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STABILIZATION OF HAZARDOUS WASTE LANDFILL LEACHATE TREATMENT RESIDUE*

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Summary

Hazardous organic wastes lend themselves primarily to destructive treatment by processes such as incineration, biodegradation, chemical oxidation, and dechlorination. When these methods are feasible, all the problems associated with long-term effects are eliminated; thus, they are high on everyone's list of preferred treatment methods. However, many industrial wastes and contaminated materials contain small amounts of toxic organics at levels which make organic destruction processes not only very expensive, but sometimes ineffective. It seems likely now that the EPA intends to establish organic levels at which stabilization can be used in soil remediation and, perhaps at RCRA central treatment, storage, and disposal facilities (TSDFs). Also, in the case of "characteristic" wastes, the Toxicity Characteristic Leaching Procedure (TCLP) test when fully in force, will make it possible to remove wastes from the RCRA hazardous waste system if they meet both inorganic and organic leaching limits. While a number of vendors of stabilization services are offering organic "stabilization," very little data has been forthcoming at least publicly. The present paper focusses on dilute aqueous hazardous waste streams treatment.

Introduction

There are five distinct types of organic-containing wastes which might be encountered in stabilization:

(1) Oil- and solvent-based wastes such as used solvent, distillation bottoms, refinery wastes, etc. which are hazardous according to RCRA. Appendix VIII [1], the waste listings, the CCW and CCWE tables, the "California List" and the Land bans.

(2) Aqueous wastes containing large amounts — 1 percent to 20 percent or more — of water soluble or insoluble, emulsified organics which are hazardous according to the above regulations.

(3) Aqueous wastes containing large amounts — 1 percent to 20 percent or more — of water soluble or insoluble emulsified organics which are not

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hazardous, or which are hazardous only by the characteristic of ignitability or are marginal (like oil).

(4) Aqueous wastes containing small amounts of non-hazardous organics — less than 1 percent and usually in the 10–1,000 mg/l range — which are of interest in stabilization only when they affect cementitious and other reactions of the stabilization system.

(5) Aqueous wastes containing small amounts of hazardous organics — less than 1 percent and usually in the 10–1,000 mg/l range.

The last waste group above is the subject of this paper. Aqueous, inorganic waste streams containing one to 10,000 mg/l levels of hazardous organics are quite common, and will become even more so as a result of land-ban regulations which require destruction of organic-based wastes but leave some organic residue which may leach above allowable levels. For these reasons, it is important to develop *fixation*[1] techniques for low-level organics.

One important category of such wastes are landfill leachates. RCRA Subtitle C hazardous waste landfills, as well as Subtitle D landfills, generate leachates which must be collected and treated before subsequent discharge or reuse of the water. Chemical Waste Management (CWM) operates seven Subtitle C landfills. These leachates may contain an unusually large assortment of RCRA hazardous constituents. Although some organics are destroyed to levels below detection limits in leachate treatment processes, others remain in the treatment residues; metals are always concentrated in the residues. This paper discusses the stabilization results from a major CWM program [2] designed to determine the treatability of hazardous landfill leachates by chemical and biological processes, including stabilization of both raw leachates and wastewater treatment residues. The project was designed to provide data to the U.S. EPA for the purpose of setting new Best Demonstrated Available Technology (BDAT) standards for hazardous landfill leachate to replace inappropriate standards which would result from application of the "derived-from" rule in the regulatory land-ban program.

Experimental

Design of the study

Nineteen leachate samples from seven hazardous waste TSDFs and three co-disposal facilities were characterized for all RCRA BDAT constituents: volatile organics, semi-volatile organics, metals, inorganics, organochlorine pesticides, phenoxyacetic acid herbicides, organophosphorus insecticides, and PCBs. Two full-scale leachate treatment plants were evaluated for their efficiencies in removing BDAT constituents, and the residues from these pro-

[1]The term "fixation" is really a misnomer in the sense that it is used for the immobilization of metals, but it is commonly used in practice.

cesses were also completely characterized both for total constituents (TCA) and leachable constituents according to the Toxicity Characteristic Leaching Procedure (TCLP). Four of the treatment residues and one untreated leachate were then stabilized with four different stabilization formulations, according to a 20-point experimental grid. The stabilized samples were also completely characterized by both TCA and TCLP analyses. For the constituents which were found in the waste samples, comparisons were made between the leachates, treatment residues (TCA and TCLP), and the final stabilized residues (TCA and TCLP) for four stabilization processes.

