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STABILIZATION OF ACIDIC REFINERY SLUDGES*

MICHAEL D. LAGREGA, JEFFREY C. EVANS, CARMEN O. ACUNA, STEPHEN J. ZARLINSKI and DIANE S. HALL

College of Engineering, Bucknell University, Lewisburg, PA 17837 (U.S.A.)

Summary

Petroleum refineries historically have generated large quantities of acidic oil sludge, a waste product from the production of fine lubricating oils. The refining process included adding sulfuric acid to crude oil to remove impurities. The waste product that remained behind after filtration was customarily disposed of in open lagoons.

The physical and chemical characteristics of this sludge vary from lagoon to lagoon and with depth. The material ranges from a solid, charcoal-like material at the bottom of the lagoons to a liquid mixture of sulfuric acid and rainwater at the surface. The sludge utilized for this study varied in pH from less than two to six and has an average loss on ignition of 78.2%. Results are presented from almost 200 separate stabilization tests.

1. Introduction

Bucknell University is in the final year of a three-year research project to investigate effective stabilization/solidification techniques for petroleum sludge. The purpose of this paper is to present selected results from almost 200 separate stabilization tests. The organic characteristics of a typical sample are shown in Table 1.

2. Research program

2.1 First year

During the first year of this investigation literature and vendor surveys [1] were conducted. From these studies, candidate stabilization agents were selected and a methodology for testing the effectiveness of the stabilized material was developed [2].

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TABLE 1

Organic analysis

Compound	Concentration (parts per billion)
Naphthalene	147
Phenanthrene	257
Phenol	2539
Methylphenol	558
Methylnaphthalene	722
Dimethylnaphthalene	815
Pyrene	109

2.2 Second year

The second year of the research focused on laboratory testing of specific stabilization mixes. During this time, 193 sample stabilization mixes were tested. The primary methods for quantification of the effectiveness of the stabilization was the Unconfined Compressive Strength (UCS) and the Toxicity Characteristic Leaching Procedure (TCLP) [3] for the leachability.

2.3 Third year

The results of the laboratory testing are being used as a basis for further studies in the third year. Mixes which most effectively stabilize the petroleum sludge have been selected for additional laboratory studies. Next, a field study using the optimum mix ingredients and proportions will be conducted. The field study will include the construction of one or more lined test cells, stabilization of the sludge, and instrumentation/monitoring of the resulting stabilized material.

3. Laboratory program

3.1 Mixing procedure and physical property tests

The sludge is received from the field in five gallon (19 l) containers. It is first mixed thoroughly before a 500 gram sample is removed for testing. The untreated sludge is characterized by measurements of moisture content, loss on ignition, unit weight and pH. Once characterized, the untreated sludge is combined with stabilization agents in a Hobart mixer and blended to achieve a uniform consistency.

The mixture is tested for moisture content, loss on ignition and pH. The mixture is then compacted in a 2.8'' diameter by 5.6'' high Plexiglass cylinder utilizing a compaction mold collar, and a 2.67 pound hammer with a twelve inch drop to apply a total of 12,400 ft.lb./ft^3, equivalent to the standard proctor compaction energy [4]. This is accomplished using a series of three equal lifts of 35 blows/lift. The compacted cylinder is then subjected to pocket penetrometer testing and unit weight determinations before it is allowed to cure at room temperature in a humid environment for 2 weeks.

After this two-week curing period, the mix is reweighed and subjected to pocket penetrometer [5] testing before being extruded from the Plexiglass mold. After extrusion, dimensions of the mix cylinder are taken and shrinkage observations recorded.

The cylinder is then loaded axially until failure in the unconfined compression test [6]. After failure occurs, the cured stabilized mix is tested for pH, moisture content and loss on ignition before it is disaggregated by passing through an ASTM E-11 (9.5 mm) sieve. The material is then analyzed for metal and organic content. A summary of physical property tests performed at each stage can be found in Table 2.

3.2 Chemical analysis

The untreated sludge and the stabilized mix undergo a modified Toxicity Characteristic Leaching Procedure (TCLP) [7]. The modified version, developed for this study, utilizes sulfuric acid in place of the specified acetic acid. This modification permits determination of Total Organic Carbon (TOC) values. A separate investigation comparing a sulfuric acid extraction with an acetic acid extraction did not identify significant differences in the resulting chemical analysis [8].

