

COMPARISON OF CONTAMINANT LEACHABILITY TO QUANTITY OF BINDER MATERIAL*

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Summary

Three separate S/S treatment technologies were applied to each waste and are differentiated by the binder additive used in the S/S process. The wastes were treated with two concentrations of each binder additive. Contaminant release properties of the treated wastes were assessed using two extraction tests; the Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET). The extraction tests were performed on the untreated wastes and on treated wastes following a twenty-four hour cure period. Treatment efficiencies (TE) were calculated for each treatment process to determine contaminant mobility reduction. The calculations were based on levels of the contaminants detected in the leachates of the untreated waste extraction tests and the leachates of the treated waste extraction tests. All data were normalized to account for dilution effects of water and binder addition during application of the S/S treatment technology. This paper discusses the results of contaminant release tests applied to the FO11 and F012 listed hazardous wastes and changes in contaminant mobility related to the amount of binder added during application of S/S. It is concluded that increased binder concentration resulted in an increase in TE in 32 of 35 S/S systems evaluated. Increase in cement binder concentrations significantly increased contaminant immobilization in 64 percent of the S/S systems evaluated; increase in kiln dust binder concentrations significantly increased contaminant immobilization in 67 percent of the S/S systems evaluated; increase in lime/fly-ash binder concentrations significantly increased contaminant immobilization in only 16 percent of the S/S systems evaluated.

1. Introduction

1.1 Background

The U.S. Army Engineer Waterways Experiment Station (WES) has been asked by the U.S. Environmental Protection Agency (EPA) to investigate the applicability of solidification/stabilization (S/S) technology to a number of listed hazardous wastes which are subject to Land Disposal Restrictions [1], and to characterize the effect of S/S on the wastes. Physical, chemical, and

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contaminant release properties of the S/S waste were evaluated to determine if the S/S treatment technology substantially reduced the amount of hazardous contaminants leached in standard leaching tests and improved the physical handling properties of the wastes.

Three separate S/S treatment technologies were applied to each waste and are differentiated by the binder additive used in the S/S process. The wastes were treated with two concentrations of each binder additive. Contaminant release properties of the treated wastes were assessed using two extraction tests: the Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET). The extraction tests were performed on the untreated wastes and on treated wastes following a twenty-four hour cure period. Treatment efficiencies were calculated for each treatment process to determine contaminant mobility reduction. The calculations were based on levels of the contaminants detected in the leachates of the untreated waste extraction tests and the leachates of the treated waste extraction tests. All data were normalized to account for dilution effects of water and binder addition during application of the S/S treatment technology. This paper discusses the results of contaminant release tests applied to the F011 and F012 listed hazardous wastes and changes in contaminant mobility related to the amount of binder added during application of S/S.

1.2 Waste of interest

The listed wastes evaluated in this paper are F011 and F012. These were generated during a metal heat treating operation that "case hardens" the surface of steel using a liquid nitriding process. The F011 waste is residual from salt bath pot cleanout used in metal heat treating operations. The F012 waste is wastewater treatment sludge from metal heat treating operations. These wastes are described in more detail below.

F011. The liquid nitriding process employs a molten salt bath in which steel parts are immersed during treatment. The salt bath becomes contaminated by the process and is periodically removed and the tank cleaned. The residue from the removal of salts and cleaning of the salt bath pots is listed as F011. The primary metal contaminants of interest in the F011 waste were total chromium (17.2 mg/l), nickel (535 mg/l), and copper (81.6 mg/l).

F012. The liquid nitriding process molten salt bath is followed by a quenching step. The treated steel parts are quenched in water, brine, or oil, depending on the final material properties desired. Listed waste F012 is the sludge generated in the spent quenching bath and *not* the wastewater itself. The primary metal contaminants of concern in the F012 waste were nickel (848 mg/l), copper (423 mg/l), and zinc (60.7 mg/l).

