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Solidification and Stabilization of Contaminated Soil

Amitdyuti Sengupta University of New Orleans

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A Thesis

Submitted to the Graduate Faculty of The University of New Orleans in partial fulfillment of the requirements for the degree of

> Masters of Science in Environmental Engineering

> > by

Amitdyuti Sengupta

B.S., Nagpur University, India, 2004 May 2007

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ABSTRACT

In-situ remediation by Solidification and Stabilization (S/S) has shown huge promise in dealing with the clean up of soils contaminated with pollutants listed as Hazardous Substances under Resource Conservation and Recovery Act (RCRA). The site discussed in this paper was contaminated with Naphthalene, heavy metals and other VOCs.

In order to find an effective remediation solution it was decided to explore the feasibility of using S/S. Research conducted included exploring Portland cement in combination with organo-clay (bentonite). Admixtures were chosen based on their advantages such as availability, previous experiences, costs and quality assurances. S/S has been found to be an effective method of remediation according to the various past and present Superfund projects. The study plan for this thesis involved bulk analysis and leachability tests to determine the initial and final level of contaminants in the soil and their potential leachability from the soil. The treated soil also underwent weight loss and air emissions (TO-3) tests.

INTRODUCTION

Large scale manufacturing requires most modern industries to store huge quantities of chemicals, raw materials and wastes before they can be used or disposed. Gas stations along with the large and small manufacturing units use Underground Storage Tanks (USTs) as a common means to store materials. Most newly constructed USTs are made of non-corrosive fiberglass, but older tanks were made of steel.

Over the years steel tanks start to corrode and leak. These seeping oils and other forms of chemical compounds slowly contaminate nearby soil and groundwater. Since half of America's population depends on groundwater for its drinking needs such contamination is a direct health hazard for millions. Compounds commonly found in hydrocarbon contaminated drinking water, such as benzene have the potential to cause damage to central nervous system, kidneys and also cause cancer. Most USTs contain hydrocarbon products which are listed as hazardous substances under Resource Conservation & Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act ("Superfund"). Leaking UST's are referred to as Leaking Underground Storage Tanks (LUST). A schematic diagram of LUST and plume spread is depicted in Figure 1.

Until 1999 the U.S. Environmental Protection Agency (EPA) monitored approximately 370,000 LUST sites in the United States. About 21,000 site cleanups were planned for fiscal year 2001. EPA funds approximately \$ 70 million per annum for the clean up of LUST sites.

Contaminated sites are not only harmful to human health it also has an adverse effect on the retail value of the property in concern. Various innovative techniques have been devised to make such contaminated sites clean by economic means. One of the established remediation methods is Solidification and Stabilization (S/S). This widely used treatment technology was initial developed in 1950's to treat radioactive wastes. Its use was further extended to treat hazardous wastes in the 1970's. Treatment procedure involves mixing one or more binding reagent into the contaminant of the media or waste. The binding material immobilizes contaminant by physical and chemical changes. EPA considers S/S as an established treatment technology including those involving hazardous waste. S/S has also found use in treating RACRA listed and characteristic wastes. Dependability of S/S is gauged by the fact that it has found application in 24% of all the superfund projects. Strengthening of US liability laws are encouraging rehabilitation of contaminated sites under the Brownfield program. S/S due to its dual ability of treatment of waste and its subsequent reuse is a popular choice in many Brownfield projects. In Boston a Brownfield site undergoing ex-situ S/S found the treated soil mixed with Portland cement to be very good binding material for a nearby parking lot. Such innovations certainly save millions of dollars apart from reaching the objective of remediation.

 Figure 1: Typical schematic diagram of LUST *Reference: Boulder Area Sustainability Information Network (BASIN)*

BACKGROUND

One of the sites in California currently waiting for remediation to clean up contaminants from a LUST has been chosen to evaluate the use of S/S as the primary remediation technique.

The site was a manufacturing facility until the 1920s. After closing, the facility was demolished and wastes were dumped into an UST. The site is currently occupied and used for commercial operation. The UST was a tank that was 40['] in diameter with the bottom of the tank located at 22' below ground surface (bgs). The groundwater fluctuates between $20' - 22'$ and the heaviest contamination extends to a depth of 30' bgs. The impacted area is expected to have very high levels of benzene and naphthalene.

SCOPE AND OBJECTIVES

Scope:

The scope of this thesis is limited to undertaking laboratory analysis of soil samples received from a client at an unknown site in California. Solidification and Stabilization (S/S) method has been investigated from the plethora of remediation techniques available to satisfy client's requirement. Due to limitation on resources and time, only Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP) methods were used to assess the leachability of metals and organics. For assessing air emission potential, TO-3 analysis was used. Bulk analysis was carried out to assess the contaminant levels in the soil before and after the treatment.

Objectives:

The main objective of this thesis was to establish an optimum mix of additives (Portland cement, bentonite and water) for S/S to be used to treat the contaminated soil samples. The effectiveness of the S/S treatment was also evaluated by undertaking various laboratory analysis.

Upon establishing the overall objective of the research the next step was to have an understanding of the specific objectives. The plan involved various laboratory experiments which would help determine the optimum mix of additives and their effectiveness to immobilize the contaminant.