The TOC of the TCLP extract is determined using a Dohrman DC-80 low temperature TOC Analyzer. Metal concentrations are determined by using an AAS IL video 12 atomic absorption spectrophotometer. To test for specific organic compounds, a base/acid methylene chloride extraction is performed on one liter of the TCLP extract. The 300 milliliter combined base and acid

TABLE 2

Physical property tests on stabilized material

Variable	Mean	Standard deviation	Minimum	Maximum
Untreated sludge				
pH	5.5[a]	1.9	0.5	7.0
Water content, %	45.6	6.5	17.5	60.6
Loss on ignition, %	78.2	14.5	14.3	98.3
Treated sample (after 2 weeks cure)				
UCS, %	32.7	52.7	0.1	505.6
Loss on ignition, %	30.5	11.9	2.3	67.5
Water content, %	24.9	6.9	5.5	48.0
Volume increase, %	66.6	38.2	20.9	288.7

[a] Geometric mean.

extract is condensed to one milliliter via a Kuderna-Danish evaporative concentrator and acenaphthene-d_{10} (internal standard) is added. Quantitative analysis of the specific organics was performed using a Hewlett Packard GC/MS 59940A chemstation.

A typical gas chromatogram is shown of the raw sludge as Fig. 1. Initially an effort was made to identify as many peaks as possible. However, the large mount in the center of the chromatogram represents alkanes and alkenes which are not separated by available chromatographic techniques. A chromatogram of one of the better mixes is illustrated in Fig. 2.

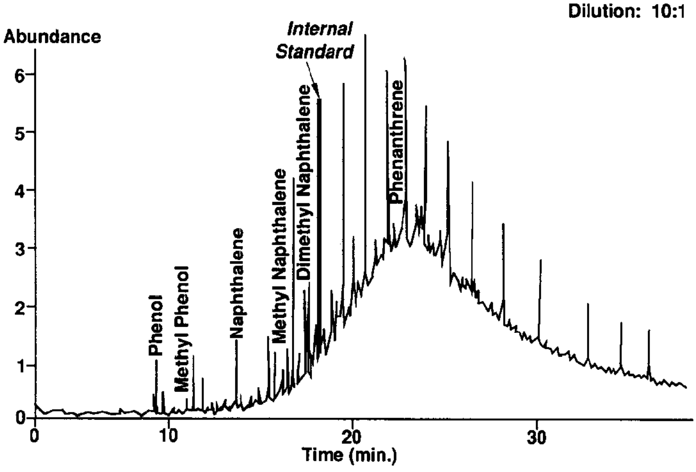

Fig. 1. Chromatogram of TCLP extract of raw sludge.

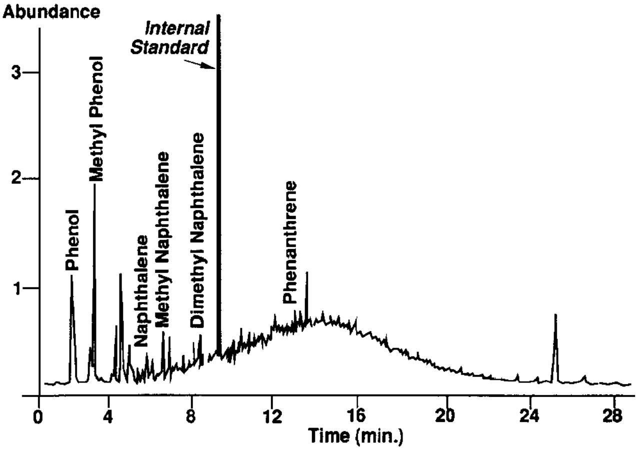

Fig. 2. Chromatogram of TCLP extract of Mix 143.

A summary of analytical data on the TCLP extract for all stabilized mixes attempted is presented in Table 3.

3.3 Complications and difficulties

Data variability has been a major hindrance in evaluating the effectiveness of various stabilization mixes. All the mixes in this study pass the TCLP requirements, thus making the passing or failing of TCLP of no use as a selection tool. Further, the data is strongly influenced by the varying nature of the petroleum sludge itself. Not only does the sludge vary in its physical character from solid to liquid, but it also varies in the amount of soil in different samples. The chemical make up is also found to be quite variable as revealed by the TOC and pH trends illustrated in Fig. 3. As shown in Fig. 3, the pH of the raw sludge used in mixes 1 through 48 was approximately 6. Also note that the higher pH values correlate with the low TOC values, and vice versa. (The table in Appendix A presents mean values of data broken down by mix groupings.)