2. Materials and methods

2.1 General approach to the investigation

This investigation was conducted in two phases and is summarized as follows:

- (a) Phase I: Preparation of test specimens. Solidification/stabilization technology was applied to the wastes and test specimens were prepared.
- (b) Phase II. Contaminant-release testing. The contaminant release properties of the treated waste were evaluated using the TCLP and the California WET.

2.2 Preparation of test specimens

Three S/S processes were used to treat each waste type and are differentiated by the type of binder material used in the process. The three processes include: Type I portland cement, kiln dust, and lime/fly-ash. The preparation of test specimens was conducted in three steps: (1) initial screening test, (2) batch preparation, and (3) test specimen curing.

2.2.1 Initial screening test (IST)

The IST is performed to help select the appropriate water/waste ratio for each S/S process and to assist in the selection of the best range of binder/waste ratios for further evaluation. The IST consists of mixing small volumes of water/binder/waste at varying ratios and placing the mixture in cylindrical molds.

The S/S waste mixtures are cured for 48 hours and a cone penetrometer test [2] is performed on the specimens. The cone penetrometer test measures resistance to penetration of a 30 degree right circular cone into the surface of the test specimen. Cone penetrometer values are reported as the force per unit area (psi) required to push the cone into a material at a rate of 72 inches per minute. The ratios chosen for subsequent study are the solidified/stabilized waste mixtures that exhibit the highest cone index values and contain the lowest waste/water/binder ratios.

2.2.2 Preparation of specimens for detailed evaluation

Based on the results of the IST, a water ratio and a range of binder/waste ratios were selected for detailed evaluation. WES prepared test specimens using the three binder processes and the water ratio and the binder/waste ratios selected on the basis of the IST results. Table 1 summarizes the ratios selected for each process evaluated in this study.

Solidified/stabilized test specimens were prepared by mixing waste, binder, and water in a Hobart K455S mixer and the resulting mixture was poured into 2 inch cubed brass molds. To remove voids, the filled molds were vibrated on a Sentron model VP61D1 vibration table. The higher binder ratio mixtures were very viscous and vibration was an ineffective method for removing voids.

TABLE 1

Water/binder/waste ratios in F011 and F012 waste types

Waste type	Water ratio	Cement ratio	Kiln dust ratio	Lime/fly-ash ratio
F011	0.1	0.1	0.1	0.11/0.11
		0.4	0.4	0.33/0.33
F012	0.1	0.1	0.1	0.1/0.1
		0.25	0.25	0.25/0.25

These specimens were compacted into the 2 inch cubed molds using a compaction hammer with a 5.74-lb weight, a 1.8 by 1.0 brass head, and a 12 inch drop. Compaction was accomplished by placing two layers of the mixture into the molds and dropping the weight five times per layer.

2.2.3 Test specimen curing

The molded, solidified/stabilized test specimens were cured at 20° and 98% relative humidity for 24 hours. Specimens were extruded from the molds for contaminant release testing.

2.3 Contaminant release testing

The contaminant release properties of the treated wastes were assessed using two extraction tests that evaluate hazardous contaminant leachability: the toxicity characteristic leaching procedure (TCLP) [3], and the California waste extraction test (WET) [4].

2.3.1 Toxicity characteristic leaching procedure

The TCLP was performed in accordance with the method prescribed in the 1986 Federal Register, Part II, Vol 40, CFR Part 261. The TCLP was performed on the untreated waste and on each solidified/stabilized test specimen.

The TCLP extraction consists of challenging waste material with a dilute acetic acid solution using a liquid-to-solids ratio of 20 to 1. The waste material is ground to pass a 9.5 mm sieve. The mixture is tumbled in a closed extraction vessel in an end-over-end fashion for 18 hours. The solid phase is separated by vacuum filtration from the leachate and the leachates are analyzed for a range of contaminants according to the appropriate U.S. EPA methods.

