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Effects of Curing Temperature on the Leachability of Lead Undergoing Solidification/Stabilization with Cement

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Curing temperature was found to dramatically affect the amount of waste leached from a solidified waste/cement matrix between 2 and 40°C. Using lead nitrate as a model waste, samples cured for 7, 14, and 28 days at a cure temperature of 40°C leached very little lead (1–3 mg/liter), while at a cure temperature of 2°C samples leached approximately 25 times more lead (20–90 mg/liter). The results indicate that curing temperature is a very crucial variable to consider when solidifying waste with cement if maximum stabilization is to be achieved.

INTRODUCTION

The hazardous waste disposal problem is a major national concern. Because of the extremely large amounts of toxic chemicals that are being released into the environment, the federal government has been forced to regulate the disposal and management of hazardous wastes. The Environmental Protection Agency (EPA) classifies a waste as hazardous if it is nondegradable, toxic, may cause detrimental cumulative effects, or poses a substantial threat to human health or living organisms (*1*). Some wastes are recycled, detoxified, or incinerated which decreases the amount of waste that must be disposed, but in almost all cases some residue still remains. One of the most cost-effective methods available for disposing of this residue along with other wastes not recycled or incinerated is placement in landfills. In 1984, the Hazardous and Solid Waste Amendments (*2*) to the Resource Conservation and Recovery Act (RCRA) (*3*) banned the placement of noncontainerized liquids in landfills. As a result, it is necessary that some form of solidification/stabilization (S/S) pretreatment be performed prior to landfilling. The process of solidification/stabilization is a recommended treatment alternative for many RCRA wastes (*4*). It is estimated that 16 million metric tons per year of waste could sustain S/S treatment and landfilling (*5*). According to the Toxic Release Inventory for 1994, 289 million pounds of toxic wastes was disposed of in landfills in 1994 (*6*). A significant portion of modern industrial waste is disposed by solidification in cements and slags each year.

The chemical reaction that takes place when Portland cement and water are mixed together is called hydration, and the heat generated, heat of hydration. This heat is a critical factor that influences the ultimate structure of concrete formed. The total amount of heat generated is dependent on the chemical composition of the cement, and the rate is affected by curing temperatures among other variables (*7*). The effects of curing temperature on the stabilization of waste in cement are examined by determining leaching rates of lead.

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MATERIALS AND METHODS

Sample Preparation

Each set of solidified samples for a particular cure temperature was prepared from a bulk batch to eliminate homogeneity problems within any particular set of samples. Bulk batches typically contained 294 g of ordinary Portland cement type I, 46 g lead nitrate [$Pb(NO_3)_2$], and 162 g deionized water, giving a composition of 10% lead by weight to cement and a water/cement ratio of 0.55. The batch was mixed in the following manner: $Pb(NO_3)_2$ was dissolved in 120 ml of water by vigorously shaking the solution. This solution was placed in a normal household blender. The cement was added to the blender and mixed with a stir rod until all cement was moist. The solution beaker was rinsed with the remaining water and placed in the blender. The mixture was blended on high speed for 5 min with periodic scraping of the sides of the blender. Approximately 20 g of the bulk batch was scooped into 20-ml borosilicate screw-cap vials. There were typically four samples made for each set of cure times (7, 14, 28 days) from a bulk batch. Care was taken to ensure that representative bulk samples from the top, middle, and bottom were obtained for each set of cure times. Once a set of samples were made, the borosilicate vials were capped, and samples were stored at a particular curing temperature until the appropriate time for the experiment.

Curing Temperature

While a set of samples were curing, the surrounding temperature was held constant. Experiments were conducted using three curing temperature ($\pm 2°C$): 40, 24, and 2°C. A standard laboratory oven was used for the 40 and 24°C samples, and a refrigerator was used for the 2°C samples.

Crushing

After the appropriate cure time, the samples were crushed in the following manner: A vial was placed into a wide-mouth plastic bottle, and the vial broken by striking it with a steel rod. The whole cement/Pb sample slug was removed from the glass. The entire sample was crushed with a steel rod, and particles between 8.0 and 9.5 mm were retained while all particles smaller than 8.0 mm were eliminated to ensure reproducibility (*8*). The mass of the entire sample was recorded (average sample mass: 9.70 g of the original 20-g bulk batch) and placed into a 250-ml Nalgene wide-mouth high-density polyethylene bottle.