The specific objectives are:

- •Develop the optimum mix for S/S.
- •Assess reduction in leachability by performing leachability tests on untreated and treated soil samples.
- •Evaluate the emissions generated during the S/S process.
- •Understand the contaminants that will (1) remain in the soil matrix, (2) expected in the leachate, and (3) potential to become airborne.

LITERATURE REVIEW

SOLIDIFICATION AND STABILIZATION (S/S)

A variety of binders and additives can be used in order to achieve S/S. In this proposed study Type 1 Portland cement and an organo-clay were considered to achieve S/S.

Solidification: A technique where a substance (for example Portland cement) is used to bind the waste involved in order to reduce its mobility. This process may or may not be chemical in nature.

Solidification as applied to fine waste particles, typically 2 mm or less, is termed microencapsulation and that which applies to a large block or container of wastes is termed macroencapsulation.

Stabilization: A chemical reaction is initiated between a binder and waste to make the latter less hazardous.

S/S involves mixing of different kinds of binders such as inorganic binders (Portland cement, lime, lime kiln dust, fly ash, slag etc.) and organic binders (asphalt, thermoplastic and ureaformaldehyde). Most of the commercial scale S/S involves the use of inorganic binders due to the cost restrictions imposed by the latter. Different S/S projects require different kinds of mix designs. This is necessitated due to the large variations in wastes and its concentrations. While choosing S/S as the option to treat contaminated soil, care must be taken to ascertain the types of contaminants involved. A table has been attached in this section which shows the efficiency of S/S over various contaminations.

Portland cement has an ability to solidify, stabilize and sometime bring down the toxicity levels in contaminant. Portland cement-based mix designs have been popular S/S treatments and have been applied to a greater variety of wastes than any other S/S binding reagent. According to Portland Cement Association, "cement is frequently selected for the reagent's ability to (1) chemically bind free liquids, (2) reduce the permeability of the waste form, (3) encapsulate waste particles surrounding them with an impermeable coating, (4) chemically fix hazardous constituents by reducing their solubility, and (5) facilitate the reduction of the toxicity of some contaminants."

The above results are achieved due to the various kinds of physical and chemical changes that happen when cement reacts with water. Portland cement when mixed with water under goes hydration and forms physical bonds with contaminants. This traps the contaminants into a matrix and eventually makes them less mobile. Such techniques can also lower the permeability of the treated material and significantly reduce the leachability. Portland cement can also initiate a stabilization process in the contaminated soil. Hydration of cement on contact with water generates calcium hydroxide Ca(OH)2 which further reacts with water and contaminants, making them somewhat less soluble and therefore less leachable. Portland cement on hydration also forms compounds of carbonates and silicates which tend to bind with the contaminants making them less soluble.

It has also been observed that toxicity of many in-organic substances such as heavy metals has been reduced by manipulating their valence through various additives and mixing techniques. Number of RACRA listed heavy metals which have failed TCLP test has been subjected to S/S. After treatment the waste is found to lose its toxicity levels in the leachate and can be safely disposed of as non-hazardous waste. S/S achieves the reduction in mobility of in-organic compounds by (1) formation of insoluble hydroxides, carbonates, or silicates; (2) substitution of the metal into a mineral structure; and (3) physical encapsulation. A case study conducted in India has been discussed in this thesis which shows formation of new hydroxides and bonds or ribs with the help of SEM photomicrographs and X-Ray diffractograms.

Organo-clay such as bentonite has been found to have micro and macro encapsulation effects. At the micro level the contaminant and bentonite are bound to each other. This is due to the organophyllic nature of bentonite. It helps the contaminant to get attached to the cementitious matrix created by Portland cement. At the macroscopic level bentonite and contaminant are found to be physically trapped in the cementitious matrix. Bentonite has an exceptional property to absorb water several times its own dry weight. This property makes bentonite an excellent sealant and water proofing material. Bentonite has been traditionally used as drilling mud for oil and gas wells, in slurry walls and water proofing. Calcium bentonite is supposed to have medical value for its cleansing properties on digestive system, however no scientific evidence was found by the author.

Fly ash is another major form of binder in use. It demonstrates a pozzolanic effect when mixed with Portland cement. Economical options include the use of Cement Kiln Dust (CKD) and slag as binders. Sometimes, the pH of the soil is of vital importance since certain contaminant show special properties (such as ability to dissolve) in particular pH range. Lime, limestone and Lime Kiln Dust (LKD) are generally used to maintain the pH suitable for S/S. Lime due to its property of high heat of hydration liberates water trapped in the pores of the contaminated soil.

S/S is sometimes used to treat free liquids for land disposal which are otherwise prohibited by RACRA. Such a case study has been discussed in this thesis were dredge sediments were treated with Portland cement before disposing in municipal waste landfill sites. Cement has the ability to chemically bond with water forming various cement hydration products.

Various kinds of organic compounds such as PCBs, VOCs, halogenated and non-halogenated semi-volatiles has been treated with the application of S/S. Treatment of organic compounds by S/S primarily involves solidification. Binding of free water, formation of monolith, drop in the hydraulic conductivity of waste are some of the mechanism by which organic wastes are treated. Large concentrations of oil and grease may sometimes form a layer over the cement particles thereby preventing hydration on addition of water. Certain hydration reaction may be exothermic; the heat liberated may volatilize certain VOCs present in the soil. Adequate off-gas collection and treatment device must be in places in such special cases.