Experimental procedures

The experimental plan for this work consisted of a matrix of five wastes and four stabilization formulations, as shown in Table 1.

The formulations all produced solids with no free water; these were cured for five days, then shipped to Radian Corp., Austin, TX, where the testing was completed. Total curing time for all samples was in the range of 10 to 20 days, with some differences between samples due to test scheduling at Radian. Each

TABLE 1

Leachate treatability study stabilization test matrix

Waste	Ref. No.	Cement[a]	Formulation activated			
			F1	F2	F3	F4
Metal precipitation	MC12-01	0.2				
sludge	-02	0.2		X		
	-03	0.2			X	
	-04	0.2				X
Spent carbon	MC13-01	0.2				
	-02	0.2		X		
	-03	0.2			X	
	-04	0.2				X
Filterpress sludge	CID7-01	0.3				
	-02	0.3		X		
	-03	0.3			X	
	-04	0.3				X
Dried biosludge	CID8-01	0.1				
	-02	0.1		X		
	-03	0.1			X	
	-04	0.1				X
Landfill leachate	EM3-01	0.3	X			
	-02	0.3		X		
	-03	0.3			X	
	-04	0.3	X			X

[a]Weight ratios of cement to formulation reagents (weight/weight)

stabilized sample was analyzed for total amount of constituent present as well as being subjected to the TCLP leaching protocol.

Stabilization methods

Stabilization treatability studies were carried out to the generally accepted industry procedures – specifically CWM Method STM 88-1.

Test methods

The standard EPA Toxicity Characteristic Leaching Test (TCLP) was used throughout this study, since the purpose of the work was to define leachability in the context of the "landban" system, where this test is mandated. It is likely that the TCLP will replace the Extraction Procedure Toxicity test (EPT) for all other uses by mid-1990. All analyses were conducted according to EPA methods and quality assurance/quality control (QA/QM) procedures as stated in SW-846 [3]. Each waste or leachate was analyzed for RCRA BDAT constituents [4].

Results

General

Leachate treatment had been found [2] to greatly diminish the concentration of organics in both effluent and residue in most cases, but to concentrate metals and inorganics in the residue, as expected in a wastewater treatment process. Stabilization decreased leachable organic constituent levels in most cases, but the degree of success in this regard depended heavily on the formulation used. At least one formulation, F4, was quite effective in meeting the lowest land-ban leaching level for any given waste for all organics except methanol. As expected, stabilization decreased the total organic constituent levels for volatile organics, presumably due to volatilization during the stabilization and curing processes. More surprisingly, since the maximum temperature rise during mixing and curing in any sample was 5 °C, stabilization also decreased the total levels of certain low-volatile organics.

Stabilization also decreased the leachability of metals for all formulations tested, although some additives were more effective than others in the low part-per-billion range tested. At least one formulation met the lowest land-ban leaching level for any of the five wastes for all metals except arsenic. Total levels for both metals and inorganics were actually increased in some cases due to the presence of these species in the stabilization reagents used.

Data analysis

Before discussing the data, some explanations and caveats are in order. Where constituents were not detected in any of the analyses, no value is reported. If a constitutent is detected in any sample, but not in all samples, the not-detected data are reported as less-than (<) detection limit (DL) values. Detection limits are not the same for all analyses for a given constituent. The laboratory reports a Limit of Quantitation (LOQ) value which is five times the DL, because the uncertainty of analysis will increase exponentially as the DL is approached. For this reason, in evaluating results, values close to the DL may have little significance when compared with each other or with a "<" value; therefore, values in this area which are within a factor of two of each other are considered essentially indistinguishable.