2.3.2 California waste extraction test

The California WET was performed in accordance with the method prescribed in the 1985 California Administrative Code, Title 22, Division 4, Environmental Health, Chapter 30, "Minimum Standard for Management of

Hazardous and Extremely Hazardous Wastes." A single WET was performed on the untreated waste and on each solidified/stabilized test specimen.

The WET extraction consists of challenging waste material with a 0.2 M sodium citrate solution using a liquid-to-solids ratio of 10 to 1. The waste material is ground to pass a 9.5 mm sieve. The mixture is tumbled in a closed extraction vessel in an end-over-end fashion for 48 hours. The solid phase is separated by vacuum filtration from the leachate, and the leachate is analyzed for a range of contaminants according to the appropriate U.S. EPA methods.

3. Methods

3.1 Data analysis

The chemical analysis of the leachates generated during the performance of the TCLP and the WET on the untreated waste was reviewed and the contaminants detected in the highest amounts were selected for further assessment in this study. Table 2 lists the contaminants of interest selected for evaluation by this study. The corresponding contaminant levels detected in the untreated wastes contaminant mobility leachates are also listed.

The data were normalized in order to directly compare the treated and the untreated wastes contaminant release tests leachate chemical analysis. Normalizing the data corrected for any dilution effects attributable to the addition of binder and water during treatment of the wastes. The data are presented as the percent of the contaminant that was immobilized as a result of treatment

TABLE 2

Contaminant levels detected by the TCLP and WET contaminant mobility tests in the leachates of untreated wastes

Waste type	Test	Contaminant of interest	Contaminant level (ppm)
F011	TCLP	Nickel	2.45
		Copper	0.049
		Chromium	0.15
	WET	Nickel	33
		Copper	7.65
		Chromium	1.85
F012	TCLP	Nickel	4.14
		Copper	0.23
		Zinc	0.3
	WET	Nickel	74.16
		Copper	42.33
		Zinc	5.16

by S/S and are referred to as treatment efficiency (*TE*). The data were normalized to the contaminant release test extract concentration per weight of the dry, raw waste extracted. The percentage values were derived using the following set of equations.

$$C_{dr} = \frac{C_r}{(W_r \times M_r)} \quad (1)$$

where

- C_{dr} = leachate contaminant mass/dry weight untreated waste, mg/g
 C_r = untreated waste leachate mass for contaminant of interest, mg. (Calculated as: extract contaminant concentration, mg/l \times extraction solution volume, l)
 W_r = net weight waste extracted, g
 M_r = solids fraction of the untreated waste used in the extraction.

$$C_{dt} = \frac{C_t}{W_t \times M_t \times B_t} \quad (2)$$

where

- C_{dt} = extract contaminant concentration/dry weight waste after S/S, mg/g
 C_t = S/S waste extract mass for the contaminant of interest, mg. (Calculated as: extract contaminant concentration, mg/l \times extraction solution volume, l)
 W_t = weight of undried S/S waste, g
 M_t = solids content of the S/S waste used in the extraction, expressed as a decimal
 B_t = weight fraction of the waste in the solidified/stabilized waste calculated as follows

$$B_t = \frac{\text{weight of waste}}{\text{weight of waste} + \text{binder}} \quad (3)$$

$$TE = \frac{C_{dr} - C_{dt}}{C_{dr}} \times 100 \quad (4)$$

where *TE* is the treatment efficiency and represents the percent of contaminant immobilized due to the application of S/S.

The *TE* of the high and low water/binder/waste ratios for all three S/S processes applied, for each waste type, were calculated. The *TE* of the high and low binder/waste ratios for each S/S process were compared to determine if the increase in binder concentration effected contaminant mobility.

