



Project Summary

Evaluation of Solidification/ Stabilization as a Best Demonstrated Available Technology for Contaminated Soils

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This project evaluated the performance of solidification/ stabilization as a means of treating soil from "Superfund" sites. Tests were conducted on four different types of artificially contaminated soil that are representative of the types of contaminated soils found at Superfund sites. For purposes of this study, the term solidification infers the conversion of a non-solid to a solid while stabilization infers reduction in contaminant leachate. Many times the terms are used interchangeable since both goals are met. The contaminated soils used for this study were synthetically prepared and termed Standard Analytical Reference Matrix (SARM). The soils were solidified/stabilized using the following three commonly used solidification/stabilization agents or binders: (1) portland cement, (2) lime kiln dust, and (3) a mixture of lime and flyash.

At 7, 14, 21, and 28 days after soil and binders were mixed, samples of the solidified material were subjected to Unconfined Compressive Strength (UCS) testing. Samples of those mixes that had a UCS minimally greater than 50 psi (pounds per square inch), or which showed the highest UCS below 50 psi, after 14 and 28 days were subjected to chemical testing such as the Toxicity Characteristic Leaching Procedure

(TCLP) and Total Waste Analysis (TWA) to determine if stabilization occurred. The results follow.

The water-to-total-solids ratio appears to be a better measure of the amount of water needed to solidify/ stabilize a given mix than the water-to-binder ratio that is commonly used. This was clearly the case for the SARM's with these binders. This needs to be confirmed on other systems.

Solidification/stabilization resulted in significant reductions in the amount of metal salt contaminants released, as measured by the TCLP. Because of the large losses of organics during the mixing process, the effect of solidification/stabilization on the organic leachate via the TCLP could not be quantitatively determined. The volatile and semi-volatile organic contaminants did appear to decrease because of the solidification/stabilization process; however, this decrease can be attributed to their release to the air during processing and curing. No correlation between UCS and the results of the leaching tests was observed.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory in Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the

same title (see Project Report ordering information at back).

Introduction

The Hazardous and Solid Waste Amendment Act (HSWA) of 1984 requires the U.S. Environmental Protection Agency (EPA) to develop treatment standards or treatment methods (called "Best Demonstrated Available Technology" or "BDAT") for listed hazardous waste before it is land disposed. Treatment methods were to be evaluated that reduce the toxicity or the likelihood of the migration of the hazardous constituents in the waste. The Superfund Amendment and Reauthorization Act (SARA) requires that remedial actions meet all applicable, relevant, and appropriate public health and environmental standards. In order to be consistent in these requirements, it may be necessary to establish the level of performance that the best available technology can achieve in the treatment of wastes from remedial actions. This project evaluated the performance of solidification/stabilization as a "BDAT" for treating soil from "Superfund" sites.

Four different types of artificially contaminated soil, which are representative of the types of contaminated soils

found at Superfund sites, were solidified/stabilized using three commonly used solidification/stabilization agents or binders. The products were subjected to UCS tests, and each blend of soil and binder that had a UCS minimally greater than 50 psi, or which showed the highest UCS below 50 psi after curing, were subjected to chemical testing such as the TCLP and TWA to determine stabilization effectiveness. The 50 psi criterion is consistent with the Resource Conservation and Recovery Act (RCRA) guidance.

The binders evaluated were commonly used generic agents that are readily available. Other binders, both proprietary and generic, are available and could possibly enhance the solidification/stabilization process. There is, at present, no set protocol for evaluating the efficacy of solidification/stabilization technologies. The TCLP was used for evaluating the level of stabilization achieved in this program. It is one of several leaching procedures commonly used at present.

Experimental Procedure and Results

The SARM's were prepared for EPA under a separate program. They are identified by the amount of organic and

metals contamination added to the soil follows:

- SARM I — low metals, high organic concentration
- SARM II — low metals, low organic concentration
- SARM III — high metals, low organic concentration
- SARM IV — high metals, high organic concentration

Table 1 presents the raw waste analysis for the SARM's received for program. Table 2 presents the metals species utilized for the contamination.