Most stabilization literature reports TCA results without correction for dilution. In this study, only the corrected value is reported. The correction factors include both reagents and water additions, where applicable. TCLP results are reported without correction since that number is the one of primary importance environmentally. However, in comparing data from raw to stabilized wastes, or from one stabilization process to another, the dilutions should be kept in mind to determine whether a difference is significant. Another number of importance in evaluating effectiveness of stabilization is the total amount of constituent leached, or the percentage leached. In making comparisons, the TCLP value must be multiplied by the total dilution factor before comparing it with the TCA value. Total dilution factor (DF) for the TCLP is:

$$DF = \frac{(\text{Weight of additions} + \text{Weight of waste})}{\text{Weight of waste}} \times 20$$

For most stabilized wastes, the TCLP factor will be in the range of 22 to 40. In many cases, the apparent destruction, loss, or immobilization of a low-level organic constituent is merely due to its dilution to below detection limits.

In view of the above, the best way to quickly determine the meaning of the results in the ability of stabilization to immobilize low-level organics is to look at reduction factors rather than absolute quantities. The reduction factor is the ratio of constituent before stabilization to constituent after stabilization, taking dilution into account. Also, in the case of TCA results on VOCs, probably loss due to volatilization must be considered. Reduction factors for TCA levels of volatile organics, TCA levels of semi-volatile organics, and TCLP levels of all organics are given in Tables 2–4, respectively. Where no factor is given, it was below the significance level for that test. Tables 5 and 6 show the absolute results for two cases – TCA and TCLP – in one waste stream.

Total constituent analysis (TCA)

The importance of TCA is that it gives an indication of whether actual loss, destruction, or change in the constituent has occurred, always with the caveat that any difference may be due to test or analytical artifacts if these cannot be absolutely ruled out. As stated in the previous section, dilution factors must always be taken into consideration. Another possible source of error is the introduction of constituents into the waste from the reagents or process water, especially when working in the low concentration ranges required by the land-

TABLE 2

Significant reductions in TCA levels volatile organics (VOCs)

Waste Ref. No.	Constituent	Reduction factor			
		Stabilization process			
		Cement	Cement/F2	Cement/F3	Cement/F4
M12	None				
MC13	Acetone	23			>14
	Methyl ethyl ketone	>118	>59	10	>59
CID7	Methanol – Significant *increase* with all samples except cement/F2 (No others tested)				
CID8	Methanol – Significant *increase* with all samples except cement/F2				
	Methylene chloride	>64	>64	>64	12
	Methyl ethyl ketone	<10	<8	~20	~20
EM3	Acetone				>5
	n-Butyl alcohol	6			>5
	Isobutyl alcohol				>10
	Methyl ethyl ketone	7	5	>5	>5
	Methyl isobutyl ketone	12	5	>5	>5

TABLE 3

Significant reductions in TCA levels semi- and non-volatile organics

Waste Ref. No.	Constituent	Reduction factor			
		Stabilization process			
		Cement	Cement/F2	Cement/F3	Cement/F4
MC12	Di-n-butyl phthalate	>4	>4	>4	
MC13	None				
CID7	Bis(ethylhexyl)phthalate	6	7	6	6
CID8	None				
EM3	Phenol	3	3	5	4
	Phthalic acid	>16	>19	>29	>32

ban BDAT standards system. This is frequently encountered in the case of metals, and it appears to have occurred in some instances in this study, as we shall see.

The first test applied to determination of the effectiveness of stabilization is whether the constituent could have been volatilized during the stabilization process. In this project, no special care was taken to prevent volatilization. Test samples were formulated by mixing in the open by standard procedures which

TABLE 4

Significant reductions in TCLP levels

Waste Ref. No.	Constituent	Reduction factor			
		Stabilization process			
		Cement	Cement/F2	Cement/F3	Cement/F4
MC12	None				
MC13	Acetone	3	3	3	>6
	Methyl chloride	2	3	3	4
	Methyl isobutyl ketone	>3	>7	>7	>7
	Pyridine	>15	>10	>160	>143
CID7	Methylene chloride		Substantial increase		
CID8	None				
EM3	Acetone	>75	395		300
	Methanol	38	69		
	Methyl ethyl ketone		>460		
	Methyl isobutyl ketone		324		

simulate, to some extent, field operations. After formulation, the sample containers were sealed until analysis or leaching was done. Previous studies [5] have shown up to 75 percent of VOCs are lost during stabilization and curing operations. Therefore, in evaluating whether any reaction is destroying or changing the constituent, we have used a rule-of-thumb that concentration of VOCs must be reduced by at least a factor of five[2] to be significant. Reduction factors less than five are not reported. Examination of results for VOCs are as shown in Table 2.

