loading. These sol-gels were subjected to TCLP with the acid extraction solution. Table 3 shows the results of AA analysis of the TCLP acid extracts from these sol-gels along with the calculated amount of immobilized lead. For comparison, if the lead completely leached from these glasses, 110 mg Pb^{+2}, 1 mg Pb^{+2}, and 0.5 mg Pb^{+2} would result in approximate measured AA values of 1450 ppm, 17 ppm, and 8.5 ppm, respectively. All sol-gels achieved greater than 97 percent immobilization of lead using the acidic extraction. However, the sol-gels formed with the greatest initial lead content failed the TCLP test since the lead concentration in the acidic extraction solution exceeded 5.0 ppm.

Table 2. Analysis of leachable lead from samples in sets A, B, and C.

Sol-Gel Set	Sample ID	Initial Pb (mg)	AA Results (ppm)	Leached Pb (mg)	Immobilized Pb (%)
A	1	109.9	630	68	38.11
A	2	1.1	29	1	0.00
A	3	0.5	4	0.45	14.90
B	4	109.9	720	76.3	30.44
B	5	1.1	13	1	0.00
B	6	0.5	6	0.5	0.00
C	7	109.9	0.2	0.01	99.99
C	8	1.1	0.3	0.027	97.56
C	9	0.5	0.1	0.008	99.00

Table 3. Analysis of leachable lead in replicate samples with three different lead loadings using the sol-gel method of Set C.

Sample ID	Initial Pb (mg)	AA Results (ppm)	Leached Pb (mg)	Immobilized Pb (%)
1	110	21.0	1.60	98.5
2	110	24.1	1.83	98.3
3	110	59.0	4.54	95.9
4	1	0.5	0.03	96.9
5	1	0.3	0.02	98.1
6	1	0.7	0.03	96.9
7	0.5	0.0	0.00	100.0
8	0.5	0.0	0.00	100.0
9	0.5	0.1	0.01	98.7

Method 4

The fourth method examined the drying period at a low temperature similar to that used in Method 2. The gels were prepared similar to Method 3 in that the aqueous components were combined and added to the alkoxide. A solution of lead acetate was used to incorporate either 55 mg or 0.27 mg Pb^{+2} into the sol-gel. The two-stage drying process of Method 2 was used with slight modification to investigate the effect of drying time on lead immobilization. After drying the gels at 70 °C for 5 days, the gels were divided into two sets, each set containing both high and low Pb^{+2} content. The glassy products of Set A were heat treated at 110 °C for 19 days while the glassy products of Set B were heat treated at 110 °C for 44 days.

Table 4 shows the analysis results of the TCLP acid extracts from these sol-gels. Sample 9 of Set B passed TCLP, but all others failed. Greater amounts of lead were retained in samples with higher initial lead loadings. The percentage of lead immobilized was in the mid-eighties regardless of the heat treatment time. In contrast, the samples with lower initial lead loadings showed better lead immobilization when heated longer.

Table 4. Analysis of leachable lead from samples in Sets A and B.

Sol-gel Set	Sample ID	Initial Pb (mg)	AA Results (ppm)	Leached Pb (mg)	Immobilized Pb (%)
A	1	54.96	205	5.95	89.2
	2	54.96	360	10.08	81.7
	3	0.27	8.75	0.25	8.5
	4	0.25	7.50	0.20	16.7
B	5	54.96	35	9.38	82.9
	6	54.96	265	7.42	86.5
	7	54.96	255	7.40	86.5
	8	0.27	6.00	0.17	37.7
	9	0.27	3.75	0.11	60.0
	10	0.27	6.25	0.17	34.7

4 Discussion and Conclusion

Based on the results, a successful method (Method 3, Set C) was obtained for the stabilization of lead in the sol-gel glass matrix. The principle criteria for success were the use of an acetate salt rather than a nitrate salt, dissolution of the salt before addition to the sol-gel precursor chemicals, and a high curing temperature. Several issues relating to the use of sol-gel chemistry as a viable S/S technique can now be discussed.