Figure 2(a & b) shows two different S/S remediation project sites. The NJ site had to treat harbor dredge. The site is Massachusetts was a Browns field site.

Figure: 2(a) S/S Treatment on harbor dredge in NJ Figure: 2(b) S/S Ex-situ site in MA

Source: EM Feature

Applicability

S/S is generally utilized for remediation of organic, inorganic compounds including radionuclide and heavy metals. It has also found successful application in sites contaminated with PCBs, organics including dioxins, VOCs and a range of heavy metals. Short term clean up criteria has been found to have been met in various Superfund sites, however long term impacts are yet to be determined.

Advantages

- •Best Demonstrated Available Technology according to EPA.
- •Cost effective if proper binders chosen
- •Applicable to wide range of contaminant like VOCs, SVOCs, heavy metals and radionucleid.

Limitations

Criteria which may impede success of S/S are as follows:

- Very deep contaminants are difficult to treat.
- An appreciable increase in volume after treatment may be a cause of concern in certain cases.
- Compatibility with the waste has to be ascertained by conducting treatability studies.
- Like all in-situ treatments, confirmatory sampling can be more difficult than for ex-situ treatments.

• Solidified material may pose problems for future site usage.

Cost

The cost factor varies extensively and depends on a range of factors such as the type and depth of contamination, availability of reagents and equipments. The cost of in-situ soil mixing/auger techniques can average \$50 to \$80 per cubic meter (\$40 to \$60 per cubic yard) for shallow applications and \$190 to \$330 per cubic meter (\$150 to \$250 per cubic yard) for deeper applications The above cost figures were obtained from Federal Remediation Technologies Roundtable (FRTR) website and should be used with caution. Author does not have confirmed data.

USEPA considers S/S to be a proven technology and has allowed its application at 24% of all the Superfund sites across the nation. EPA considers S/S the Best Demonstrated Available Technology (BDAT) for fifty RCRA listed Hazardous wastes compounds. Figure 3 shows a sketch of a S/S site where an augur mixes predetermined quantities of cleanup material and water into the contaminated soil.

Figure 3: Schematic Diagram of a Typical In-situ S/S Process *Source: Envirotools*

Figure 4 lists the top five source control treatment technologies at the superfund remedial sites. According to this list S/S has an individual share of 24% among all the available control technologies which are currently in use at various superfund sites. Figure 4 shows the various types of binders that are in use such as organic, inorganic and a combination of both. From the pie chart it is evident that majority (94%) of S/S projects currently underway use inorganic binders (e.g.: Portland cement, fly ash, lime etc.)

Soil Vapor Extraction	28%	
Solidification/Stabilization	24%	
Incineration (off-site)	13%	
Bioremediation	11%	
Thermal Desorption	9%	

 Figure 4: Top 5 Source Control Treatment Technologies at Superfund Remedial Sites *Source: Cluin.org*

 Source: Cluin.org

In figure 5 the pie chart splits out the share of various contaminants types which were successfully treated by S/S. Most success was reported in treating metals (52%) followed by organics (32%); other important contaminants to be treated are combination of metals and radioactive elements. This data was based on a total of 163 project sites and the figures in bracket signify the number of individual projects.

Figure 6 shows pie chart representation of the percentage distribution of types of contaminants in the various S/S remediation sites. The expected efficiency of S/S on various kinds of contaminant like organic, in-organic and radio-nuclide is shown in figure 7.

Case Studies

In-situ Stabilization/Solidification of PCB-Contaminated Soil. *(Mark K. Stinson and Stephen Sawyer)*

One of the first field demonstrations of in situ stabilization/solidification process was undertaken in April 1988. The site involved was General Electric Co. electric service station in Hialeah, FL. The site was contaminated with Polychlorinated biphenyls (PCBs) and localized concentrations of VOCs and heavy metal contaminants. The binders used were HTW-20 a cementitious mix and water. The two primary objectives of this project were to; immobilize the PCBs and potential long-term integrity of the soil strata. In order to estimate the effectiveness of immobilization three types of leachability test was performed including TCLP. The PCB concentration was generally around 300 mg/kg the maximum being 950 mg/kg. On additive injection of HTW-20, mixing of higher contaminated soil with lower contaminated soil and water brought down the concentration of contamination to a maximum of 170 mg/kg with the majority of samples readings below 110 mg/kg. Treated soil leachability showed values less than the detectable limit of 1µg/l. On further reduction of the detectable limit to 0.1µg/l only four of the seven most contaminated samples showed data above the new detectable limit. The researchers assumed the low detection limit of PCBs in the leachate may be due to the immobilization caused by the HTW-20 binders. The effect of the binders could not be proved conclusively since the researchers felt the values of concentration measured were too low. The maximum concentration of VOCs such as ethlylebenzene, chlorobenzene, and xylene were found in three of the samples to maximum values of 1485 mg/kg. Post remediation the maximum VOCs was reported at 41mg/l. The leachability test of untreated soil stood at 2.5-7.9 mg/l which on treatment was 0.32- 0.61 mg/l. Similar reduction in concentration was recorded for certain heavy metals such as lead, zinc, copper and chromium. Pre treatment concentration were 5000 mg/l and post treatment it was reported in the range of 80-270 mg/l. Leachability tests for the heavy metals also showed declining trend from pre-treatment range of 0.32-12.65 mg/l to a post treatment range of 0.12- 0.21 mg/l. Researchers felt due to limited data and low soil concentrations, immobilization of heavy metals cannot be ascertained for sure. However, past experience has shown that cementitious process indeed immobilizes heavy metals. Permeability test data showed an appreciable reduction from un-treated soil $(1.8 \times 10^{-2} \text{ cm/s})$ to treated soil $(10^{-6} \text{ to } 10^{-7} \text{ cm/s})$. According to the researchers the four to five times reduction of permeability will route the ground water around the solidified monolith rather than through it.