From the data in Table 2 it appears that, of the constituents found in the raw waste, acetone, methyl ethyl ketone, methylene chloride, n-butyl alcohol, isobutyl alcohol, and methyl isobutyl ketone in certain wastes show significant reduction in TCA after stabilization. The cement/F4 system was the most consistently effective, although it did not always give the best results. Perhaps the F4 additive holds certain compounds so tightly that they cannot be extracted during analysis. Methanol showed substantial increases in two waste streams with most stabilization reagents. Whether this is due to experimental error, to laboratory contamination, to introduction of methanol into the system by reagents or other means, or by production of methanol from other constituents by the stabilization process is not ascertainable from the evidence at hand. The latter possibility would require the elucidation of a reaction path-

[2]Reduction of a factor of four for volatilization plus a factor of one for experimental and analytical error. This is somewhat arbitrary, since there is no evidence to show that such volatilization occurs to the same extent at these low levels.

way. The presence of methanol at these levels is important, however, because it is above the lowest BDAT treatment standard in two wastes. Methylene chloride and methyl isobutyl ketone also fail to meet BDAT standards in at least one waste, although their TCA values are not increased by stabilization.

For semi-volatile and other organic compounds, volatilization should be minimal under the conditions of this program. Therefore, a factor of two was applied as the criterion of significance. Examination of results for these compounds are as shown in Table 3.

In a number of instances, there may have been reductions in TCA for other constituents, but the results cannot be analyzed due to substantial differences in detection limits and less-than values for the raw waste. Interestingly, the reductions observed are all for compounds that may be reactive in the stabilization environment – organic acids, esters, and phenol. In general, additive F4 was of no special advantage with the semi- and non-volatile organics. None of these organics were present in above BDAT concentrations in any stabilized samples.

TCLP analysis

In evaluating the results of stabilization by means of a leaching test such as the TCLP, two comparisons must be made:

(1) Stabilized waste TCLP versus stabilized waste TCA, taking into account dilution by the TCLP by a factor of 20, and

(2) stabilized waste TCLP versus raw waste TCLP.

The first factor tells us whether or not we are just diluting the constituent, not accomplishing any useful purpose by stabilization. If the first evaluation shows possible usefulness of stabilization, then the second factor shows whether stabilization is working to reduce mobility. Therefore, we have used a rule-of-thumb that TCA-to-TCLP concentrations must be reduced by at least a factor of 20 to be significant. If the result passes this test, then a significant reduction in leaching (TCLP) from raw to stabilized waste would indicate immobilization of the constituent. This reduction factor is taken to be 2, to allow for experimental uncertainty. Examination of results of this evaluation are as shown in Table 4.

Only methanol failed to meet BDAT standard for TCLP in two wastes: CID dried biosludge (2.000–3.300 mg/l) and Emelle landfill leachate (2.200–5.000 mg/l). Acetone, methanol, methylene chloride, methyl isobutyl ketone, and pyridine all showed significant reductions in leachability with various stabilization reagents. This was especially evident in the stabilization of Emelle landfill leachate where substantial concentrations of acetone, methyl ethyl ketone, and methyl isobutyl ketone were present in both raw and stabilized wastes (see also Tables 5 and 6). In the CID filter press sludge, methylene chloride leaching level was substantially increased when additive F4 was used, indicating contamination from some source in this test.

