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Effects of Particle Size and Contact Time on the Reliability of Toxicity Characteristic Leaching Procedure for Solidified/Stabilized Waste

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Inconsistency in leaching results using the Toxicity Characteristic Leaching Procedure (TCLP) indicates that the procedure should contain specific guidance with respect to the following parameters: (1) minimum particle size, (2) contact time limit between leachant and waste. Experimental data show that there is approximately a 50% decrease in the amount of waste leached when a minimum particle size of 8 mm is applied. Results indicate that as the contact time between leachant and waste increases, the amount of waste leached increases drastically. The results suggest that restrictions should be set on these two parameters for TCLP results to be reliable and comparable for solidified/stabilized waste.

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 was 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, and poses a substantial threat to human health or living organisms. Some wastes are recycled, detoxified, or incinerated which decreases the amount of wastes 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. The 1984 Amendments of the Hazardous and Solid Wastes Act (*1*) to the Resource Conservation and Recovery Act (RCRA) (*2*) banned the placement of noncontainerized liquids in landfills. As a result, it is often 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 (*3*). It is estimated that 16 million metric tons per year of waste is a candidate for S/S treatment and landfilling (*4*). According to the Toxic Release Inventory for 1994, 289 million pounds of toxic wastes was disposed of in landfills in 1994 (*5*). Approximately 40% of all wastes that are disposed of in landfills is pretreated by S/S processes.

Before solidified/stabilized waste can be landfilled, it must be analyzed by the EPA Toxicity Characteristic Leaching Procedure (TCLP) (*6, 7*) to determine the leachability of a solidified waste encountering typical environmental conditions. The TCLP test was

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designed to determine whether a waste, if mismanaged, has the potential to pose a significant hazard to human health or to the environment due to its propensity to leach toxic chemicals. During the TCLP test, waste samples are crushed to particle size less than 9.5 mm and extracted with a leachant. The leachant depends on the alkalinity of the waste. A liquid leachant-to-solid ratio of 20:1 is used for an extraction period of 18 h. The leachate is filtered prior to conducting the contaminant analyses. The results are compared with an established standard to determine if the solidified/stabilized waste can be landfilled. The standard TCLP requires that all samples be passed through a 9.5-mm screen before leaching. This requirement may not be appropriate for solidified/stabilized wastes. Solidified/stabilized wastes have been solidified to withstand the environmental stresses encountered in a landfill, and well-stabilized waste may remain more or less intact whereas poorly stabilized wastes are significantly degraded (*8*). The net result may be that solidified/stabilized waste does not need a preliminary size reduction of samples or, at the minimum, a range of size particles to maintain comparable TCLP results. There is also no mention of contact time limit between leachant and waste. Once a sample is prepared for TCLP by adding the leachant solution, the leaching process begins prior to the 18 h of rotation and continues until the leachate is filtered, removing the waste contamination source. The TCLP does not contain specific guidance with respect to the following parameters: (1) minimum particle size, (2) contact time limit between leachant and waste. Experimental data show that drastic differences in final concentration of waste leached can be obtained when these two parameters are not considered and restrictions are necessary.

MATERIAL AND METHODS

Sample Preparation

Each set of solidified samples 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, 56 g lead nitrate [$Pb(NO_3)_2$], and 175 g deionized water, giving a composition of 12% lead by weight to cement and a water/cement ratio of 0.60. The batch was mixed in the following manner: $Pb(NO_3)_2$ was dissolved in one-half the water with minor heat. This solution was placed in a normal household blender. The solution beaker was rinsed with the remaining water and placed in the blender. The cement was added to the blender and mixed with a stir rod until all cement was moist. The mixture was blended on high speed for 5 min with periodic scraping of the sides of the blender. The bulk batch was then scooped into 20-ml borosilicate screw-cap vials. Once a set of samples were made, the borosilcate vials were capped, and samples were stored in a cabinet until the appropriate time for the experiment. For the particle size experiment, there were typically 21 samples made per bulk batch; 7 samples each for 7, 14, 28 days of cure time. Care was taken to ensure that representative bulk samples from the top, middle, and bottom were obtained for each set of cure times. Each set of samples for a particular cure time typically included 3 samples containing 10 g of bulk batch that were crushed to particle sizes less than 9.5 mm, 3 samples containing 20 g of bulk batch that were crushed to obtain 9 to 10-g samples with particle sizes between 8 and 9.5 mm, and 1 sample containing 10 g of bulk batch that was not crushed but left in solidified form ($\approx$ 24 mm diameter $\times$ 10 mm high cylinders). For the contact time experiment, one set of 24 samples was prepared that included 6 samples each for four different time experiments.