As the first step in the program, apparent water content of the SARM was determined by drying them to constant weight and attributing the weight loss to water removed by evaporation although organic material loss not occurred in addition. The results were: SARM I — 31.4%, SARM II — 8.9%, SARM III — 19.3%, and SARM IV — 22.1%. Then the amount of water required to form a satisfactory solidified product was defined to be that mix which gave the product most resistant to penetration (U.S. Army Corps of Engineers, 1984).

Table 1. Results of TWA for SARM Samples Received for this Program

Analyte	Metals Concentration (mg/kg)			
	SARM I High Organic, Low Metal	SARM II Low Organic, Low Metal	SARM III Low Organic, High Metal	SARM IV High Organic, High Metal
<u>Volatiles</u>				
Acetone	3,150	230	220	13,000
Chlorobenzene	330	9.2	8.9	270
1,2-Dichloroethane	380	3.9	3.1	830
Ethylbenzene	3,350	74	100	2,500
Styrene	1,000	26	24	540
Tetrachloroethylene	710	16	13	540
Xylene	4,150	210	150	3,700
<u>Semivolatiles</u>				
Anthracene	940	275	265	770
Bis(2-ethylhexyl) phthalate	600	34	140	500
Pentachlorophenol	135	62	15	70
<u>Inorganics</u>				
Arsenic	18	18	904	81
Cadmium	17	23	1,280	1,430
Chromium	27	37	1,190	1,650
Copper	193	260	9,650	13,300
Lead	190	240	15,200	16,900
Nickel	27	32	1,140	1,360
Zinc	392	544	53,400	28,900

Table 2. Chemical Identification and Solubility of SARM Metal Contaminants

Chemical Type	Solubility in Water
Lead sulfate ($PbSO_4$)	Slightly soluble
Lead oxide (PbO)	Insoluble
Zinc oxide (ZnO)	Insoluble
Cadmium sulfate ($3CdSO_4 \cdot 8H_2O$)	Soluble
Arsenic trioxide (As_2O_3)	Slightly soluble
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	Soluble
Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$)	Soluble
Nickel nitrate ($Ni(NO_3)_2$)	Soluble to very soluble

Penetrometer test after 24 hr, was determined.

The testing showed that water-to-binder ratios were not good indicators of the amount of water that should be used to form the SARM's into a monolithic solid suitable for hardness testing. The ability of the product to set up could be correlated reasonably well to the water-to-total-solids ratio (W/TS) of the mix. This ratio is simply the mass of water used versus the sum of the solid component of the SARM and of the solidifying agent. In virtually all cases tested, a W/TS ratio of 0.4 to 0.5 resulted in an acceptable product, regardless of the soil or the binder used.

The next phase of the program was intended to determine the minimum binder-to-soil (B/S) ratio that would result in a sample of solidified soil with an unconfined compressibility greater than 50 psi. Actually, with some binders this UCS level could not be achieved with any ratio tested within the 28-day curing time set under this program. In that case, the sample that achieved the highest UCS level was used for subsequent testing.

The B/S ratio tests were performed by mixing each soil (4 soils) with each binder (3 binders) at three B/S ratios. Each mixture was split into a number of samples. On each of the 7th, 14th, 21st and 28th days after mixing, the samples were subjected to UCS testing. On the 14th and 28th days, the samples that had either minimally satisfied the 50-psi UCS requirement or, if none had achieved 50 psi, the one that had the highest UCS reading, were also subjected to TWA and TCLP analysis. The program resulted in a total of 648 samples.

At 14 and 28 days after mixing, the organic volatile and semivolatile emissions from the solidified samples were

qualitatively measured to track the loss of organic components from the samples into the surrounding air by withdrawing a sample of the air from the polyethylene bag in which the samples were allowed to cure and injecting it into a gas chromatograph. Because no gas flux measurements through the plastic bags were made, these concentrations cannot be used to calculate the emission rate of the organics and should be construed as qualitative in nature.