 Stabilization of Fuel Oil Contaminated Soil-A case study. *(Sanjay Shah, A V Shroff, Jignesh V. Patel, K. C. Tiwari and D. Ramakrishnan)*

This particular case study had a primary focus to increase the geotechnical properties of the contaminated soil by stabilization. However, lechability tests showed a reduction of various oil based compounds when the soil was treated with inorganic binders such as lime, cement and fly ash. The site in concern is in the city of Vadodara in the state of Gujarat, India. A point source led to contamination of sub-soil area of approximately 200m². In order to prevent the further spread of the plume, impervious bentonite dykes were constructed. In order to fully reclaim the land, remediation of the site was proposed. The study undertaken by researchers^{*} from MS University Baroda, India, tried to use various kinds of binders in order to improve the stability of the contaminated soil. Leachate from four different samples was analyzed. The samples

comprised of untreated soil, 5% cement treated, 10% lime treated and a mixture of 10% lime, 5% cement, 5% fly ash. The leachate comprised of 380 mg/l from untreated soil, 107 mg/l for soil treated with 5% cement. The leachate reported concentration of 51 mg/l for soil undergoing 10% lime. The lowest reported concentration of 31 mg/l was reported for soil treated with admixture. Researchers believe progressive decrease in the above concentration is associated with the formation of metal and polycyclic aromatic hydrocarbons.

 Researchers further analyzed the admixture-soil with the help of X-Ray diffraction to determine the structural properties. X-Ray diffractograms *(FigureNo.8)* showed new peak formation (d =3.353, 3.232, 3.180 etc.) in the stabilized soil. This proved that some of the new peaks such as d $= 3.353$ and $d = 3.029$ were created due to the formation of Calcium Silicate Hydrate (CSH). Other new peaks were due to the formation of Calcium Aluminate Hydrate (CAH) and Calcium Alumino-Silicate Hydrates (CASH).

Further analysis of the soil structure with the help of SEM reveals the formation of cement coating *(Figure: 9)* on the soil structure. This stabilizes the soil further apart from trapping the contaminant in itself. Rib formation is seen *(Figure No. 9a)* to form after the admixture is mixed in the contaminated soil. This further enhances the stability of the soil structure.

Source: MS Unv. Of Baroda

S/S Treatment of Dredge Material from the Port of San Diego *(Robert S. Austin and Charles M. Wilk)*

Cement based s/s was undertaken to the material dredged out of the bay in Port of San Diego. The dredged material taken out of the bottom of the bay was contaminated with the below hazardous levels of PCBs, copper, zinc, lead and pesticides. Such dredged are generally disposed off in special Confined Disposal Facility (CDFs). Such alternatives involving CDFs involves dedicated land space. S/S of the dredged material was suggested in order to save land and also safely handle the contaminated sediments. Finally, the treated sediments can be disposed in municipal landfill sites rather than hazardous landfills. A clam shell dredge *(Figure: 10a)* was used to lift the silt off the bay surface. The water being lifted was back filled into the dredge area. The silt was dumped into a barge floating along side the clam shell were a S/S head *(Figure: 10b)* mixed 2%-5% of Portland cement to the sediment by the mixing head (*Figure 10c)* Among the other tangible benefits of using S/S to treat sediments includes using the treated sediment as landfill cover, structural fill material and roadway pavement base.

Figure: 10© (a): Dredging from Bay; (b): S/S of sediments on barge; (c): Close-up of Mixer *Source: Portland Cement Association*

METHODOLOGY

The test samples which were excavated from the site had been preserved in a frozen environment during transportation and storage. A representative sample was used for lechability tests to determine the mobility of constituents of concern. Leaching procedures to be used include EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) and EPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP).

Soil samples were mixed with various quantities of Portland cement, bentonite and water to evaluate the reduction in the leachability of contaminant of concern. During the mixing of cement and bentonite with the contaminated soil, it was expected that a certain fraction of the VOCs in the soil will be volatilized either due to heat of hydration or due to mechanical stirring. The test was then subsequently divided in three phases.

In phase-I, various quantities of water were tried such as 5%, 10%, 15% and 20% by weight of the soil sample to achieve the best workability. It was determined that a water content of 15% made the sample most workable. 15% of water content was thereby standardized for remaining tests. A matrix involving various percentage quantities of Portland cement and bentonite was developed to plan the total number of weight analysis tests to be performed. Based on the matrix, various quantities of Portland cement and bentonite was mixed to a fixed weight of soil sample. On mixing; the initial weight of the soil along with additives and water was noted. As a precaution the mixture was not stirred before taking the first weight reading. To standardize the stirring procedure a predetermined number of clockwise and anti-clockwise movements were performed. This was done to create uniformity among various soil samples which were subjected to stirring. Finally, the soil sample weight was taken every thirty minutes for two and half hours and the corresponding weight losses were recorded. An overnight weight loss data was also recorded for each sample which was left exposed to atmosphere. Along with the weight loss data, the temperature of all the samples was noted for various intervals of time for one hour. It was expected that on hydration of cement there may be a change in temperature. The temperature rise would obviously be more initially so the first few readings were taken in close proximity to each other followed by longer durations.