4. Discussion of results

The treatment efficiencies (degree of contaminant leachability) were calculated using the results of the chemical analysis of the TCLP leachates and

TABLE 3

Treatment efficiencies for F011 and F012 wastes treated with various binders

	F011			
	TCLP		WET	
	low (%)	high (%)	low (%)	high (%)
<i>Cement binder</i>				
Nickel	50.5	98.9	38.7	87.2
Copper	33.0	— ^a	29.0	84.0
Chromium (total)	-119.0	-78.1	-16.12	39.9
<i>Kiln dust binder</i>				
Nickel	34.5	98.8	26.7	81.7
Copper	40.2	58.2	15.2	76.2
Chromium (total)	54.1	58.3	-1.1	75.4
<i>Lime fly-ash binder</i>				
Nickel	98.6	98.7	66.9	94.0
Copper	50.4	54.6	45.1	85.4
Chromium (total)	26.1	22.6	2.7	69.8
	F012			
	TCLP		WET	
	low (%)	high (%)	low (%)	high (%)
<i>Cement binder</i>				
Nickel	97.2	99.4	30.9	95.9
Copper	90.6	92.7	2.4	89.9
Zinc	59.8	69.1	84.0	56.6
<i>Kiln dust binder</i>				
Nickel	44.8	99.4	34.8	98.1
Copper	80.3	92.8	24.6	87.3
Zinc	55.4	76.8	62.1	91.0
<i>Lime/fly-ash binder</i>				
Nickel	99.4	99.5	87.3	91.8
Copper	90.9	88.7	77.7	86.6
Zinc	62.0	69.2	85.3	86.9

^aData not available.

of the WET leachates. As shown in Table 2, the contaminants of interest investigated for the F011 waste were nickel, copper, and total chromium, and for the F012 waste were nickel, copper, and zinc.

Table 3 lists the *TEs* calculated for each binder/waste ratio for each S/S process applied to both wastes based on the TCLP and the WET leachate chemical analysis. Figure 1 is a graphical representation of the high versus the low kiln dust binder concentrations for nickel, copper, and chromium (total),

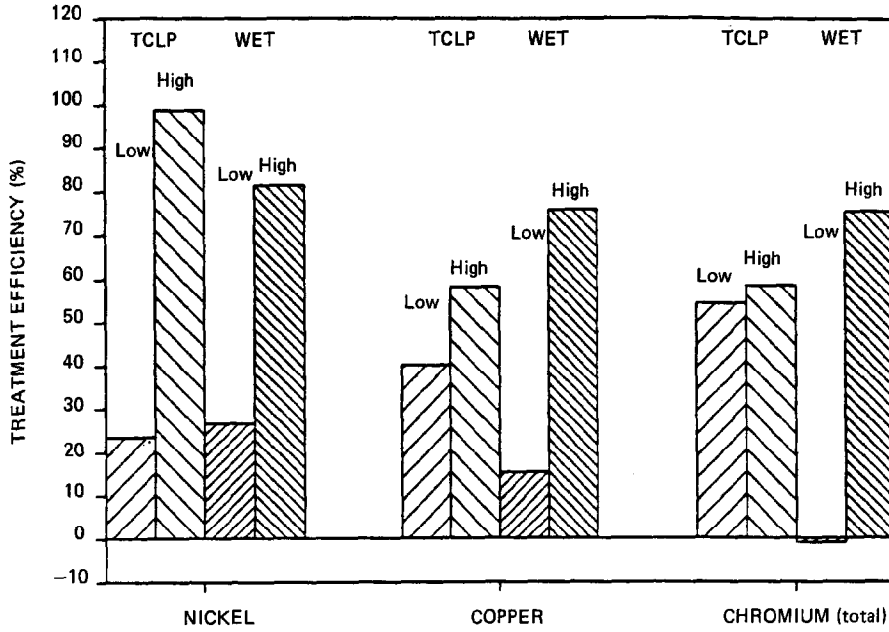


Fig. 1. Treatment efficiency versus kiln dust binder concentration for F011.