TABLE 5

Leachate treatability study, landfill leachate, total constituent analysis (TCA)[a]

Type	Constituent	Unstabilized sludge EM2.02 TCA (mg/kg)	Stabilized sludge				Treatment standard-lowest land-ban level TCA (mg/kg)
			Portland Cement EM3-01 TCA (mg/kg) Corrected[b]	Cement/F2 EM3-02 TCA (mg/kg) Corrected[b]	Cement/F3 EM3-03 TCA (mg/kg) Corrected[b]	Cement/F4 EM3-04 TCA (mg/kg) Corrected[b]	
Volatiles:							
	Acetone	54.000	17.670	14.272	19.000	<10.00	0.370
	n-Butyl alcohol	39.000	6.270	5.798	9.690	<2.000	0.370
	Isobutyl alcohol	20.000	6.840	8.251	10.070	<2.000	
	Methanol	148.000	83.600	86.970	89.300	86.000	0.370
	Methyl ethyl ketone	53.000	7.980	10.704	<10.000	<10.000	0.370
	Methyl isobutyl ketone	53.000	4.560	9.589	<5.000	<5.000	0.370
	Dibenzo(a, e)pyrene	<0.00026	0.139	0.083	<0.0025	<0.0025	
	Dibenzo(a, i)pyrene	<0.0057		0.350	<0.055	<0.055	
	3-Methylcholanthrene	<0.00026	0.020	0.011	<0.0025	<0.0025	
	Phenol	140.000	47.500	42.370	<28.500	32.000	2.700
	Phthalic acid	41.000	<2.600	<2.200	<1.400	<1.300	28.000
	2,4,6-Trichlorophenol	<4.500	<0.690	<0.600	0.836	<0.350	
Organochlorine pesticides:							
	Kepone	<0.010	<0.532	<0.033	0.494	0.480	
Organophosphorus insecticides:							
	Disoifoton	0.0037	<0.200	<0.200	<0.200	<0.200	
	Methyl parathion						
	Phorate	0.0035	<0.150	<0.150	<0.150	<0.150	

[a]Dilution factor $= \frac{\text{(Weight of waste + Weight of reagents)}}{\text{Weight of waste}}$.

[b]Corrected TCA = Measured Value × dilution factor.

TABLE 6

Leachate treatability study, landfill leachate TCLP analysis

Type	Constituent	Unstabilized sludge EM2-02 TCLP (mg/l)	Stabilized sludge				Treatment standard-lowest land-ban level TCLP (mg/l)
			Portland Cement EM3-01 TCLP (mg/l)	Cement/F2 EM3-02 TCLP (mg/l)	Cement/F3 EM3-03 TCLP (mg/l)	Cement/F4 EM3-04 TCLP (mg/l)	
Volatiles:							
	Acetone	75.000	< 1.000	0.190	1.200	0.250	0.590
	n-Butyl alcohol	39.000	< 2.000	< 2.000	< 2.000	< 2.000	5.000
	Isobutyl alcohol	20.000	< 2.000	< 2.000	< 2.000	< 2.000	5.000
	Methanol	152.000	4.300	2.200	5.500	5.000	0.750
	Methylene chloride	4.500	< 0.050	< 0.005	< 0.025	0.013	0.960
	Methylethyl ketone	46.000	< 1.000	< 0.100	0.620	< 0.100	0.750
	Methylisobutyl ketone	22.000	< 0.500	0.068	0.280	< 0.050	0.330
	Pyridine	< 2.000	< 0.028	0.0067	< 0.013	< 0.0027	0.330

Conclusions

(1) Stabilization of low-level organic constituents in aqueous/inorganic waste matrices appears to be feasible with many waste streams. Of the organics tested in the Leachate Treatability Study, only methanol was not stabilized to land-ban BDAT standards.

(2) Stabilization not only immobilizes at least some organics to acceptable levels, but certain constituents apparently can be chemically altered by standard stabilization formulations or by the use of additives. However, such reactions must be characterized so that unacceptable by-products are not generated or, if they are generated, can be immobilized.

(3) The issue of volatile organics will need to be addressed in future stabilization work. It is likely that emission controls for organics will be required on some stabilization systems in the future.

(4) The possible mechanisms of immobilization have not been discussed in this paper; however, their determination is of utmost importance if the credibility of organic stabilization is to be established.

(5) While a number of organic stabilization products and services are being marketed, little technical information is available. It is likely that the development of generic systems will prove much more cost effective in most cases. Claims of vendors and some researchers in this area should be treated skeptically, because little control data is presented. This is especially true of claims that organics are destroyed in stabilization treatment which, although possibly true, have not been proven conclusively to date.

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