In phase-II, three samples were chosen to be re-prepared this time in an air tight glove box. The three samples were chosen based on highest, medium and lowest weight losses from the samples weighed in phase-I. The three samples were prepared individually inside the globe box. The samples were allowed to settle for thirty minutes for equilibrium to be attained with respect to VOCs. A gas syringe was then used to extract air sample from the glove box through a self sealing septum valve. The gas sample was quickly transferred from the syringe to Tedlar bags. These air samples were then analyzed for VOCs by TO-3.

Phase-III involved testing the untreated and treated soil samples for TCLP and SPLP. The mixture showing the highest air emissions from the TO-3 underwent TCLP and SPLP tests. Untreated soil sample were also subjected to the TCLP and SPLP tests to get a baseline data of the type of contaminant and their expected concentration.

Synopsis of the Test Methods

Toxicity Characteristic Leaching Procedure (TCLP)

This test was developed to simulate conditions of rain water percolating through a soil mass thereby interacting with the contaminants present in the soil. The leachate collected from the test soil sample undergoes chemical analysis to determine if one or more of the hazardous substances listed under RCRA are present. By legal definition the detection of a single contaminant defines the leachate as hazardous.

Synthetic Precipitation Leaching Procedure (SPLP)

It is generally similar to the TCLP test procedure; however the kind of extraction fluid used is different. According to EPA this procedure provides a more realistic result as it better simulates actual conditions associated with rain or snow. Also the pH of the solvent used in the test varies from 4.2 for sites located east of Mississippi River to 5.0 for sites located west of the Mississippi River.

The choice between the two tests depends on numerous factors. In order to ascertain the correct type of test a study was conducted by Chih-Shin Shieh from Florida Institute of Technology (August 2001). Comparative tests where performed and the paper reported large variations in detection limits of Lead (Pb) by both test methods at higher pHs of 10.5. Also detection of elements such as selenium and chromium (Cr) showed large variations in measurements in both tests. The paper concludes that the type of leaching procedure to be performed depends on the following:

- Waste disposal practice
- Type of leachate to be expected and its pH
- SPLP is recommended for very low organic content waste and TCPL is recommended for higher organic content waste.
- Types of elements expected in the contaminated soil
- Location of site corresponding to the Mississippi River

In this particular case it was decided to perform both TCLP and SPLP tests as the type of elements, metals or compounds expected in the soil was uncertain. Additionally the following tests were preformed as listed below:

TCLP/ SPLP Zero Headspace Extraction

The waste is identified as liquid and solid waste depending on the percentage of solids found. If the waste is liquid, it is filtered through glass fiber and TCLP extract is separated for further analysis (A). If higher percentage of solids are found it is first milled to reduce the size and solid phase is extracted by an extraction fluid 20 times the weight of solid phase. Typical extraction devices (Agitation apparatus or Zero-Head space extraction vessel; ZHE fig. 11 & 12) are employed when testing the volatile analytes. Again the liquid is extracted using glass fiber of pre-determined size and another sample of extract (B) is now available. If both samples A & B are compatible (no multi-phase formation) they are mixed together for analysis otherwise they are analyzed separately and results are compiled mathematically by volume-weight average concentration.

Figure 11: Rotary Agitation Device

TCLP/SPLP for BTEX

This method was used to determine VOCs in a variety of solid wastes. According to EPA "This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludge, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments." The samples can be injected into the GC using Direct Injection or Purge and Trap. The peaks were recorded and the type of compound is analyzed. If interference is suspected the samples were reanalyzed using a second GC column. If peak response is off scale it is required to dilute and re-analyze the second aliquot of sample.

TCLP/SPLP TPH Gasoline by Purge & Trap

This method is used to identify certain non-halogenated volatile and semi-volatile compounds. Samples were recognized as fuels or analytes and then introduced into GC by direct injection, purge and trap or vacuum distillation. A predetermined column and temperature were used in the GC to separate the various organic compounds. A flame ionization detector (FID) achieves the detection. To determine petrochemical hydrocarbons, a fused silica capillary column is recommended.

TCLP/SPLP RACRA (8) Metals

This method uses inductively coupled plasma-atomic emission spectrometer (ICP-AES). It is utilized to determine the presence of trace elements including metals in a solution. Initial digestion of the solution is required in most of the cases using appropriate sample preparation method. Unique emission spectra were emitted when the samples got excited by the plasma torch. These spectra were dispersed by a grating spectrometer and the intensities of the spectral lines were monitored by photosensitive devices.

TCPL/SPLP Polyaromatic Hydrocarbons

This method helps to determine the various semi-volatile and poly-aromatic hydrocarbons. Samples were prepared using appropriate methods and the semi volatile compounds were introduced into the GC/MS. The GC column has pre-programmed temperatures to isolate the various analytes. These different analytes were finally detected by MS. Analytes were differentiated by their mass spectra compared with the electron impact spectra of authentic standards.