TCLP leachate analyses were performed for both organics and metals; however, because of the significant losses of the organic constituents during mixing and handling, the results of the TCLP analyses for organics proved inconclusive. The results of the TCLP analyses for metals are presented in Table 3. It lists the SARM type (I through IV) and the sample number that was tested in the first column. The second column identifies the type of binder used. "RAW" is the contaminated SARM without solidification/stabilization and PC, KD, and LF are the three binders. The numbers in parenthesis identify the day the analyses were performed—14 or 28 days after mixing. The final columns present the TCLP results for each metal: (a) giving the parts per million (ppm) of that metal found in the extract, and (b) giving the percent decrease that this represents over the raw SARM. The values in the (b) column correct for the decrease in the concentration of that metal that is due to dilution by the binders.

Discussion of Results and Conclusions

The results indicated that the portland cement formed a much stronger matrix than the other two binders. Typically, the portland cement resulted in a UCS exceeding 1,000 psi (the upper limit of measurement with the available equipment) for three out of the four SARM's. Further, it achieved these levels at far lower B/S ratios than the other two binders, possibly resulting in a smaller volume of waste requiring ultimate disposal. The strength of the product solidified/stabilized with portland cement was significantly lower for SARM IV than for the other three SARM's. The SARM IV had been contaminated with very high levels of both organic compounds and metal salts and it appears that this combination resulted in a large amount of interference to the solidification/stabilization process.

The lime kiln dust and the lime/flyash mixtures used for these tests did not result in values of the UCS as high as those observed with portland cement. The strength (UCS) values were initially low, however, the values continued to increase during the course of these tests. The trend in the data was very clear and confirmed the general impression that lime-based binders will continue to harden over time.

The SARM samples stabilized with lime and lime kiln dust/flyash continued to cure over time. The UCS values for these samples started very low but as time progressed, they increased. The test suggests that the curing time for these binders should have been extended to determine their ultimate strength. The trend in the data suggested that these samples would continue to show increases in their UCS beyond the 28-day period.

An observation made during the initial screening tests of this program appears to be useful for further work. These tests showed that a water/solids ratio of approximately 0.4 would result in a solidified/stabilized product regardless of the binder used—within the overall context of the experiment. This observation, if confirmed with other systems, may result in a significant reduction in number of experiments required to test a given water/binder ratio.

The results of the TCLP for the metals on the treated SARM's were very encouraging. In general, the data show that the metals leaching from the SARM's are reduced significantly by the solidification/stabilization process. In fact, the reduction approached 100% for many of the compounds.

The TCLP results on the raw (untreated) contaminated SARM's were lower than the expected values for almost all of the metals. This made the data difficult to interpret as many of the analyses were being made at or near the detection limits. Nevertheless, the results clearly indicate a significant reduction in the TCLP of the metals in almost all cases. The TCLP results of the raw SARM's showed that the matrix itself prevented a large portion of the metals from being released to the TCLP. Many analyses of the raw, contaminated material approached the minimum level of sensitivity of the analyses. Many of the metal salts appeared to be attenuated by the SARM itself, possibly because of the clay portion of the soils.