TABLE 3

Chemical test data

Parameter	TOC (ppm)	Phenol (ppb)	Methyl phenol (ppb)	Naphthalene (ppb)	Chromium (ppm)	Lead (ppm)	Cadmium (ppm)
Mean	187.3	1350.6	255.5	16.3	0.38	0.05	0.01
Std. Dev.	117.7	989.6	198.0	7.4	0.55	0.10	0.03
Minimum	2.5	16.0	8.0	3.6	0.00	0.00	0.00
Maximum	574.4	4981.0	877.9	47.9	3.00	0.80	0.30

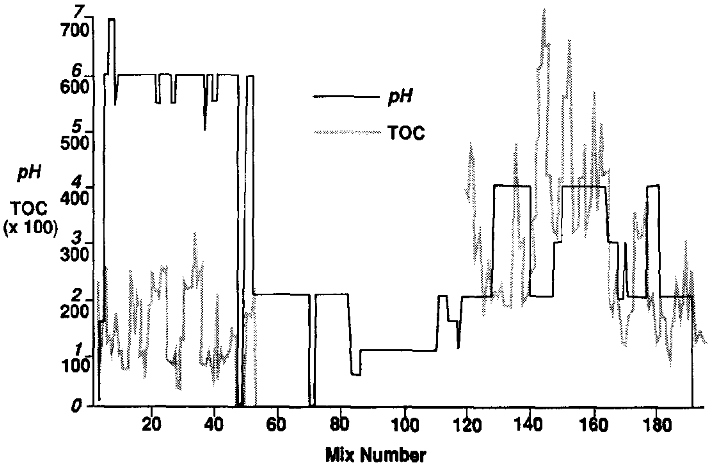

Fig. 3. Raw sludge pH and TOC of TCLP extract as a function of mix number.

TABLE 4

Stabilization agents evaluated

Fly-ash and lime	Cement
Organically modified clays	Bentonite
Cement kiln dusts	Attapulgite
Soluble sodium silicate	Proprietary mixes

Laboratory contamination is also a concern. Phthalates were initially found in blank samples. These compounds are normally associated with plastics, and steps were taken to prevent plastic labware from contacting samples. The continuing practice of running blanks is part of an overall laboratory Quality Control Program.

4. Stabilization materials

As shown in Table 4, a wide range of materials were evaluated in the initial phase of this study. Organically modified clays [9,10] and microfine cements [11] proved to be the most effective at minimizing the leaching of organics, but neither material is cost-effective for the high organic content sludges encountered in this study.

5. Evaluation of laboratory studies

The selection of candidate mixes is perhaps the most difficult part of applying stabilization to real sites. There is no consensus on which tests define "effective stabilization," and decisions must be made on a site by site basis. In this study, all of the mixes evaluated passed the TCLP. Therefore, in all cases the stabilized mass does not constitute a hazardous waste. The TCLP is the most commonly reported test in the stabilization literature. It was utilized in this study to allow comparison to published results. The TCLP test was designed to simulate the placement of the stabilized waste in a municipal landfill where it would be subject to acidic leachate. This is hardly appropriate for most stabilization applications.

51. Selection criteria used

The criteria utilized in this study are shown in Table 5. Unconfined compressive strength (UCS), was not considered a major factor in that the strength of the mix is not related to the ability to prevent leaching of organics. Once organics are tied up, it is relatively inexpensive to increase UCS, if an increase is warranted by proposed future use of the site. Volume increase is of major consequence in that the site has space limitations. Some of the earlier mixes

TABLE 5

Selection criteria

Physical measurements:
- Volume increase
- Unconfined compressive strength

TCLP extract:
- Total organic carbon
- Phenol
- Methylphenol
- Naphthalene
- Chromium
- Lead

Cost

TABLE 6

Candidate mixes

Mix	Unconfined compressive strength (psi)	Volume increase (%)	Phenol (ppb)	TOC (ppm)	Cost ($/ton)
Attapulgite + cement (V)	16	31	331	193	50
Cement (I)	2.8	48	294	63	80
Cement (I) + kiln dust	11	60	199	116	9
Attapulgite + fly-ash + quicklime + cement (I)	69.6	124	444	151	99

had a volume increase approaching 300%. There is simply not enough room at the site to implement such a solution.