AIR EMISSIONS

In order to determine the type and quantity of organics volatilized during the actual S/S process, air samples were analyzed by TO-3. The captured air samples were introduced into a heated injector and passed through a separating column by an inert gas. A series of peaks were recorded when the various elements or compounds got excited and fell back to stable orbits at different energy levels. Thus various peaks were observed when the components exit the column. The working principle of a GC is depicted in *(Figure 13)* below.

Figure 13: Schematic Diagram of Gas Chromatography *Source: www.teaching.shu.ac.uk*

RESULTS

The initial TCLP/SPLP and Total or Bulk tests were conducted to ascertain the baseline parameters for the contaminated soil samples. The tests gave the preliminary data which was later compared to the treated soil (using the optimum mix) data from TCLP, SPLP and Bulk analysis. Hence, a conclusion can be established regarding the success of additives used in the S/S treatment. This research involved the use of both TCLP and SPLP data since initially the type of contaminant involved and their concentration levels were uncertain.

Results from the laboratory analysis of Bulk, SPLP, TCLP, and air samples are presented in Appendix 1, 2, and 3. Table 1 summarizes the results in a format to be able to answers the following questions which is included as Appendix 4.

Efficiency of S/S on SPLP contaminant reduction Efficiency of S/S on TCLP contaminant reduction Contaminant levels in treated soil Air contaminants (mass) released to the environment Comparison of contaminant quantities in untreated and treated soil

A sample quantity of 30 g or 15 g was used to be able conserve the limited soil sample available for the research. For easy understanding and comparison, all results are converted to a sample mass of 100 g which is presented in Table 1.

The preliminary test Method 8021 VOAs data showed very high concentrations of Benzene at 62300 ug/l, Ethylbenzene at 1100 ug/l and Toluene at 6440 ug/l. Various types of derivatives of the above two compounds were also detected at high levels. Method 8021 VOAs showed high concentration of m&p-Xylene at 31600 ug/kg. Extremely high concentration of Naphthalene (9400000 ug/kg) was detected by conducting Method 8270 SVOAs.

Leachate analysis by ICP showed presence of certain heavy metals such as Barium (Ba) at 270 ug/l and Lead (Pd) at 10.9 ug/l. Method 8015 extractable detected a substantial concentration of Diesel Organic Compound (C10-28) at the range of 53700 mg/kg. Other organics with higher concentration are in the range C28-40 at 4820 mg/kg.

All figures presented correspond to 100 g soil to make the comparison easy and understandable.

Figure 14: Method 8021 VOAs

Figure 14 shows the various levels of concentration of Benzene, Ethylbenzene and Toluene in TCLP/SPLP samples which were analyzed using Method 8021 TCLP/SPLP tests. TCLP data shows a higher concentration than corresponding SPLP data for all the three pollutants. Benzene has a far higher concentration than the other two compounds.

Figure 15: Metal ICP Lechate

Figure 16: Method 8270 SVOAs

Results from Method 8270 SVOAs have been represented in Figure 16. Here the major pollutant is Naphthalene. Both TCLP and SPLP indicate high Naphthalene content at approximately 800ug/l.

Figure 17: Method 8015 TPH Extractable

Method 8015 TPH Extractable was performed to detect the presence of fuel oil. Figure 17 shows the illustration of the major contaminants such as Gasoline Organic Range (C6-10) and Diesel Range Organic (C10-28). Clearly Gasoline Range (C6-10) has a significant presence reported by both TCLP and SPLP.

Figure 18: Method 8021 Bulk Analysis

The pie chart, figure 18, shows the bulk analysis data reported by Method 8021. The percentage representation clearly indicates Benzene to be predominant at 42% followed by Toluene at 22%. Other major contaminant detected are Ethylbenzene (13%) and m&p-Xylene (8%).

Figure 19: Method 8270 Bulk Analysis

Figure 19 shows the various contaminants detected by Method 8270. SPLP was specifically performed to detect those contaminants which remain undetected by TCLP. Here various contaminants are shown in this bulk analysis test. The major share of the contaminant is clearly Naphthalene; other major contributors include Benzene and Fluorene.

Further, an additive mixture matrix table was created which detailed the various kinds of Portland cement and bentonite mixture applied to contaminated soil samples. The matrix had twenty different ratios of admixture combinations. A number of water ratios were also experimented to determine the most workable mixture. Finally; 15% water content was ascertained to be the best to make the samples workable. All the twenty soil samples treated with various admixture ratios were recorded for weight loss every 30 minutes for two and half hours. An overnight weight loss data was collected for each sample. From the weight loss data recorded, three samples were chosen for second round of TCLP, SPLP and Bulk analysis. These samples were the ones which recorded the highest (12.51%), medium (7.96%) and lowest (0.47%) weight loss among all the treated samples.

Figure 20*: Weight Loss of Treated Soil Samples

**1) This data has been generated out of a few samples to preserve simplicity of the chart. 2) All the above sample has 15% water content. 3) ON: Overnight data.*

Figure 20 shows the various weight loss data gathered from the different soil samples post treatment by admixtures. Mixture ratio of 20, 20 (20% Portland cement- 20% bentonite) shows the minimum dip on weight scale over a time period.