All of the binders reduced the leachability of the cadmium, copper, nickel,

Table 3. Summary of TCLP Results for Metals

SARM Sample No.	Binder (Day)	Arsenic		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	RAW	ND	-	0.53	ND	ND	+	0.61	81	0.49	75	0.27	70	9.2	96
1	PC(14)	ND	-	ND	0.06	0.06	+	0.07	81	0.15	100	0.04	100	0.23	94
14	KD(14)	ND	-	ND	0.06	0.06	+	0.04	81	ND	100	ND	100	0.27	94
27	LF(14)	ND	-	ND	0.02	0.02	+	0.03	98	ND	100	ND	100	0.14	94
1	PC(28)	ND	-	ND	0.06	0.06	+	0.06	83	0.15	75	0.04	70	0.49	91
15	KD(28)	ND	-	ND	0.09	0.09	+	0.03	98	ND	100	ND	100	0.62	73
27	LF(28)	ND	-	ND	0.02	0.02	+	0.03	98	ND	100	ND	100	ND	100
II	RAW	ND	-	0.73	ND	ND	+	0.89	92	0.7	82	0.4	83	14.6	99
4	PC(14)	ND	-	ND	0.03	0.03	+	0.04	92	0.15	+	0.04	100	0.09	97
16	KD(14)	ND	-	ND	0.08	0.08	+	0.07	79	0.44	+	ND	100	0.25	99
30	LF(14)	ND	-	ND	ND	ND	-	ND	100	ND	100	ND	100	0.22	99
4	PC(28)	ND	-	ND	0.03	0.03	+	0.06	89	0.15	83	0.04	83	0.54	94
16	KD(28)	ND	-	ND	0.05	0.05	+	0.09	89	0.37	+	ND	100	0.78	89
29	LF(28)	ND	-	ND	ND	ND	-	0.03	90	ND	100	ND	100	0.02	100
III	RAW	6.39	100	33.1	ND	ND	+	80.7	100	19.9	95	17.5	100	359	100
7	PC(14)	ND	100	ND	0.07	0.07	+	0.15	100	0.63	+	ND	100	0.58	95
21	KD(14)	ND	100	ND	0.22	0.22	+	1.02	96	13.3	+	ND	100	4.38	96
33	LF(14)	0.81	52	0.02	0.03	0.03	+	2.96	87	51	+	ND	100	3.81	100
7	PC(28)	ND	100	ND	0.07	0.07	+	0.09	100	ND	100	ND	100	0.69	95
21	KD(28)	0.21	98	ND	0.12	0.12	+	0.85	96	18.3	+	ND	100	4.07	96
33	LF(28)	0.79	51	0.02	0.07	0.07	+	2.59	87	51	+	0.03	99	3.97	96
IV	RAW	9.58	100	35.3	0.06	0.06	+	10	100	70.4	99	26.8	100	396	100
10	PC(14)	ND	100	ND	0.06	0.06	+	0.04	100	0.39	43	ND	100	0.39	97
23	KD(14)	0.16	95	ND	0.11	0.11	+	1.88	97	12.4	+	ND	100	4.57	96
	LF(14)	1.61	50	ND	0.07	0.07	+	1.92	96	91.8	+	ND	100	3.22	100
10	PC(28)	ND	100	ND	0.06	0.06	+	0.17	100	0.37	99	ND	100	0.74	97
23	KD(28)	0.27	92	ND	0.12	0.12	+	1.67	97	21.4	9	ND	100	3.72	96
	LF(28)	0.98	59	0.02	0.07	0.07	+	2.18	95	65	+	ND	100	3.64	96
Detection Limit		0.15		0.01	0.01	0.01		0.02		0.15		0.04		0.01	

Notes: (a) TCLP results in ppm

(b) percent reduction, corrected for dilution

ND - below detection limit

+ - increase over raw SARF

and zinc. In all of these cases, the solidified/stabilized SARM's resulted in only trace amounts or less of these metal salts in the leachate. The TCLP results for lead was less consistent. All of the samples that were solidified/stabilized with portland cement showed very large reductions in the leachability of this ion. The kiln dust caused some reduction in the leachability of the lead, although the reduction was not as great as for the portland cement.

The lime/flyash binder did not appear to reduce the leachability of the lead. In fact, the results actually showed an increase in the leachability after correcting for dilution. The increase is most likely because of the error introduced by the large amount of binder used for these samples and the resultant large dilution factor, rather than it being an actual increase.

The arsenic was stabilized well by the portland cement and the kiln dust. The lime/flyash binder also reduced the arsenic's leachability, but only by approximately 50%.