The basic tool used to determine the ability of a mix to tie up organics was the TCLP. As noted above, this test is not necessarily realistic and the ANS 16.1 is currently being used to test the more successful mixes (see also Section 7.5). While the TCLP protocol specifies a specific list of organics to be evaluated, this study used the entire range of organics identified in GC/MS analysis.

In addition to quantification of specific organic molecules, a visual inspection of the chromatograms proved to be useful. While it was not possible to quantify the various compounds that make up the bulge in the center of the chromatogram, it is evident that the mix shown in Fig. 2 has effectively tied up most of these compounds when compared to the raw sludge (Fig. 1). It should be noted that the chromatogram of Fig. 1 has been diluted 1:10, and the ordinate is actually an order of magnitude higher.

The cost of additives considered vary from fly-ash, at less than a penny per pound to highly specialized organophilic clays that cost over two dollars per pound. The mixes evaluated represent a wide range of chemical costs, extending from under ten dollars per ton to several thousands. Cost was therefore a significant factor in the selection of a suitable mix.

5.2 Candidate mixes

In reviewing all of the above criteria, the series of mixes shown in Table 6 were selected for further study. The data shown in Table 6 are preliminary results of some of the selection variables.

6. Statistical analyses

6.1 Non-normality/unequal variances

Two studies involving random allocation of sludge samples were carried out. The first one consisted of a replicate study involving sixteen mixes to compare two types of sorbents and two types of binders, with four replicates allocated to each sorbent–binder combination. The second study involved 27 mixes (three additives at three levels each, without replication).

The first step in the analysis was to look at histograms and summary statistics for all the variables under study. In most cases the histograms showed severe skewness or bimodality, and outliers. Figure 4 illustrates a normal probability plot for methyl/phenol residuals.

Even adjusting for differences in group averages, the data for the most part showed marked departure from normality. This was typical of many of the variables examined as part of this study.

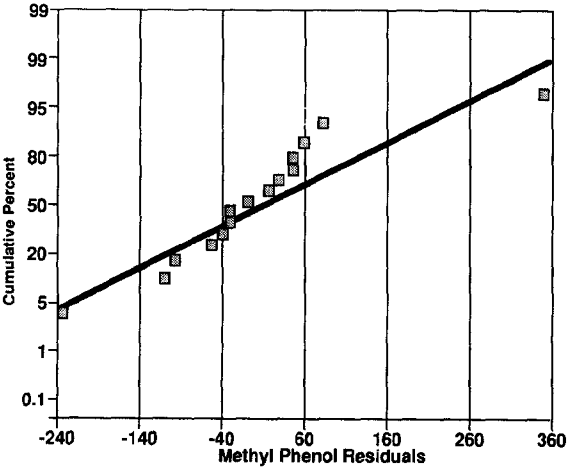

Fig. 4. Normal probability plot of methylphenol residuals.

TABLE 7

Standard deviations of replicate mixes

Variable	Bentonite fly-ash quick-lime	Bentonite cement	Attapulgite fly-ash quick-lime	Attapulgite cement	Ratio (high/ low)
Volume increase (%)	6.6	1.8	5.2	1.4	4.7
Unconfined compressive strength (psi)	5.6	0.35	11.4	9.2	31.4
TOC (ppm)	98.5	44.4	67.3	92.8	2.2
Phenol (ppb)	578.6	783.9	175.0	470.7	4.5
Methylphenol (ppb)	55.2	305.0	67.8	48.4	7.0
Naphthalene (ppb)	5.4	2.6	1.4	2.8	3.9

In addition to looking at the summary statistics of the data as a whole, special attention was given to the variability of the data within homogeneous groups. From the binder–sorbent study it was possible to obtain estimates of the variability of the measurements based on four observations. Standard deviations for selected variables are given in Table 7.

Table 7 shows that the variability of the data changes from group to group. It should be noted that for the variables depicted there always exists a group whose standard deviation is at least twice of that of the other groups. Therefore the assumption of equal variances, as required by many standard statistical techniques, is not met.

The lack of normality and inequality of variances are possibly related, and have prompted the use of non-parametric methods of data analysis. In the sorbent–binder study, an equivalent non-parametric test did not exist, therefore the standard parametric analysis (the F-test) was carried out. Caution must be exercised when interpreting these results. Specifically, the departure from the standard assumptions increases the probability that statistically significant differences will not be identified.