The samples were also subjected to temperature change measurement immediately after mixing of admixtures. No substantial temperature variations were recorded in any of the samples. Most of the soil temperature measured around 23 $\mathrm{^{0}C}$ which later had very minor temperature variations over a period of an hour after admixtures were applied. Mixture ratio (10% Cement-10% bentonite-15% water) showed a drop in temperature from 24 to 22 $\mathrm{^0C}$ within an hour of treatment of soil. Another soil sample (15% Cement-15% bentonite-15% water) was the only sample to show appreciation of temperature from 23 to 23.7 $\mathrm{^{0}C}$.

Figure 21*: Temperature Variations of Treated Soil Sample

Figure 21 depicts the temperature variations observed on a time scale measured in minutes. The temperature variations are not extreme but random as shown above.

The three samples previously identified were prepared again in an air tight glove box. This was done to prevent any interaction of the air emissions generated during mixing with ambient air. The samples were left undisturbed inside the glove box for thirty minutes so that equilibrium could be reached inside the glove box. Air samples were taken out from the glove box with the help of a syringe. These air samples were immediately transferred into a tedlar bag. These three air samples underwent TO-3 air toxicity tests for VOCs. TO-3 tests included the identification of Benzene, Ethylebenzene, Toluene, m&p-Xylene and o-Xylene.

Figure 22 (a, b $\&$ c) shows the air sample results of the emissions generated from the soil sample after treatment. The air samples underwent TO-3 tests. All the different samples show high concentration of Benzene. Other contaminants present are Toluene and Ethylbenzene. The highest emissions were indicated to be emitted from Sample 1 (20% Portland cement- 20% bentonite-15% water) followed by Sample 3 (20% Portland cement-15% bentonite-15% water) and Sample 2 (20% Portland cement-5% bentonite-15% water).

^{*}*This data has been generated out of a few samples to preserve simplicity of the chart.*

Figure 22©*

Figure 22 (d) shows the stacked concentrations of contaminants over various samples. Sample 1 has the highest level of contaminants followed by Sample 3. Least air emissions were observed from Sample 3.

Figure 22 (d)^{*}: Air Emissions

** Note: The above graphs (figure 22: a, b, c & d) show concentrations in mg/m³ . Air emissions concentrations were later standardized to ug/100g for easy comparison with the leachate and bulk analysis concentration data.*

Air Emissions Test (T0-3) Data

The concentration data of air emissions from Sample 1 was standardized to ug/100 g and used in the summary table. Analysis of the air emissions data indicated presence of Benzene, Ehylbenzene, Toluene, m&p-Xylene and o-Xylene. The concentrations of each of this contaminant in air was found to very insignificant ranging from a high of 0.001115 ug (Benzene) to a low of $4.42x10^{\circ}$ (-5) ug (m&p-Xylene).

Other VOCs, SVOCs and metals that were detected in the Bulk, SPLP and TCLP were not traced in air sample.

Effectiveness of S/S

Sample 1 with 20% cement, 20% bentonite and 15% water (weight by soil mass) was analyzed for Bulk and TCLP/SPLP tests. On treatment, sample 1 showed a huge reduction in the concentration of most contaminants in the soil matrix and leachate.

Efficiency of S/S on SPLP and TCLP

The summary table (Table 1) lists the percentage reduction of various contaminant found in leachate analyzed by SPLP and TCLP before and after S/S. Various contaminant achieved different levels of reduction efficiency. The percentage reduction for Benzene, Ethylbenzene, and Toluene were found to be in the high 99 %. Moderate reduction efficiency (50%) was achieved in Diesel Range Organics (C10-28). Leachate from the treated soil showed extremely low traces of heavy metals like Lead and Barium again indicating higher reduction efficiency due to S/S.

The concentration of most metals was found to be Below Detection Limit (BDL) after S/S and hence reported as zero. The efficiency was thus mathematically calculated as 100%, although the actual reduction efficiency is expected to be slightly lower than 100%. Certain exceptions such as Acenaphthene experienced very low treatment efficiency of 7.41% (SPLP) and 12% (TCLP). Other VOCs and SVOCs analyzed by SPLP/TCLP were found to be BDL in both untreated and treated soil mass.

Figure 23 shows a comparative sketch of the concentration values determined by SPLP tests on both untreated and treated soil. Substantial drop was detected in concentrations of various VOCs, Diesel Range Organics and heavy metal.

Figure 23* : S/S Effectiveness on SPLP

Similarly Fig 24 shows the effectiveness observed in controlling the leachate by TCLP test procedure. Again a significant slump was observed in the concentration of contaminant after S/S treatment.

Figure 24*: S/S Effectiveness on TCLP

* *Note: In figure 23 and 24 the bar representing the untreated concentration of leachate is almost invisible. This is due to very high treatment efficiency (higher 99%) achieved by S/S. The efficiency calculations can be found in the summary table (Appendix 4).*

Overall, it was found that the treatment efficiency was high for most VOCs and heavy metals especially BTEX and Lead respectively. Moderate efficiency was achieved for fuel oil compounds. However, S/S efficiency was found to be low for certain VOCs likes Acenaphthene.

Bulk Analysis

Comparative study of bulk analysis data from untreated and treated soil showed a reduction in the concentration of contaminant for all the cases [Benzene -70% , Ethylebenzene 50%, Toluene 68.1%, m&p-Xylene 51.42%, o-Xylene 41.42%, Diesel Organic Range (C10-28) 41.5 %, Barium 3.17% and Lead 64.9%].