Samples contained 15 g of bulk batch and were crushed after 28 days of cure time to obtain 5 to 9-g samples with particle sizes between 8 and 9.5 mm. Note that the mass of sample for the contact time experiment between 8 and 9.5 mm after crushing has a large range, 5–9 g. Expertise in crushing was gained in later experiments as can be seen in the mass of particles, 9–10 g, retained in the particle size experiment.

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 was broken by striking it with a steel rod. The whole cement/Pb sample slug was removed from the glass. If the initial sample contained 10 g of bulk batch, the entire sample was crushed with a steel rod until all particles could pass through a 9.5-mm sieve. The mass of the entire sample was recorded (typically between 9.60 and 9.95 g) and placed into a 250-ml Nalgene wide-mouth HDPE bottle. If the initial sample contained 15 or 20 g of bulk batch, the entire sample was crushed with a steel rod, and the particles between 8.0 and 9.5 mm were retained while all particles smaller than 8.0 mm were eliminated. Typically, 9.00–10.00 g of the original 20-g bulk batch sample was retained for the particle size experiment and 5–9 g for the contact time experiment. The mass of each sample was recorded and placed into a 250-ml Nalgene wide-mouth HDPE bottle.

TCLP Procedure

To each sample, a volume of TCLP leachate 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 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. For the particle size experiment, the samples were filtered within 2 h of the 18-h extraction period. 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).

Contact Time Experiment

The regulations do not state any specific time constraints for contact time between sample and leachant fluid; therefore, a second experiment was conducted concerning contact time. For the contact time experiment, samples were prepared and the TCLP test was conducted as stated earlier with the exception that the time between crushing, agitating, and filtering was varied. There were four different trials as illustrated in Fig. 1: (1) crushing of sample and retention of particles between 8 and 9.5 mm (typically 5–9 g of sample), addition of leachant, immediate TCLP for 18 h, and immediate filtering of sample; (2) crushing of sample and retention of particles between 8 and 9.5 mm (typically 5–9 g of sample), addition of leachant, 14-day contact time between sample and leachant, TCLP for 18 h, and immediate filtering of sample; (3) crushing of sample and retention of particles between 8 and 9.5 mm (typically 5–9 g of sample), addition of leachant, immediate TCLP for 18 h, 14-day contact time between sample and leachant, and filtering of sample; (4) crushing of sample and retention of particles between 8 and 9.5 mm