6.2 Binder sorbent study

6.2.1 Description

The performance of four different types of mixes was studied by carrying out an experiment involving 16 runs. The goal of the study was to compare the performance of two types of sorbent (bentonite and attapulgite) and two types of binder (fly-ash/quicklime and cement). All mixes contained the same proportions of sorbent and binder. The experimental layout is shown in Table 8.

This experimental design can be described as a completely randomized factorial experiment with two factors, each factor at two levels. This type of experimental design allows comparison of the performance of the two sorbents,

TABLE 8

Binder–sorbent study

Stabilization agent	Level (weight additive/weight sludge)
Two binders:	
Cement	0.3
Fly-ash + quicklime	0.3 + 0.1
Two sorbents:	
Bentonite	0.4
Attapulgite	0.4

4 Replicates of each combination, total = 16 tests

TABLE 9

Summary statistics

Variable	Sample size	Mean	Standard deviation
Volume increase	16	38.6	8.0
UCS	14	33.1	19.0
TOC	16	367.2	86.3
Phenol	15	1349.0	487.2
Methylphenol	15	238.2	194.0
Naphthalene	15	19.9	13.3
Chromium	16	0.5	0.5
Lead	16	0.06	0.09

the performance of the two binders, and also the performance of the individual mixes.

As noted in the previous section, the data does not meet the assumptions underlying the analysis of this type of experimental design. However, since the design is balanced, the results are valid due to the robustness of the F-test [12].

6.2.2 Results

Table 9 provides summary statistics for all the variables under study. No significant differences in the average performance of the mixes were found for the variables phenol, chromium, and lead. Therefore, for these variables, the mean values shown in Table 9 provide the best estimates.

Analysis at the 1% level of significance showed that the volume increase is affected by the type of binder used in the mix. In particular, mixes that use fly-ash and quicklime as a binder exhibit a significantly higher average volume increase than those which use cement as a binder. The unconfined compressive strength (UCS) is significantly affected by the type of sorbent and also by the type of binder used. However, only one statistically significant difference in mean UCS exists among individual mixes. The value 5.1 is significantly less than the other three mean values, but no difference is observed among the values 31.5, 53.3 and 36.4 (Table 10).

Notice that the observed differences are mainly due to the low readings for mixes in the bentonite/cement cell and that no significant differences exist among the other three types of mixes.

The analysis also showed that the total organic carbon is significantly lower (p value <0.10), for the attapulgite/fly-ash/quicklime mixes. Summary statistics for this analysis are given in Table 11. Table 12 shows group averages for methylphenol. The analyses of these two variables indicated significant differences among individual mixes (p value <0.05), as well as sorbent and binder effects (p value <0.10). These observed differences are due mainly to the high readings in the bentonite/cement cell; there is no difference in the average methylphenol among the other three mixes.

To summarize, the volume increase is larger when the binding agent is fly-ash/quicklime. This binding agent also appear to tie up the organic carbon better and provide an increased unconfined compressive strength. Except for the bentonite/cement mixes, all the other mixes are equally effective in tying up the methylphenol and the naphthalene. Overall it is important to notice that, except for the volume increase, most of the observed differences are due to the poor performance of the bentonite/cement mixes.

TABLE 10

Unconfined compressive strength

		Binder		
		Fly-ash	Cement	
Sorbent	Bentonite	31.5 (4) 2.8	5.1 (3) 0.2	20.2 (7) 5.5
	Attapulgite	53.3 (4) 5.7	36.4 (3) 5.3	46.1 (7) 5.0
		42.4 (8) 5.1	20.8 (6) 7.4	Mean (Replicates) Std. error

TABLE 11

Total organic carbon

		Binder		
		Fly-ash	Cement	
Sorbent	Bentonite	393.3 (4) 49.2	362.8 (4) 22.2	378.0 (8) 25.7
	Attapulgite	291.5 (4) 33.7	421.2 (4) 46.4	356.3 (8) 36.1
		342.4 (8) 33.7	392.0 (8) 26.2	Mean (Replicates) Std. error

TABLE 12

Methylphenol

		Binder		
		Fly-ash	Cement	
Sorbent	Bentonite	153.4 (4) 27.6	525.5 (3) 176.1	312.9 (7) 101.5
	Attapulgite	186.3 (4) 33.9	159.5 (4) 21.7	172.9 (8) 19.3
		169.8 (8) 21.2	316.4 (7) 100.2	Mean (Replicates) Std. error

6.3 Effect of additive level

6.3.1 Description

An experiment designed to investigate the effect of different levels of additives was carried out.