As S/S process is expected to release contaminants into air, air samples were analyzed as explained in the methodology section. Sum of the masses of contaminant in the treated bulk soil sample and air sample was compared with the mass of the contaminant in the untreated bulk soil sample. Ideally, these two values should be close however a big difference was noticed. This could be due to a number of factors such as, (1) contaminant release would have occurred during much longer period (sample was collected only over 30 minutes in this research), (2) soil samples used was non-homogeneous, and other unknown factors.

Figure 25 shows the S/S effectiveness on bulk analysis of the soil.

Figure 25* : S/S Effectiveness on Bulk Analysis

** Note: Bar representing air emission is invisible due to their extremely low values.*

CONCLUSION

Based on the literature review from various sources and available test data, certain conclusions can be drawn. The initial TCLP/SPLP test data showed presence of compounds such as Benzene, fuel oil, heavy metals and various other VOCs in high concentration. Both TCLP and SPLP tests were undertaken to ascertain the presence of most of the major contaminants mixed in the soil samples. Apart form benzene, other BTEX compounds such as ethylebenzene and toluene were also detected above the reporting limits.

Client requirement for S/S was substantiated by literature review, previous research work, and standardized matrix developed by Federal Remediation Technology Roundtable (based on past project experiences). Choices of admixtures used were based on past knowledge of their individual physical, chemical and structural properties. Twenty different admixture ratios were used to treat the contaminated soil and the weight loss was recorded for each sample. The sample which had a highest percentage of Portland cement and bentonite had the lowest percentage weight loss. Lack of bentonite in the certain admixtures showed a higher percentage weight loss ranging from 3%-12%. Also, a few samples were treated with only bentonite. Weight loss data from five such samples showed a consistently high weight loss ranging from 6%-9%.

Temperature was measured for each sample for specific interval of time. However, no major temperature variations were recorded. Thus rise in temperature is not expected be a factor.

Finally, the thesis concludes by referring to the objectives and the extent to which they were achieved. The overall objective of this thesis was to find an optimum mix based on its ability to control leachate from the soil matrix. Leachability data from both TCLP and SPLP tests showed appreciable reduction in the concentrations of most of the contaminants. Contaminants with high initial concentrations such as Benzene, Toluene, and heavy metals (lead) showed as much as 99% reduction in leachability.

Air emissions generated during the S/S was evaluated by TO-3 tests. Highest emissions were generated from Sample 1 (20% Portland cement-20% bentonite-15% water) followed by Sample 3 (20% Portland Cement-15% bentonite-15% water) and Sample 2 (20% Portland cement-5% bentonite-15% water). The differences in the emission levels generated needs to be further investigated with additional sampling and analysis.

Large amounts of BTEX, fuel oils, Naphthalene and its derivatives were found to be encapsulated in the soil matrix due to S/S. Compounds such as Benzene, Ethylbenze, Toluene, m&p-Xylene have a potential to be airborne during the S/S process (as indicated by air emission data). Although their concentration was found to be extremely low, off-gas collection and treatment facilities may be adopted on-site to satisfy any specific regulatory issues. The leachate tests indicate extremely low concentrations of contaminants like Toluene, Ethylebenzene and other VOCs. Naphthalene due to its extremely high concentration in untreated soil finds major presence in the leachate even after S/S.

LIMITATIONS

The thesis faced certain limitations most of which can be attributed to the very nature of the project. The site awaiting remediation is located in California making it difficult to avail soil samples in substantial quantity here at New Orleans. This imposed restrictions on the number of test trials.

Soil made available by the site owners was observed to be generally non-homogenous. This led to certain variations in the bulk and leachate analysis of the data. However, the major contaminant present in the site was less affected due to their higher concentration and greater homogenous presence across the site.

Thesis deadline and limited funds also imposed additional embargo on the overall exhaustiveness of the samples tested.

Appendices

Appendix 1 (Bulk, TCLP & SPLP Data)

Method 8021

Metal ICP Lechate

Method 8270

Appendix 1 (Cont.)

Method 8021 VOAs (Bulk)

Method 8015 TPH Extractable

Method 8270 SVOAs (Bulk)

Appendix 2 (Bulk, TCLP & SPLP Data from Treated Soil)

Method 8021 VOAs

Metal ICP Lechate

Method 8270 SVOAs SIM

Method 8021 VOAs

Method 8015 TPH Extractable

Method 8270 SVOAs

Appendix 3 (TO-3 Air Sample Analysis) *(This Air Sample was extracted from Soil treated with 20% Portland Cement and 20% Bentonite)*

Table 1

Note:
1) m&p-Xylene and o-Xylene: More sensitive reporting limit was adopted while analyzing treated soil sample (RL for Treated soil 10ug/L & RL for Untreated
soil 2000 ug/L) *1) m&p-Xylene and o-Xylene: More sensitive reporting limit was adopted while analyzing treated soil sample (RL for Treated soil 10ug/L & RL for Untreated soil 2000 ug/L)*

2) X: Non-homogenous soil produced incompatible data for untreated and treated soil sample *2) X: Non-homogenous soil produced incompatible data for untreated and treated soil sample*

3) All units in $ug/100 g$ *3) All units in ug/100 g*

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Vita

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