TCLP Procedure

To each sample, a volume of TCLP leachant No. 2 (5.7 ml/liter glacial acetic acid aqueous solution at pH 2.88) was added at a volume of 20 times the weight of the sample. The extraction period for the sample was 18 h under rotary agitation at 30 rpm. Subsequently, the sample was filtered using Grade GF/F 0.7-μm glass-fiber filter paper. The sample was filtered within 2 h of the 18-h extraction period to ensure reproducibility (*8*). The filtrate was acidified using concentrated nitric acid and analysis for lead was performed using a Perkin–Elmer Model 5000 atomic absorption spectrometer at 283.3 nm. If all lead is extracted from $Pb(NO_3)_2$ waste/cement matrix, concentration of lead in leachate will be approximately 3000 mg/liter. This procedure differs from the EPA TCLP experiment in that one-tenth of the amount of sample was used (10 g instead of 100 g) (*9, 10*).

TABLE 1
Effects of Curing Temperature on Amount of Lead Leached

	Pb leached (mg/liter)[a]		
Days cure	40°C	24°C	2°C
7	Not recorded	6.7 ± 1.3	87 ± 3
14	3.1 ± 0.4	4.9 ± 1.2	82 ± 6
28	1.1 ± 0.2	3.8 ± 0.5	19 ± 1

[a] Mean ± SD, $n = 4$.

RESULTS AND DISCUSSION

The effects of curing temperature on the amount of lead leached in a $Pb(NO_3)_2$ waste/cement matrix are summarized in Table 1. Curing temperature was found to dramatically affect the amount of waste leached from a solidified waste/cement matrix between 2 and 40°C. Using lead nitrate as a model waste, samples cured for 7, 14, and 28 days at 40°C leached very little lead (1–3 mg/liter), while at 2°C samples leached approximately 25 times more lead (20–90 mg/liter). Curing temperature is inversely proportional to the amount of lead that leaches from a lead waste/cement matrix. This can be further verified by examining Fig. 1, which clearly shows that the lower the temper-

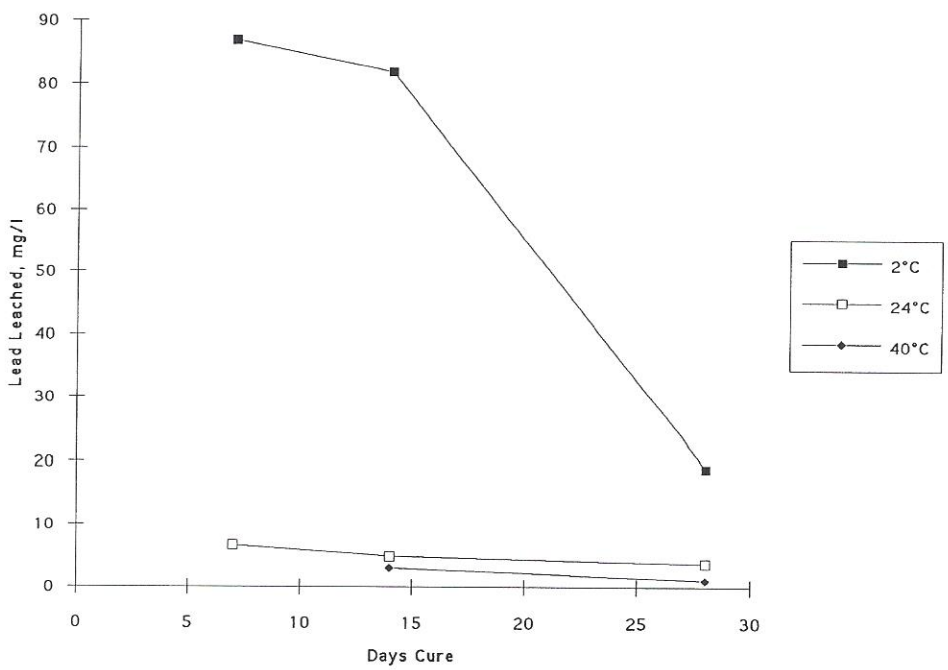

FIG. 1. Effects of curing temperature on amount of lead leached.