Twenty-seven mixes were randomly allocated to one of the 27 possible combinations shown in Table 13. It is important to note that no mixes were replicated and only one mix corresponds to each possible combination of levels. Therefore while the effect of each individual component (attapulgite, fly-ash/quicklime, and cement) can be measured, the effect of interactions cannot.

TABLE 13

Effect of additive level

Additive	Levels (weight/additive/weight sludge)		
Attapulgite	0.4	0.6	0.8
Fly-ash	0.25	0.5	0.75
Cement	0.25	0.5	0.75

One mix at each possible combination = 27 tests.

TABLE 14

Summary statistics

Variable	Sample size	Mean	Standard deviation
Volume increase	27	123.8	46.3
UCS	27	69.6	34.5
TOC	27	151.2	43.5
Phenol	24	1037.5	502.6
Methylphenol	26	172.4	72.2
Naphthalene	24	13.9	3.4
Chromium	27	0.88	0.58
Lead	27	0.09	0.13

The statistical analysis was carried out using the Kruskal–Wallis [13,14] test which is a non-parametric equivalent of the one-way analysis of variance (ANOVA). This test was chosen because the variables under study departed markedly from the assumptions underlying the traditional one-way ANOVA (normality and equality of variances).

6.3.2 Results

Summary statistics for all variables under study are given in Table 14. Unconfined compressive strength, naphthalene and lead are not affected by the additive level, that is, all mixes show the same performance with respect to these variables with any observed differences being due only to chance variation. Also the pH of the untreated sludge is homogeneous for all the groups (geometric mean of pH = 3.2).

The analysis showed that the level of fly-ash/quicklime has a statistically significant effect on the average volume increase (Table 15). The *p*-value for this test was 0.0032. The level of cement and attapulgite in the mix do not significantly affect the percent volume increase. The multiple comparisons

TABLE 15

Volume increase (%)

Levels	Attapulgite			Fly-ash			Cement		
	0.4	0.6	0.8	0.25	0.50	0.75	0.25	0.50	0.75
Sample size	9	9	9	9	9	9	9	9	9
Mean value	104	117	151	94	130	148	114	120	137
Standard error	8.8	8.0	22.1	7.7	21.4	8.4	8.7	13.0	22.3

TABLE 16

Total organic carbon (ppm)

Levels	Attapulgite			Fly-ash			Cement		
	0.4	0.6	0.8	0.25	0.50	0.75	0.25	0.50	0.75
Sample size	9	9	9	9	9	9	9	9	9
Mean value	179.0	144.1	130.6	166.8	152.5	134.3	159.2	143.8	150.7
Standard error	14.1	8.6	15.9	13.1	18.5	10.2	17.9	12.8	13.5

TABLE 17

Methylphenol (ppb)

Levels	Attapulgite			Fly-ash			Cement		
	0.4	0.6	0.8	0.25	0.50	0.75	0.25	0.50	0.75
Sample size	9	9	9	9	9	9	9	9	9
Mean value	165.3	172.9	179.0	209.4	197.9	109.9	160.0	176.4	180.7
Standard error	25.1	24.9	25.5	22.0	19.0	18.0	25.7	27.9	20.9

test [13] shows that for fly-ash/quick lime, the levels 25% and 75% are significantly different. The statement is true for levels 25% and 75% of the fly-ash/quicklime factor.

The total organic carbon is affected only by the level of attapulgite in the mix (p value = 0.0104). The multiple comparisons test showed that mixes with 60% attapulgite are as effective as those with 80%, whereas those with 40% attapulgite content do not perform as well. Summary statistics are given in Table 16.