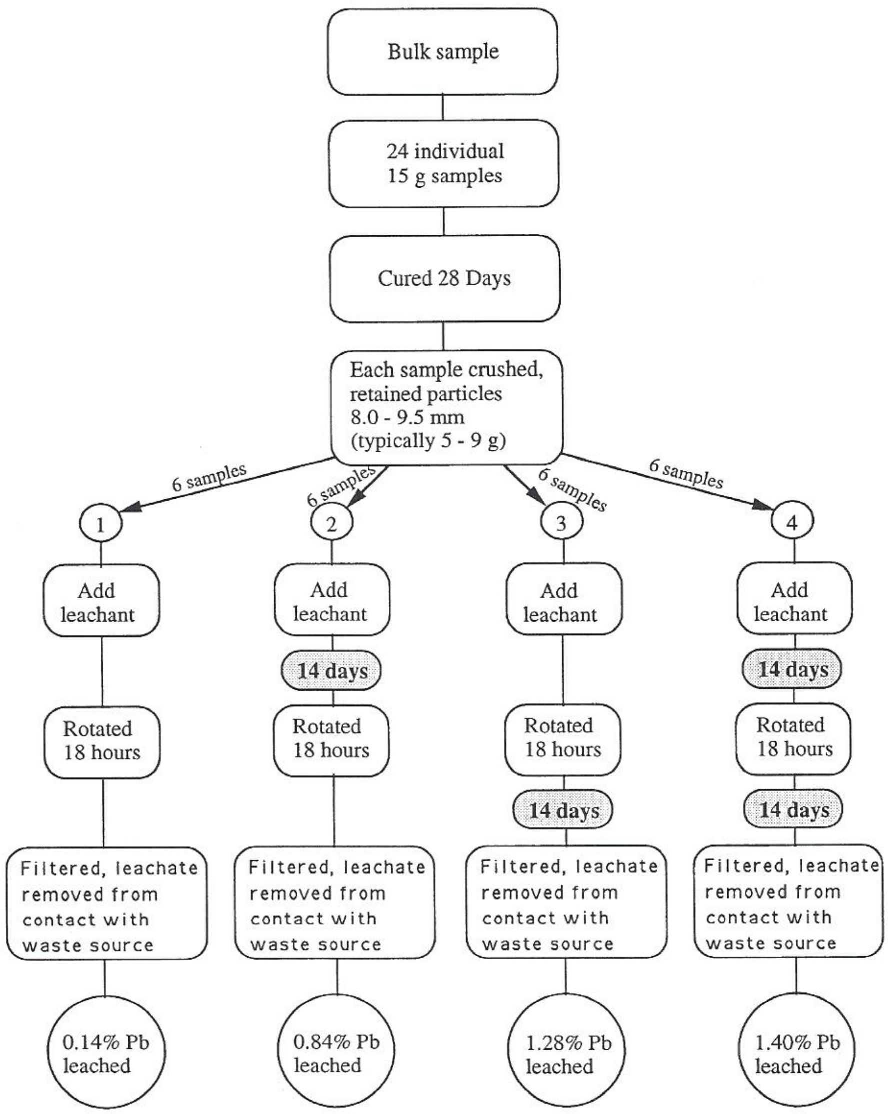

FIG. 1. Effects of contact time between leachant and waste.

(typically 5–9 g of sample), addition of leachant, 14-day contact time between sample and leachant, TCLP for 18 h, 14-day contact time between sample and leachant, and filtering of sample.

RESULTS AND DISCUSSION

Table 1 contains the data obtained for the particle size experiment. There is a major difference in the amount of lead leached at all cure times between the samples that were

TABLE 1
Effects of Particle Size on Amount of Lead Leached

	Pb leached (%)		
Days cure	<9.5 mm	8–9.5 mm	Whole
7	0.52 ± 0.11[a]	0.28 ± 0.05[a]	0.05 ± 0.05[b]
14	0.34 ± 0.08[a]	0.16 ± 0.03[a]	0.06 ± 0.04[b]
28	0.23 ± 0.07[a]	0.09 ± 0.03[a]	0.04 ± 0.03[b]

[a] Mean ± SD, $n = 12$.
[b] Mean ± SD, $n = 4$.

crushed to particle sizes less than 9.5 mm (per regulations) and samples that had a range of particle sizes of 8–9.5 mm. There is approximately a 50% decrease in the amount of lead leached and in the standard deviation for all time periods of cure. The larger standard deviation is attributed to the larger range of results obtained for each cure time. The samples crushed to sizes less than 9.5 mm have results that span ranges of 0.39, 0.33, and 0.25% Pb leached (7, 14, and 28 days of cure) as can be seen in Fig. 2. Samples crushed to particle sizes between 8 and 9.5 mm have results that span ranges of 0.15, 0.10, and 0.10% Pb leached (7, 14, and 28 days cure). This is a clear indication that better precision can be obtained using minimum and maximum particle sizes, making the TCLP test more valid.

It has been mostly assumed that bulk diffusion from cement-based systems is the driving force for contaminant release. Recent research has shown that the dissolution of

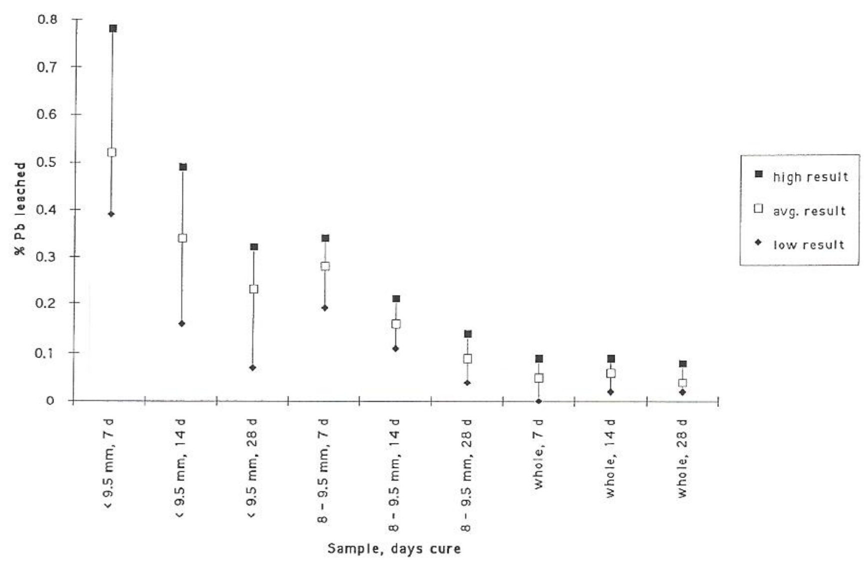

FIG. 2. Spread of percentage lead leached for each set of samples.