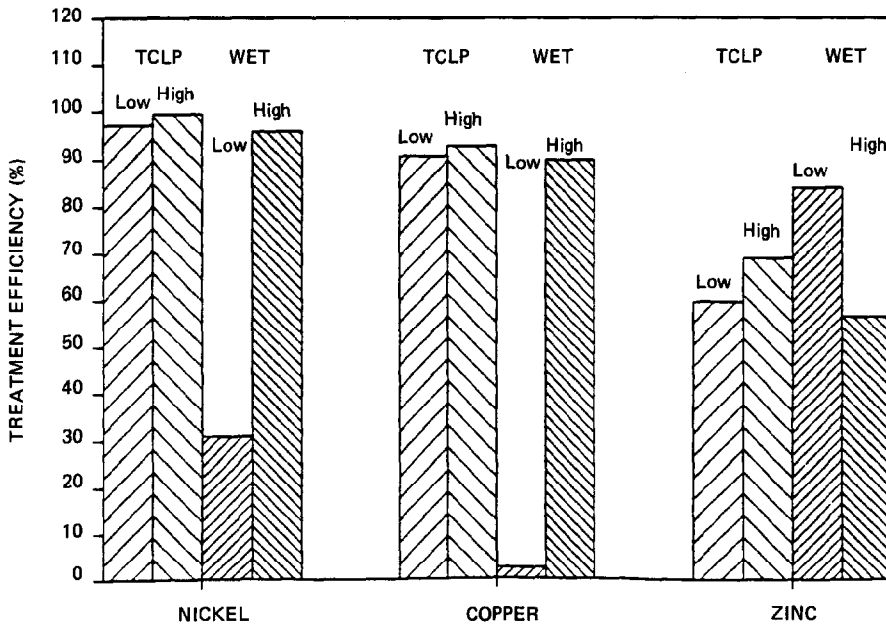


Fig. 2. Treatment efficiency versus cement binder concentration for F012.

for the F011 waste. Figure 2 is a graphical representation of the high versus low cement binder concentrations for nickel, copper, and zinc, for the F012 waste.

A total of thirty-five comparisons were made between the high and low binder concentrations. In all but three cases, contaminant mobility was decreased by using higher binder concentrations.

Treatment efficiency improvements range from a 0.1 percent to a 64 percent increase. There was an average increase in treatment efficiency of 17.3 percent resulting from using higher binder concentrations calculated from the TCLP leachate chemical analysis. There was an average increase in treatment efficiency of 41.8 percent resulting from the higher binder concentration calculated from the WET leachate chemical analysis.

A negative *TE* was calculated from the TCLP leachate chemical analysis for the F011 waste type, low concentration lime/fly-ash binder, total chromium contaminant, and for the F012 waste type, low concentration lime/fly-ash binder, copper contaminant. A negative *TE* was also calculated for the WET leachate chemical analysis for the F012 waste type, high concentration cement binder, zinc contaminant.

For the purposes of evaluation, a change in *TE* exceeding 40 percent when the binder concentration is increased, will be indicative of significant contaminant immobilization due to the use of large quantities of binder material. When cement binder concentrations were increased, *TE* increase was > 40 percent in seven of eleven S/S systems evaluated. In the remaining four S/S systems evaluated that used cement binder, *TE* increase < 10 percent. When kiln dust binder concentrations were increased, *TE* increase was > 40 percent in eight of twelve S/S systems evaluated. In the remaining four S/S systems evaluated that used kiln dust binder, *TE* increase was < 21 percent. When lime/fly-ash binder concentrations were increased, *TE* increase was > 40 percent in two of twelve S/S systems evaluated. In the remaining ten S/S systems evaluated that used lime/fly-ash binder, *TE* increase was 27 percent in one and < 10 percent in the other nine.

5. Conclusions

- (1) Increased binder concentration resulted in an increase in *TE* in 32 of 35 S/S systems evaluated.
- (2) Increase in cement binder concentrations significantly increased contaminant immobilization in 64 percent of the S/S systems evaluated.
- (3) Increase in kiln dust binder concentrations significantly increased contaminant immobilization in 67 percent of the S/S systems evaluated.
- (4) Increase in lime/fly-ash binder concentrations significantly increased contaminant immobilization in only 16 percent of the S/S systems evaluated.

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