Methylphenol concentrations are affected by the levels of fly-ash/quicklime (p value = 0.0026), mixes with 75% fly-ash/quicklime have the lowest average concentration. Phenol concentrations are affected by the levels of fly-ash (p

TABLE 18

Phenol (ppb)

Levels	Attapulgite			Fly-ash			Cement		
	0.4	0.6	0.8	0.25	0.50	0.75	0.25	0.50	0.75
Sample size	9	9	9	9	9	9	9	9	9
Mean value	960.4	956.0	1196.1	1305.0	1147.9	659.6	1122.9	1104.3	885.3
Standard error	201.6	177.7	119.5	107.3	181.0	136.4	160.9	178.3	170.8

TABLE 19

Chromium (ppm)

Levels	Attapulgite			Fly-ash			Cement		
	0.4	0.6	0.8	0.25	0.50	0.75	0.25	0.50	0.75
Sample size	9	9	9	9	9	9	9	9	9
Mean value	1.1	0.60	0.93	1.11	0.68	0.84	1.22	0.49	0.92
Standard error	0.28	0.16	0.06	0.27	0.15	0.12	0.23	0.15	0.12

value = 0.0116), mixes with 75% fly-ash have significantly lower average phenol content. The percentage of cement in the mix significantly affects the concentration of chromium in the extract. The multiple comparisons test shows that mixes containing a 50% cement are significantly more effective in tying up chromium than either 25% or 75%. Group averages, sample sizes and standard errors are given in Tables 17, 18 and 19, respectively.

To summarize, the statistical analysis indicates that the following mixes show the most promise for effectiveness: 60% attapulgite, 25% fly-ash/quicklime, and 50% cement or 60% attapulgite, 50% fly-ash/quicklime, and 50% cement.

7. Ongoing studies

It is recognized that although a particular stabilization mix may be effective in laboratory studies, degradation may occur under long-term environmental stresses. Therefore, durability tests are being conducted to evaluate long-term environmental effects on the stabilized material. The results of these durability studies are presented elsewhere [19].

7.1 Curing-time study

Under current laboratory procedure, the stabilized sludge samples cure in a humid environment for two weeks before any further testing is conducted. A study was conducted to determine whether the test results are significantly affected by the curing time. Individual samples are tested at weekly intervals up to four weeks and monthly thereafter. With the exception of the curing time, the physical-chemical testing methodology remaines unchanged.

7.2 Wet/dry tests

To further study long-term environmental effects, a wet/dry study was conducted. The wet/dry tests [15] allow for the determination of the durability, the moisture changes, and the volume changes of the stabilized sludge sample as produced by cycles of wetting and drying. Each sample is placed in a bath of water for six hours and oven-dried for forty-two hours.

7.3 Freeze/thaw tests

Since the project is located in the mid-Atlantic region, the stabilized material may also be subjected to freeze/thaw climatological stresses. The freeze/thaw test [16] determined the same parameters as the wet/dry analysis except that the samples are frozen for six hours and thawed for forty-two hours. Likewise, the process is repeated on each sample for a total of twelve cycles.

7.4 One-dimensional consolidation

The consolidation test [17] is used to predict the total deformation due to an applied load of overlying material. These data are also used to predict time-rate of settlement.

7.5 American Nuclear Society (ANS) 16.1 procedure

The ANS 16.1 [18] procedure is used to determine the long term leaching potential of stabilized sludge samples. This method may more precisely model the conditions which will be present *in situ*. The method is less aggressive than the TCLP procedures. The results may also be used to estimate the effective diffusivity of various contaminants from the stabilized material.

8 Conclusions

8.1 Additives

In a comparison of binders (Cement vs. fly-ash+quicklime) and sorbents (bentonite vs. attapulgite) fly-ash and attapulgite provided the best overall mix. The total organic carbon in the extract is lower when the binding agent is fly-ash/quicklime.

In a study comparing the levels of three additives, the analysis showed that the levels of fly-ash/quicklime have a statistically significant effect on the average volume increase, but the level attapulgite and of cement in the mix do not. The nature of the materials is such that fly-ash/quicklime add significantly to the volume. The total organic carbon is affected only by the level of attapulgite; lower TOC values are associated with the highest level of attapulgite.

Based upon the studies to date [9] it is concluded that organophilic clays are the most effective at stabilizing the organic components of the waste. However, for the highly organic waste sludge of these studies, organically modified clays are not cost-effective. The cost-effectiveness improves when considering lower organic concentrations, such as contaminated site soils. Organophilic clays are particularly suited for the heavy organics, and are less effective for the volatile organics.

Studies have shown that adding some cement to fly-ash/lime mixes enhances the retention of organics, as measured by TOC. The fly-ash/lime mixes with some cement out perform those with cement only or fly-ash and lime only. These studies have also shown that attapulgite mixes outperform bentonite mixes. The attapulgite clay has a greater affinity for organics than the bentonite clay.

8.2 Testing

Unconfined compressive strength is not a reliable indicator of the effectiveness of stabilization. Further, many materials with an unconfined strength of zero are quite stable (e.g. sand).