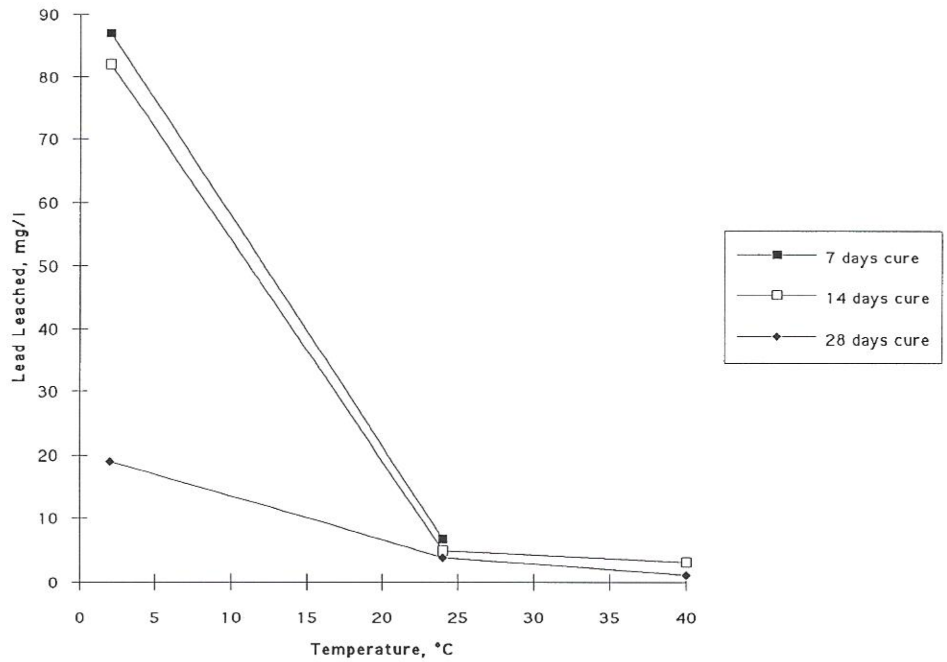

FIG. 2. Effects of curing time on amount of lead leached.

ature, the higher the lead leach rates. The same trend occurs for a particular cure time as can be seen in Fig. 2. There is also an inverse relationship between cure time and amount of lead leached. Although the 2°C data clearly show a high leach rate for lead at all cure times, there is a drastic decrease in the amount of lead leached at 28 days as compared with 7 and 14 days. During crushing of these samples, 28-day samples were harder in texture than 7- and 14-day samples, which tended to be very mushy. This is an indication that the 2°C samples may bind the lead over longer cure times.

The objective of the solidification/stabilization process using waste/cement is to reduce the mobility of the waste by forming a granular or monolithic solid that incorporates the waste. The solid matrix forms because of the hydration of silicates in the cement. Tricalcium/dicalcium silicates are major crystalline compounds and tricalcium aluminate/calcium alumnoferrite are minor components present in Portland cement (*11*). The cementation process binds free water, increases the pH, and alters other chemical properties of the mixture. Once water is added to a waste/cement mixture, the cementation process begins. The water hydrates the calcium silicates and aluminates in the cement to form calcium silicate hydrate. Inert material and unreacted cement grains are entrapped by densely packed fibrils of silicate growing out from the cement grains. Hydration of tricalcium and dicalcium silicates results in the formation of tobermoite and crystalline calcium hydroxide (*12*). The rate of cement hydration is rather insensitive to temperature in the range 0–40°C (*13*); however, for the hydration process to proceed the cementation reagents must react after being wetted with water. The addition of an impurity such as a hazardous waste to the matrix may inhibit the setting and curing of the cement by interfering with the wetting process by coating the reacting surfaces. In fact, the rate-retarding effect of lead salts on cement hydration may be due to the rapid formation of a gelatinous coating of mixed lead salts around cement clinker grains (*14, 15*). This agrees well with our results here. The lower curing temperature of the lead waste/cement matrix decreases the solubility of lead salts formed in the cement, resulting in an increase in gelatinous coatings on grains. This increase of coating at lower curing temperatures causes less contact between the cement grains and water, retarding the hydration process and solidifying/stabilizing power of cement. By varying the curing temperature, the solubility of waste salts formed directly influences the heat of hydration and ultimately the holding power of cement for added waste.

CONCLUSIONS

The results indicate that curing temperature is a very crucial variable to consider when solidifying waste with cement if maximum stabilization is to be achieved. Whether the waste/cement matrix is cured during winter or summer months drastically affects the extent that the waste has been solidified/stabilized. Similar results seem to be obtained at the two higher experimental temperatures; however, the 40°C results are well below the EPA leaching standard for lead of 5 mg/liter (*10*) at shorter cure time while 24°C results are borderline. Curing at higher temperatures (incubate waste/cement matrix) results in maximum and rapid binding of waste in cement, while low cure temperatures result in waste leaching that could be prevented.

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