the outer shell of the waste form results in solubilization and release of contaminants from the leached shell (*9, 10*). This is referred to as the shrinking unreacted core. The inward diffusion of acid species into the alkaline-depleted leached shell controls the rate of contaminant leaching. This coincides very well with what is occurring here. The smaller the particle size, the more surface area that is exposed to the leachant, resulting in higher concentrations of Pb being leached. When samples are crushed to less than 9.5 mm, a wide range of particle sizes are obtained from micrometers to 9.5 mm. This was verified further by conducting TCLP analysis on samples that were not crushed, but left in their solidified form ($\approx$ 24 mm diameter $\times$ 10 mm high cylinders). Note in Table 1 that the results for whole samples cured for 7, 14, and 28 days gave similar percentages of Pb leached. This is attributed to all these samples having very similar, extremely small surface areas. Even if the particle size is given a range, there still will be a variation in surface area and final percentage waste leached. However, to control precision and to make the TCLP test more reliable, a minimum size particle should be used.

Similarly, the same effect is occurring in the contact time experiment. In the second trial, the 14 days of exposure to the leachant occurs prior to rotation of the sample. The particles are still between 8 and 9.5 mm which gives less surface area for acid exposure compared with the third trial, in which rotation produced smaller particles and, hence, a larger surface area prior to the 14 days of leachant exposure. It is expected that trial 3 should leach more lead than trial 2 because of the increase in surface area. As can be seen in Fig. 1, trial 3 leached 1.28% Pb whereas trial 2 leached 0.84%. In trial 4, it is expected that an even larger surface area will be obtained and, hence, a larger percentage of Pb leached, 1.40%. There is a major difference in percentage of Pb leached between trial 1 (leachant contact time during rotation only) and the other trials. In trial 1 0.14% Pb was leached. Once a sample is prepared for TCLP by adding the leachant solution, the leaching process begins prior to the 18 h of rotation and continues until the leachate is filtered, removing the waste contamination source. This is a clear indication that contact time with leachant is a crucial parameter that must be stated to obtain reliable and comparable results.

CONCLUSIONS

Solidified/stabilized wastes have been solidified to withstand the environmental stresses encountered in a landfill, and well-stabilized waste may remain more or less intact whereas poorly stabilized waste is significantly degraded. The results for uncrushed samples are an example. The net result may be that solidified/stabilized waste does not need a preliminary size reduction of samples or, at the minimum, a range of size particles to maintain reliable and comparable TCLP results. The results of this experiment indicate that some restrictions should be set forth by EPA with respect to minimum particle size and contact time between sample and leachant. Drastic differences in final concentration of waste leached can be obtained using the present procedure, which lacks these restrictions. If the TCLP test is used as the leaching test to determine whether a sample is hazardous or not, it must have restrictions on these two parameters for results to be reliable and comparable for solidified/stabilized waste.

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REFERENCES

1. *Fed. Regist.,* 1985, **50** (105), 23250–23258.
2. *Resource Conservation and Recovery Act,* 1976, PL 94–580.
3. *Comprehensive Environmental Response, Compensation and Liability Act of 1980,* 1980, PL 96–510.
4. Conner, J. R. *Chemical Fixation and Solidification of Hazardous Wastes.* Van Nostrand Reinhold, New York, 1990.
5. *Chem. Eng. News,* July 15, 1996, 29.
6. *Standard Methods for the Examination of Water and Wastewater,* 16th ed. APHA, AWWA, WPCF, 1985.
7. *Fed. Regist.* 1986, **51,** 21672–21692 (No. 114, Friday, June 13, 1986).
8. Means, J. L.; Smith, L. A.; Nehring, K. W.; Brauning, S. E.; Gavaskar, A. R.; Sass, B. M.; Wiles, C. C.; Mashni, C. I. *The Applications of Solidification/Stabilization to Waste Materials.* CRC Press, Boca Raton, FL, 1995.
9. Hinsenveld, M. *A Shrinking Core Model as a Fundamental Representation of Leaching Mechanisms in Cement Stabilized Waste.* Ph.D. dissertation, University of Cincinnati, Cincinnati, OH, 1992.
10. Baker, P. G.; Bishop, P. L. *J. Hazard. Mater.,* 1997, **52,** 311–333.