The pass/fail application of the TCLP is of limited usefulness. Further, substitution of sulfuric acid allows TOC to be measured. It is recognized that TOC is high for large molecules that may not be related to toxicity.

For this study, waste nature and variability were more important than any other parameter. For example, subsequent sampling of the same location in the same lagoon using identical sampling methods yielded very different results. Implementing stabilization with a very limited treatability program may therefore result in unsatisfactory field performance.

Of the organics present in this acidic sludge, phenolics are the most difficult to immobilize.

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Appendix A

TABLE A1

Test averages for stabilization mix groupings

	Number of mixes	TOC (ppm)	Phenol (ppb)	Napthalene (ppb)	Pocket penetrometer	Volume change	Wet density	Dry density	Pocket penetrometer	Compressive strength	Unit strain	Total cost
Attapulgite												
(1-48)[a]	6	183.72	475.67	4.33	26.16	57.02	1.25	0.94	49.31	16.59	3.60	$89.93
(49-193)[b]	50	230.73	1209.73	13.97	34.09	90.87	1.39	1.06	58.27	61.04	3.09	$91.69
(1-193)[c]	56	226.10	1154.97	13.39	33.83	88.53	1.38	1.04	57.53	55.43	3.18	$91.24
Bentonite												
(1-48)	8	151.45	333.96	13.23	6.76	36.60	1.41	1.04	27.40	30.76	12.27	$144.77
(49-193)	17	308.34	1659.38	24.45	12.17	39.17	1.42	1.03	40.44	15.69	11.59	$85.33
(1-193)	25	246.34	1165.28	19.46	10.82	38.38	1.41	1.03	37.15	23.75	11.52	$121.83
Cement												
(1-48)	23	112.61	292.17	9.52	10.00	42.30	1.36	1.02	38.90	16.90	8.10	$812.50
(49-193)	91	218.33	1670.12	16.88	18.82	80.56	1.44	1.10	37.85	37.42	8.07	$346.09
(1-193)	114	185.02	1392.11	15.93	17.04	72.84	1.42	1.08	38.07	32.28	8.08	$440.19
Fly-ash												
(1-48)	15	147.84	418.36	9.16	15.30	45.50	1.29	1.00	35.90	11.70	8.10	$395.40
(49-193)	48	208.49	1360.04	15.41	31.69	94.27	1.36	1.06	56.86	51.42	3.37	$66.16
(1-193)	63	101.33	1135.83	13.92	27.79	82.66	1.35	1.05	51.87	41.97	4.50	$220.74
Organoclay												
(1-48)	24	76.21	248.91	8.67	13.40	45.10	1.27	0.97	43.60	21.50	6.00	$968.18
(49-193)	58	NA	2212.82	17.91	6.74	67.44	1.59	1.27	25.23	15.64	9.62	$736.27
(1-193)	82	NA	1638.02	15.20	8.69	60.90	1.49	1.18	30.61	17.35	8.56	$804.15
Sodium silicate												
(1-48)	6	121.17	197.00	17.50	11.80	58.70	1.38	1.06	51.00	22.40	3.50	$813.71
(49-193)	13	NA	1022.30	14.14	20.37	64.06	1.21	0.89	44.13	33.00	7.12	$181.33
(1-193)	19	NA	761.68	15.20	17.67	62.37	1.26	0.94	46.30	29.65	5.98	$381.03
Cement kiln dust												
(1-48)	5	156.84	258.20	18.00	5.30	49.40	1.50	1.20	42.40	9.50	4.70	$94.40
(49-193)	5	NA	2690.20	24.19	14.03	74.96	1.46	1.14	31.53	11.35	6.07	$247.20
(1-193)	10	NA	1474.20	21.10	9.66	62.18	1.48	1.17	36.96	10.43	5.38	$170.80
Proprietary												
(1-48)	7	105.87	69.17	7.75	5.80	42.20	1.35	1.03	30.60	18.10	9.10	$441.62
(49-193)	23	209.11	1605.57	16.81	22.13	56.97	1.29	1.04	38.41	20.29	5.15	$540.50
(1-193)	30	141.61	1247.08	14.69	18.32	53.52	1.30	1.04	36.58	19.78	6.07	$517.43

[a] Means of mixes 1-48 only. [b] Means of mixes 49-193 only. [c] Means of all 193 mixes.