Temperature

The results of Table 3 clearly illustrated the treatment temperature of the glass to be the dominant parameter for increased immobilization of lead. A 700 °C curing temperature created the most stable monolith. This result can be directly related to the gel structure. For any constituent to leach, it must first dissolve in the pore water of the solid matrix or in the leachant permeating the solid (Spence 1993), implying that the constituent must be present at the solid-liquid boundary. It has been shown that heat treatment of gels at elevated temperatures reduces the number of pores and their connectivity (Hench and West 1990). In addition, faster drying rates create glassy products with smaller surface areas and smaller pore volumes (Schwartz 1989). It is not surprising that increasing the gel processing temperature results in a glass that is denser and, therefore, better at immobilizing lead. Higher treatment temperatures may continue to improve the stabilizing character of the glass.

A comparison of results from sol-gel Set B in Table 2 to the results in Table 4 indicates that longer treatment times at a low temperature also improves performance. As the gel ages, the pore structure condenses and the glass densifies preventing the leachability of lead. These gels would slowly approach, but would not reach, the final characteristics of gels heated at elevated temperatures. Unfortunately, the need to heat treat the gel to improve its S/S characteristics eliminates one of the expected benefits of sol-gel chemistry over vitrification. These temperatures are beginning to approach the levels needed for glass melting of 1200 °C and above (Vance 1986).

One further comment can be made regarding heating and drying of gels. Drying stresses can introduce catastrophic fracture of the final gel (Hench and West

1990). Problems with cracking and crazing of the glass has limited its applications. On several occasions during these experiments, it was observed that catastrophic fracturing had caused the final gel to actually explode out of its beaker. This behavior increases the surface area of the final product and allows additional leaching of lead from newly exposed sites.

Sensitivity of Sol-Gel Chemistry

Numerous references have indicated the sensitivity of the sol-gel chemistry with differences in gel structure as a function of preparation conditions (Schwartz 1989). The pH of the solution has a dramatic effect on the glass structure, creating monolithic structures under acidic conditions versus spherical particles under basic conditions (Dave and Maccrone 1986). It has been shown that acidic gels and low water conditions will result in greater bulk density with lower pore volume than the same acidic gels with high water conditions (Schwartz 1989). Differences in rates of hydrolysis relative to the rates of condensation during gelation produce a very different polymer structure (Brinker et al. 1982). This research did not observe great effects on the stabilization ability of the glass related to the pH conditions; none of these glasses worked well. Reproducibility was sometimes a problem directly related to reaction sensitivity. Nevertheless, it is not useful to use an S/S technique that is sensitive to the initial conditions, especially since the chemistry of the heavy metal contaminated waste may vary dramatically.

Counter Ion Effects

Other work has shown that metal ions have been incorporated into sol-gel matrices from the metal acetate in aqueous solutions. Copper ions have been incorporated as structural probe ions in the glass (Dave and Maccrone 1986) and even lead has been incorporated into a titanate matrix (Schwartz 1989), but these require careful control of the chemistry. The high treatment temperatures for the gels are needed to degrade the acetate from the matrix. Results from Method 1 indicate that lead from the nitrate can interfere with the gelation process and precipitate from the glass without immobilization. There would be no control over the metal counter ion in actual waste samples.

Loading Capacity

It is important to consider the loading capacity when comparing methods. Loading capacity is the amount of waste that can be stabilized by a given amount of matrix. Low loading rates where little chemical or physical encapsulation occurs can be regarded as merely dilution of the waste to pass TCLP. In sol-gel chemistry, mixing components and waste on a molecular level should maximize chemical interactions and optimize the loading capacity. Other research that shows chemical and physical interactions between the gel and an entrained metal are usually interested in dopant levels of the metal, which are much lower than S/S levels. Using the best result in Table 2, 110 mg of Pb+2 were effectively loaded into 2.44 g of matrix for a loading rate of less than 5 percent. This sample passed a modified TCLP extraction using water, but a similar sample failed when using the acidic extraction fluid. The 5 percent value can thus be considered as an upper bound to loading capacity in these experiments. This result can be compared to Portland cement where a typical loading capacity is a 1:1 mixture of waste to cement, or 50 percent (Conner 1990).