The solidification/stabilization process had virtually no effect on the chromium in this program. In fact, as with the lead (solidified/stabilized by the lime/flyash mix), the concentration of chromium in the leachate appeared to increase after correcting the results of the TCLP for dilution. Once again, this increase is most likely an artifact of the experiment. Further research into the chemical mechanisms involved in the solidification/stabilization process is needed to correlate these observations.

Another observation of the TCLP data is that the results for each sample at 14 days was the same (to within sampling and analytical error) as that for the same sample at 28 days. If this correlation could be confirmed, significant reductions in the time required for such testing could possibly be realized. This result is also of interest because it indicates that, at least for the lime/flyash and the lime kiln dust, the UCS may not be a good indicator of how well metals are immobilized for the SARM's. The UCS of the samples formed with these binders continued to increase even though there was little change in the TCLP.

The variability owing to the analytical method used for metal analysis can be estimated by examining the difference between the TWA for the metals for each mix after 14 and 28 days. For example, SARM III solidified/stabilized with portland cement (PC) after 14 days showed 528-ppm arsenic. The same sample at 28 days showed 584 ppm. Generally, comparison of the metals analyses for each sample at 14 and 18 days showed a similar consistency. This type of variability is quite small, indicating that the mixing procedures used in this program resulted in a homogeneous product and that the analytical protocol appeared to give reasonably consistent results.

The analysis of the volatile and semi-volatile organic compounds in the headspace by gas chromatography/flame ion detector (GC/FID) seemed to indicate that the volatile organic emissions occur mostly during mixing and then continue at a steady rate after curing in a sample, dropping as the organic content of the solidified/stabilized material is reduced.

The solidified/stabilized SARM's generally showed a lower TCLP value for the volatile organic contaminants than the original SARM's. This should not, however, be attributed to the solidification/stabilization process binding the volatile compounds. Rather, this is most likely because of a simple release of the volatile compounds during the mixing process and during the sample preparation prior to extraction.

The TWA analyses for the volatile organics showed the same pattern as the TCLP. The TWA analyses, however, showed the results magnified. That is, the solidified/stabilized SARM's contained on the order of 80% to 90% less volatile organics than the original material. This is consistent with the hypothesis that the volatile organics were released to the air rather than trapped in the solid. Had the volatile organics truly been stabilized, then the TWA would have shown a constant value for these materials while the TCLP would have shown a decrease.

The TCLP for the semivolatile organics, in general, showed a significant decrease because of solidification/stabilization. The results show that the percent decrease in

the TCLP analyses for the semivolatile organics is greatest for SARM's I and IV (those contaminated with high levels of organics) and least for II and III. SARM's II and III also show a greater variability for the semivolatile reduction, but this is most likely because of analytical errors caused by the low concentration of the semivolatile compounds.

The TWA results for the semivolatile organics was unexpected. Solidification/stabilization appeared to result in an apparent increase in almost all of the values. This is most likely an artifact of the analytical method. The TWA results appear to have a very wide variation in them. The reason for this is unclear, but it may be because of the physical nature of the semivolatile compounds. They are heavy solids that go into solution slowly. As a result, the amount of each constituent in the liquid after the extraction for analysis may be more of a function of how much of the material actually dissolves than of the total amount of that compound in the waste. Under normal conditions, this error is not significant; however, in this case, the TWA values are corrected for dilution. This results in a "leveraging" of any error and a much higher degree of uncertainty for the TWA results.

In conclusion, it appears that solidification/stabilization can significantly reduce the leachability of many metals of the SARM's matrices. In this specific case, when no effort was made to match the solidification/stabilization process to the contaminant, most of the contaminants were effectively immobilized as determined by the TCLP. It is therefore likely that with a proper choice of binder, it may be possible to better stabilize the inorganic contaminants and, possibly, even some of the organics.

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The complete report, entitled "Evaluation of Solidification/Stabilization as a Best Demonstrated Available Technology for Contaminated Soils," (Order No. PB 89-169 908/AS; Cost: \$15.95, subject to change) will be available only from:

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