Limited Applicability

To maximize the potential success of sol-gel chemistry as an S/S technique, this research focused only on stabilization of solutions where the metal alone is present and in cationic form. Clearly, no real waste will be as pure and controlled as this type of solution. Some aqueous wastes contaminated by metals may result from industrial processes such as electroplating baths or from extracting the metals from solid wastes in a wash solution, but such instances are few. Sol-gel processes have been used to encapsulate particulates to impart desired bulk characteristics to the glass product (for example, soot for blocking infrared radiation (Lux et al. 1990)). However, based on the need for tightly controlled chemistry and glass fracture at boundary surfaces, sol-gel encapsulation of solid wastes is not a likely application. Vitrification is primarily used in the highly specialized area of low-level radioactive waste stabilization. Sol-gel chemistry would similarly need a specialized niche to be useful.

Cost

Final comments can be made regarding cost. One reason the siloxane glasses TEOS and TMOS were used in these studies is that they are the least expensive precursors. TMOS costs $33.20 for 100 g. Using a loading capacity of 5 percent, it would cost $664 to encapsulate 100 g of lead. For comparison, 100 g of lead

could be encapsulated in Portland cement at a cost of about 20 cents using the same 5 percent loading capacity.

Conclusion

The results reported in this document have shown that sol-gel processing can minimally stabilize lead from solutions. The successful stabilization results indicate that some metal can be encapsulated in the glass matrix. Due to the numerous problems listed earlier, however, it is unlikely that sol-gel chemistry will provide a useful S/S tool. It is too sensitive to chemistry, too limited in application, and too expensive to compete with common cementitious processes.

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REPORT DOCUMENTATION PAGE

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of Information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 2000	Final

4. TITLE AND SUBTITLE
Sol-Gel Stabilization of Heavy Metal Waste

5. FUNDING NUMBERS
62720
D048
U79

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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Champaign, IL 61826-9005

8. PEFORMING ORGANIZATION REPORT NUMBER
TR-00-6

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers (USACE)
20 Massachusetts Avenue, NW.
Washington, DC 20314-1000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

9. SUPPLEMENTARY NOTES
Copies are available from the National Technical Information Service, 5385 Port Royal Road, Springfield, VA 22161

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

The Army is continually faced with the disposal or treatment of media contaminated with heavy metals such as lead, chromium, and cadmium. The types of media are varied and include soils, ashes, and sludges. Waste having a leachable metal concentration above the Toxicity Characteristic Leaching Procedure limit established by the U.S. Environmental Protection Agency can be treated to render it non-hazardous.

Several stabilization/solidification (S/S) processes are used for the treatment of hazardous wastes. Vitrification, for example, incorporates hazardous waste into glass, but the high temperatures needed to make the glass are undesirable. Sol-gel chemistry is a means to make glass at low temperatures. Also, the heavy metals can be chemically incorporated in the glass matrix rather than merely encapsulated. This work examines the ability of sol-gel chemistry to replace vitrification as an S/S technique. A recipe was formulated for immobilizing lead in glass by the sol-gel process. The merits of the process are discussed.

Results showed that sol-gel processing stabilized some lead from solutions and encapsulated some metals in a glass matrix. However, sol-gel was found to be too sensitive to chemistry, too limited in application, and too expensive to compete with current S/S processes.

14. SUBJECT TERMS
hazardous wastes; sol-gel; waste disposal; heavy metals; stabilization solidification

15. NUMBER OF PAGES
24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR