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Field Treatment of Soils Contaminated with Lead

Final Report

Richard P. Long, Professor

Nikolaos P. Nikolaidis, Associate Professor

Rony Bruell, Graduate Student

September, 1999



University of Connecticut

School of Engineering

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JHR 99-271

Project 96-1

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16. Abstract <p>There are two problems with contaminants in soils. If the contaminant is mobile it can leach into the water supply, and soil particles carrying the toxins are small enough to enter the body by inhalation or ingestion. To render contaminated soil benign one must address both of these issues. Previous research used the mineral Apatite to treat a Connecticut soil contaminated with lead. The Apatite reduced the mobility of the heavy metal through precipitation, the soil was then solidified to prevent ingestion. This treatment had been shown effective. A soil contaminated with lead, removed from a former skeet shooting area, appeared to be ideal for this research; it was within DEP limits for total lead but failed the TCLP test, indicating that the lead is mobile. This soil however proved difficult to treat with the techniques used in the previous research. Three remediation techniques were investigated to reduce lead mobility below the Connecticut Remediation Standard Regulations. The first technique involved stabilization of Pb with apatite; the second was heating of soil at 400°C and the third was solidification of the soil with Portland cement. Reduction of lead mobility to acceptable levels was achieved only by heat treatment.</p>					
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
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LENGTH

in	inches	25.4	millimetres	mm
ft	feet	0.305	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km

AREA

in ²	square inches	645.2	millimetres squared	mm ²
ft ²	square feet	0.093	metres squared	m ²
yd ²	square yards	0.836	metres squared	m ²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	kilometres squared	km ²

VOLUME

fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	Litres	L
ft ³	cubic feet	0.028	metres cubed	m ³
yd ³	cubic yards	0.765	metres cubed	m ³

NOTE: Volumes greater than 1000 L shall be shown in m³

MASS

oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

TEMPERATURE (exact)

°F	Fahrenheit temperature	5(F-32)/9	Celsius temperature	°C
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APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
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LENGTH

mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi

AREA

mm ²	millimetres squared	0.0016	square inches	in ²
m ²	metres squared	10.764	square feet	ft ²
ha	hectares	2.47	acres	ac
km ²	kilometres squared	0.386	square miles	mi ²

VOLUME

mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m ³	metres cubed	35.315	cubic feet	ft ³
m ³	metres cubed	1.308	cubic yards	yd ³

MASS

g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T

TEMPERATURE (exact)

°C	Celsius temperature	1.8C+32	Fahrenheit temperature	°F
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°F	Fahrenheit temperature	5(F-32)/9	Celsius temperature	°C
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* SI is the symbol for the International System of Measurement

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Executive Summary

There are two problems with contaminants in soils. If the contaminant is mobile it can leach into the water supply and soil particles carrying the toxins are small enough to enter the body by inhalation or ingestion. To render contaminated soil benign one must address both of these issues.

Previous research used the mineral Apatite to treat a Connecticut soil contaminated with lead (Long et al). The Apatite reduced the mobility of the heavy metal through precipitation, the soil was then solidified to prevent ingestion. This treatment had been shown effective in numerous publications (Ma ...).

The original objective of this research was to apply this process to a CONNDOT field site. Meetings with representatives of the Department of Environmental Protection and CONNDOT's Section for Environmental Compliance showed that a field trial was not feasible. In addition no active CONNDOT site could be identified as contaminated with lead. It was hoped at that time that samples in the laboratory could be solidified in such a manner that they could be used as aggregates in the field.

A soil contaminated with lead was located in Bridgeport on land that is owned by the DuPont Corporation. The soil that was removed from the former skeet shooting area appeared to be ideal for this research; it was within DEP limits for total lead but failed the TCLP test, indicating that the lead is mobile. This soil however proved difficult to treat with the techniques used in the previous research.

The soil is non-plastic with about 30% of the particles by weight smaller than 0.075 mm. Other characteristics of the soil include pH of 5, organic carbon of 2.5% by weight, and 400 ppb of total lead. Sequential extraction of the metals revealed that over 40% of the total lead is held at exchangeable sites and in the organic fraction of the soil. TCLP, SPLP, and pH-Edge batch experiments examined lead mobility. The soil leached more lead than allowed under Connecticut standards for mobility by both TCLP and SPLP tests. An amphoteric behavior was established in the pH-Edge test with maximum mobility at a pH of 3, minimum at pH of 6 and increasing mobility at values of pH greater than 7.

Three remediation techniques were investigated to reduce lead mobility below the Connecticut Remediation Standard Regulations. The first technique involved stabilization of Pb with apatite; the second was heating of soil at 400°C and the third was solidification of the soil with Portland cement. Reduction of lead mobility to acceptable levels was achieved only by heat treatment.

A. Introduction

I. Background

There are two considerations in dealing with soil contaminated with heavy metals: mobility and exposure. The concern about mobility considers the hazardous substance moving through the soil to the groundwater and its effect on the biomaterial with which it comes in contact. Exposure considers the effects of physical contact with the contaminant, including possible ingestion of the contaminated material.

Project 93-3, "Strategies for Using Stabilized Wastes in Construction," addressed these problems in two ways: soil washing and Stabilization/Solidification. Stabilization/Solidification worked well on a soil recovered from the upper two inches of backfill in the vicinity of Bridge No. 03038 on I-95 in New Haven, CT. The lead in this soil stabilized easily with the addition of the mineral apatite, and cement served as the solidification agent. This combination of treatments reduced the mobility of lead to such an extent that only a few percent leached out of the treated soil even when the solidified soil was crushed. Other researchers also found apatite effective in decreasing the mobility of lead.

The original intent of this research was to adapt the same techniques to the field. This presented several difficulties. There were no active construction sites that contained an adequate supply of lead contaminated soil, and the Department of Environmental Protection discouraged any activity that might leave behind a slab of solidified contaminated soil. It was decided therefore to investigate the production of solidified spheres that could be used as aggregate or fill in construction.

An adequate supply of lead-contaminated soil to study was found on the site of the former Remington Arms factory in Bridgeport, CT. This soil was scraped from the surface of a skeet shooting-range. In preliminary tests the soil appeared ideal for this investigation in that it passed the limits for total lead but did not pass the TCLP.

The lead in this soil did not, however, respond to the mineral apatite. A review of the research with apatite and lead in the literature showed that most experiments were conducted with soils that had been artificially laced with lead in the laboratory. The investigation was shifted therefore, to understand why the lead in this soil behaved differently than the soil in the previous study. In this search it was revealed that heating the soil reduced the mobility of this heavy metal. This study did not allow time for finding field applications

II. Problem Statement

The Hazardous and Solid Waste amendment to the Resource Conservation and Recovery Act (RCRA) required corrective actions for the release of hazardous materials. Corrective actions range from source control to full scale clean up. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) requires the clean up of hazardous wastes on superfund sites. Over the years, solidification/stabilization (S/S) techniques were used for the remediation of 30% of superfund sites and were widely used for RCRA facilities (EPA 1996).

S/S technologies are based on incorporating wastes, both physically and or chemically, into a solid waste form. Cement, lime, soluble silica and fly ash are often used. This research addresses Portland cement as the solidifying matrix since it is used mostly in commercial and research applications.

The goal of S/S is to create a solid, easy to handle product that will not leach contaminants to the environment. Standard tests and their modifications are used to evaluate physical and chemical characteristics of products. Although in use for many years for nuclear wastes, S/S processes started to be implemented for other hazardous waste in the seventies. Recently, S/S processes are combined in "train treatment" with other technologies usually as the final stage.

Since organic compounds negatively alter cement properties they are rarely treated in S/S processes. This report addresses the applications of S/S to metals wastes.

B. Literature Review

I. Background

a. Definitions

S/S processes can treat a variety of contaminants but have proven to be mostly effective in treating nuclear and inorganic wastes such as sludge, soils and industrial streams. The goals of these processes are to reduce the toxicity and mobility of the waste and to improve its handling. Both solid and liquid wastes can be treated. The processes have been used for more that 20 years and many terms have been given to the different steps included in the process as well as to the groups of chemicals being used. This report uses the following definitions:

- **Hazardous Waste** - a group of solid waste that was defined in the CFR as a waste that can "cause an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or

otherwise managed. (40 CFR part 261)". The EPA regulates wastes that exhibit one of the four characteristics: ignitability, corrosivity, reactivity, and toxicity. A standard procedure, Toxicity Characteristic Leaching Procedure (TCLP), tests whether a waste is toxic. It sets limit to leaching of metals for 18 hours under acidic conditions. S/S processes usually treat wastes that are defined as toxic wastes (Grasso, 1993).

- **Solidification** - treatment that results in a solid waste form that has a high structural identity. The product can be as big as the waste site or small as a stone. Binders and additives are added to create the solid form. The contaminant does not necessarily interact with the solidifying reagents. It can be mechanically locked inside the solid formed by this process (EPA, 1986a).
- **Stabilization** - techniques designed to limit the mobility or solubility of contaminants with or without change in the physical properties of the waste. Stabilization usually involves the addition of materials to the hazardous waste and the creation of a product that is less hazardous (EPA 1986a).
- **Binders** - cement, or cement like material, or resin used to hold particles together. Addition of water or other additives is possible. The binder creates the majority of the stabilized waste form (Means et al., 1995). Portland cement is the binder most widely used in S/S processes.
- **Additives** - materials added to the binder to improve the S/S process. Additives such as silicates, can alter the rate of hardening, clays can improve retention of water or contaminants, and surfactants can improve the incorporation of organic compounds. Additives are usually added in small amounts (Means et al., 1995).
- **Waste form** - this term is used for the product of the S/S process.

b. Performance Goals

Solidification/Stabilization processes are designed to accomplish one or more of the following goals (EPA, 1986a):

- Reduce the contaminant's mobility or solubility;
- Improve handling and physical characteristics of the waste by creating a solid matrix with no free water; and,
- Decrease the wastes surface area across which transfer or loss of contaminant may occur. Standard or modified tests are used to verify whether the goals were met. Three groups of tests are commonly used for the evaluation of S/S processes (Means, et al., 1995).
- **Physical** - including moisture content, bulk density, compaction, strength, and durability.

- **Chemical** - including pH, redox, acid neutralization capacity, alkalinity, metals, VOC's and organic compounds content, and organic carbon.
- **Leaching** - including TCLP, multiple extraction procedure, dynamic leaching, synthetic acid precipitation leaching procedure (SPLP), and sequential extraction.

A successful S/S treatment will be one that creates a strong and durable solid form that would not leach metals (in short and long terms). The effects of the different parameters on achieving the goals are interrelated.

Fine grains have high surface area from which metals can leach to the environment. Additionally, a negative correlation between size and metal concentration is usually found in soils and other solid wastes. Zhang (1995) found that the smaller the particles the more they leached in TCLP test.

Waste forms with low strength and compaction are likely to deteriorate with time, break down into smaller particles and, therefore enhance the risk of increased leaching. Waste forms must be durable under changing environments and must exhibit a strong resistance to wet/dry and freeze/thaw cycles.

Measuring the chemical components of the waste form is important for the determination of short and long term leachability. Generally, it is assumed that in high pH metals are less mobile. Acid rain for example, can reduce the stability of exposed waste forms unless they have high acid neutralization capacities, which means they have high pH and alkalinity.

Other factors, like cost, are also important in determining the applicability of S/S. High moisture content will reduce the amount of water needed for the cementation. Large particle can be a benefit in strength and durability of the cement form, but can be a problem for in-situ applications because of adverse effect on mixing.

Upon setting of the cement its volume changes and a network of pores is established. The water to cement ratio is important since it effects the size of the pores (high ratio = larger pores) and the volume change. Small pores can be important in S/S processes since contaminants can be trapped inside resulting in a mobility reduction of the waste. Permeability is another property of S/S forms effected by water to cement ratio. Low permeability will be beneficial, causing reduction in contaminant mobility.

Although the concrete product is considered to be durable over time, deformation from chemical and physical attacks can occur. Typical concrete will have about 30% lime (calcium hydroxide). The lime is the most important component in the concrete that resists acid attack. Concrete has high acid naturalization capacity of 8-20 meq/gr. This produces base pore solution with a pH of 12 to 13. When the cement is attacked by acids lime leaches out. If the acid neutralization capacity is exhausted, the metals mobility may increase.

Advantages of using cement for S/S are:

- Consistent composition from source to source.
- The reactions of setting, hardening and fixation are clearer than in other pozzolans.
- Existing data on environmental leaching from the nuclear field makes the prediction of the process outcome easier.
- Most studies are done with Portland cement, generating more knowledge of its behavior
- Low cost.

Generally, organic compounds can reduce the mechanical strength of waste forms. Therefore, in organic compounds remediation with cement based S/S is limited.

II. Binding Mechanisms

Metals react in different ways in the cementation process resulting in a variety of bonds, compounds, and complexes. Successful design for S/S treatment must be based on understanding of the nature and mechanisms of metal-cement bonds. Otherwise the goals of the process will not be met. In order to create a stable, strong and durable product the metals have to be properly bound or incorporated in the form.

Leaching tests are often used in research as a tool for behavior characterization of cement-metal waste forms in different environments. Conclusions drawn from leaching tests are used for explanation of other phenomena such as metal location in the waste, strength alternation and durability. Other tools used to describe metals bonds and interactions with cement are X-ray photoelectron spectroscopy (XPS), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and fourier transform infrared techniques (FTIR).

The major bounding mechanisms suggested by different researchers are precipitation and other surface reactions, including adsorption, absorption, and complexation. Alkaline environment and its effects on metal chemistry should be addressed when trying to explain the reactions in cement.

a. Ion Exchange

Ion exchange is not considered to be an important mechanism for binding heavy metals in cement. This is a reversible process that when used in wastewater treatment, for example, removes metals from the water by changing the resin. In S/S processes the metals stay in the cement form. Also, to prove the existence of ion exchange, one needs to find evidence for releasing of one metal in exchange to another.

Ortego (1990) reported that XPS showed potassium migration to the surface when

cement is hydrated in the presence of metal-nitrate salts. As the doped metals incorporated in the cement form, the electrical balance with the nitrate has to be maintained, presumably by potassium.

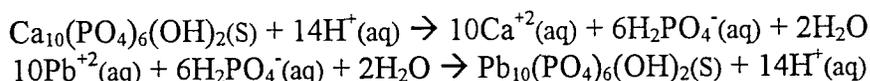
b. Precipitation

Containment of heavy metals in cement can rely on pH controls, since metals are known to be less soluble in high pH. However, some metals exhibit amphoteric behavior, that is high solubility in low and high pH's. The optimum pH for hydroxide precipitation is metals-specific, as are the solubilities of the hydroxides. Actual precipitation in cement was found to be different from calculated values (Conner, 1990).

Cartledge et al. (1990) reported that Cd/cement systems involves the formation of CdOH₂ which provides nucleation sites for calcium hydroxide and C-S-H gel, resulting in cadmium in the form of an insoluble hydroxide. Pb/cement systems involve hydroxide, sulfate and nitrate mixed salts which form impervious coatings on the cement grains and retard cement setting as well as soluble lead salts.

Many researchers are exploring the possibility of precipitation of heavy metals prior or during S/S treatment. Those processes are based on combining known precipitation reactions and cementation.

Calciumphosphate (apatite) was found to immobilize lead very efficiently (Ma et al, 1993, 1994a, 1994b, 1995, 1996, and Laperch et al. 1996). The reaction is thought to be dissolution followed by precipitation:



Lead removal was found to be rapid; 93% removal within half a minute in aqueous solution and 90% removal of aqueous lead in contaminated soils after five hours.

Chen et al. (1997) also investigated the effect of apatite on contaminated soils. They leached the soil in TCLP extraction fluid (pH=4) for 24 hours. The liquid phase was separated and reacted with apatite. They concluded that apatite was extremely effective in removing lead (about 100% removal) and was moderately effective in sorbing cadmium (49%) and zinc (29%). Apatite was able to reduce the metal concentrations in TCLP from solution. It was also found that after the reaction, the precipitants were highly immobile under wide pH ranged environments.

Hydroxylfluoropyromorphite was found to precipitate out of solutions, suggesting that precipitation is the mechanism controlling lead immobilization. Adsorption, and/or formation of amorphous solids is thought to be the mechanism for cadmium and zinc immobilization. Those findings are in agreement with Xu et al. (1994), who reported their

findings on hydroxyapatite sorption of cadmium and zinc.

Zhang (1995) investigated the possible use of this process for immobilization of lead in S/S treatment. He found that Apatite addition to contaminated soil prior to solidification with cement decreased the leachability of lead from the solidified form (Fig. 7A).

Jacson (1991) studied the influence of additives, such as sulfide, phosphate and latex on S/S of lead, cadmium, and chromium. He found that phosphate additive reduced leachability of metals with lead being the most effected. This supports the hypothesis that precipitation of metals, as phosphate salts, can improve S/S processes.

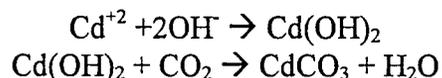
III. Other Surface Reactions

Ortego (1990) investigated the bonds formed by metals when stabilized in cement. Fourier Transform Infrared Techniques (FTIR) revealed the following:

- Mercury forms mercuric oxide (HgO), a relatively soluble and volatile species,
- FTIR results suggest that barium forms insoluble sulfate (BaSO₄) which will probably decrease the strength of the form.
- Zinc was found to have negative effect on hydration probably through carbonate formation, which inhibits the hydration process.
- Lead was found by photoelectron spectroscopy XPS and FTIR to be present as sulfate or hydrosulfate species on the surface of the cement form.
- Chromium according to XPS studies incorporates into the cement matrix and does not appear to be a surface species.

Cocke (1990) also found by spectroscopic methods that in waste forms, chromium incorporated into the solid and lead on the silica matrix. Wen (1992) reported similar results.

McWhinney and Cocke (1993) report their findings on solidification of zinc, mercury, and cadmium using XPS, SEM and EDS. Carbonate formation on the surface was found to increase significantly for all metal doped forms. Cadmium is a strong surface species that forms oxides and carbonates depending on pH, time, and concentrations. Carbonate formation occurs through the absorption of carbon dioxide:



Mercury stabilization was found to be mainly through physical interaction in the matrix forming highly concentrated deposits.

Some heavy metals are amphoteric in nature. They have soluble forms in low and high pH ranges (Conner, 1990). Cheng and Bishop found that the amphoteric nature of lead and cadmium did not appear when S/S waste form were leached by acetic acid. They investigated the possibility that the metals have been sorbed onto the silica skeleton which remained after leaching. Sorption patterns of silica (SiO_2) and amorphous silica were found to be similar to those calculated from the leaching test. As long as the pH in the pores was above nine, high percentages of the metals initially present in the solidified waste remained sorbed. Arsenic was found to be highly bonded to the waste form with only 70% leached in a pH of 4.5. It can be assumed that arsenic is physically bound to the solid matrix or strongly adsorbed in the structure.

IV. Effects of Heavy Metals on Cement Properties

a. Leaching

One of the most important goals of S/S processes is the reduction of contaminants leachability to a minimum. Disposal sites for S/S products should be designed such that the waste forms would not be in contact with groundwater, rain or runoff water. However, one can not rely on the end disposal site, and must make sure that the product will be strong, durable, non-permeable, and will leach as little as possible.

Experience with radioactive waste disposal indicates that some hazardous contaminants have leached over time, especially those exposed to mildly acidic solutions. Predicting leaching rates and constituents, is the focus of many researches. Short and long-term leachability of S/S waste forms is often predicted by using results of short term leaching tests and mathematical models. Some of the most used models are presented in Appendix 1. This chapter describes some of the observation and mechanisms regarding leachability of waste forms, mainly in the short term.

Due to S/S products high alkalinity, concern has been raised regarding its resistance to acidic conditions. Calcium hydroxide provides as much as 20 meq alkalinity per gram solid (Shively et al., 1986; Poon, 1989; Jacson 1991).

Bishop (1988) discussed the metal-binding mechanisms in S/S products based on batch and continuous leaching tests. He found that both batch and column studies gave comparable results. Cadmium was found to leach out from the waste at a much greater rate than chromium and lead. This was suggested to be an outcome of the metals different binding mechanisms and location in the waste form.

The leaching of chromium and lead is correlated to the breakdown of silica in the cement form. Cadmium was found to leach in a similar pattern to the alkalinity release. Extraction studies (Shively 1984, Tashiro 1977, Bishop 1988) showed that the leaching of heavy metals from S/S waste forms, is often lower than the amount calculated from solubility products. Those findings can be explained only by assuming other binding mechanisms than hydroxide and sulfide precipitation.

Leaching is limited mostly by four rate controlling process:

- Diffusion limitations from the pores and the interface to the reaction front.
- Shortage of hydrogen supplies near the surface due to buffering capacity of the waste form or weak extraction fluid.
- Accumulation of metals in the leachate can reduce the concentration gradient that caused the leaching. and,
- Slow chemical reactions mobilize species from the S/S form (Cote, 1986).

A solidified waste form is a porous solid, saturated with water and gases. Contaminants can be in equilibrium with many phases. They can be dissolved, precipitate, and volatile (in the case of mercury). Leaching due to groundwater convection, run-off water, and/or acid rain precipitation will disturb equilibrium conditions. As a result, concentration gradients will form and diffusion of species will start. Chemical reactions such as dissolution of precipitants desorption, and complexes destruction can also start with in wet environments. In the inner pores contaminant can precipitate or sorbed due to a leachate attack that will release calcium hydroxide providing hydroxides and ion exchange site.

In secure landfills liners, impermeable caps, and pipe systems prevent contact of groundwater, rain and runoff with the waste forms. Diffusion due to small amounts of water is the main cause for leaching. In a case where the S/S product will be landfilled with municipal or untreated waste, acidic fluids can be present and can induce leaching.

Cheng and Bishop (1992a) investigated the changes occurred when S/S waste forms extracted by acidic fluid. A semi dynamic and a static leaching test were used. The extraction fluid was replaced periodically in a semi dynamic test and was not renewed in a static test. Acid Penetration Depth (APD) was defined as the depth from the surface to the center of the solidified sphere in which the pH changed due to acid penetration.

The development of a leaching layer can be summarized as three steps process:

- Acid diffusion from the bulk to the surface;
- Diffusion from the surface to the leaching boundary; and,
- Diffusion combined with reaction at the leaching boundary.

Diffusion of acids controls the inward movement of the leaching boundary. It was found that in the static tests, all samples had shorter APD than in the semi dynamic tests. The APD was positively correlated to acid strength (Table 2). The physical and chemical properties of the leached layer were reported in Cheng and Bishop (1992b). SEM/EDXA results showed chemical changes caused by acid on the surface of the waste form. Calcium was removed while silicon, iron and aluminum remained on the surface. Those remnants are known for their sorption qualities and can adsorbed the free metals ions leached by the acid. Calcium when leached can diffuse to the bulk or reprecipitate due to high pH in the pores. Calcium hydroxide precipitation can resist further acid attacks.

TABLE 2A - COMPARISON OF TWO LEACH TEST RESULTS
(CHENG AND BISHOP, 1992A)

Water/Cement	Acid [N]	STATIC TEST		SEMI DYNAMIC TEST	
		Time [day]	APD [cm]	Time [day]	APD [cm]
0.6	0.2	6.2	0.11	8.0	0.13
0.6	0.3	11.1	0.17	8.0	0.17
0.6	0.4	19.0	0.26	15.0	0.34
0.6	0.5	28.0	0.34	29.0	0.56

Acid digestion on the leached layer, the kernel, and control samples proved changes of metal concentrations only in the leached layer.

Particle size of the waste correlates to the amount of metal leached through available surface area. Wen (1992) compared diffusion from different sizes of lead-doped cement forms. He found that the smaller the particles the quicker the amount of lead leached drop. Based on those results he concluded that S/S products should have high surface area to volume ratio (S/V) to reduce leaching potential.

Brown et al. (1986) used upflow column tests to study the alkalinity, pH and metal changes in the leachate when flushed with 0.2ml/min of 0.01N acetic acid. They found that in columns containing large particles (4.8-9.5mm) the acid attack advanced faster than in columns packed with small particles (0.3-0.6mm). A color change was also observed with the large particles turning from gray to orange within the first day of leaching. Small particles changed color from gray to orange and then to white in a much slower process that progressed through the column.

At first the metals leached in a slow rate from the small particle columns, then the leaching rate rose rapidly after a while. The large particle columns leached metals in a steady rate with cadmium leaching much more than lead and chromium.

All findings were explained by the change in alkalinity available for acid neutralization and the surface area of the particles. Smaller particles have greater surface area and so have higher alkalinity available for acid neutralization. In large particles the release of alkalinity is slower and so the acids progress through the column converting its color to orange and leaching metals in constant rate. Small particles release alkalinity faster, and therefore, the conversion to white color is believed to be related to exposure of silica matrix when alkalinity is depleted. These findings are in agreement with the finding of Bishop (1988) and Conner (1990).

b. Strength

Compressive strength is an important characteristic of S/S product. Although in a well-designed landfill the waste should not support structures and buildings, it may have to support the cap and equipment. Reuse of solidified waste requires high strength and

durability. It is a common practice to test S/S products for their unconfined compressive strength. Regulations require durable shear strength of at least 50psi (EPA 1986b).

Metals that form sulfate salts are likely to decrease the strength of cement. Gypsum (CaSO_4) is added to clinker to inhibit flash setting. If metals react with sulfate to form precipitants excess calcium will be present in the solution and flash setting is possible (Ortego, 1990).

Ortego (1990) reported that samples containing 20% and 30% $\text{Zn}(\text{NO}_3)_2$ and cured for three months, crumbled with slight pressure between ones fingers. Lead doped samples were much stronger. FTIR results showed that the silicate bonds in samples doped with Zn were almost like those bonds in dry clinker. Apparently zinc inhibits the condensation process and produced a solid without strength.

Ortego et al. (1991) investigated Zn and Pb doped cement samples with NMR and FTIR. They also found that Pb initially inhibits the setting of cement but the effect is overcome after four weeks. The cement doped with lead continued to harden for one year after curing. Zinc doped samples showed the same bonding as in clinker even five months after curing. Zinc doped samples had no strength.

Murat and Sorrentino (1996) who investigated the effect of heavy metal addition to the clinker also found the same. Additionally they reported that chromium first increases the strength of cement but this effect is only short term. After 38 days cement strength was less for the samples with greater chromium.

Lead stabilized samples that were dried in air lost 11% of water used in making them, and zinc samples lost over 60%. This proves that most of the water in zinc doped samples does not react with the cement (Ortego et al., 1991).

Wang and Vipulanandan (1996) reported that the compressive strength of solidified forms decreased with addition of lead nitrate to cement and cement/fly ash mixtures. This effect can be explained in the light of interference with cement hydration. Strength development was delayed by inhibition of hydration.

c. Setting Time

Setting time is one of the factors influencing concrete strength. In a regular cement processes setting rate is controlled by gypsum. Gypsum prevents flash set and allows for the hydration process to build up the C-S-H that gives the final product its strength. In hazardous waste applications, metals can interfere with setting, causing a weaker product.

Tashiro et al. (1977) studied cement hardening when heavy metals were added to the cement mixture. They found that Zn, Pb, and Cu inhibited the initial hardening when

5-25% heavy metals were added (as solid minerals, by weight). In the case of 0.5% addition, no inhibition was observed. In fact, lead, when added in such small amounts accelerated the hardening of the cement.

Yousuf et al. (1995) developed a reaction model to explain retardation of cement setting and surface coating. They tested Zn-doped waste forms and found that in highly alkaline environments zinc is present as negative charge ions, $\{Zn(OH)_3^- \text{ and } Zn(OH)_4^{2-}\}$. In the presence of sufficient calcium ions, the zinc hydroxyl anions are transformed into $CaZn(OH)_6 \cdot H_2O$ that covers the cement grains completely. In Cd-doped waste forms they found the formation of $CaCd_2(OH)_4$ acts the same way.

Further hydration of the cement was prevented by the precipitants. The chemistry of other metals such as barium, silver and chromium suggest that these metals do not form negative charge ions in highly alkaline environments, and therefore, do not effect the hydration of cement.

Murat and Sorrento (1996) confirmed the above findings and reported an increase in setting time with addition of lead, zinc, and cadmium and an initial decrease in setting time in the presence of chromium.

Wang and Vipulanandan (1996) tested the immobilization of lead in cement and in cement mixed with fly ash. They found that addition of lead nitrate increased the setting time in cement and cement/fly ash systems. The setting time change was found to be related to the concentration of lead nitrite added). It was found that the concentration of calcium and silica in the pores increased with the addition of lead. Lead may interfere with the hydration reaction.

d. Durability

Wet/dry and freeze/thaw cycles effect the breakdown of the waste forms and increase available surface area for leaching. The ASTM standard tests (ASTM D-559-82 and D-560-82) were developed for construction uses and represents much harsher conditions than expected in a S/S disposal sites. During the tests, wastes are exposed to 24-hour cycles of saturation/drying and freezing/thawing. Weight and strength losses are measured after each cycle. In a landfill the waste will be placed under a cap with low permeability and should not go under such extreme cycles. However, the tests provide a good way of comparing and can imply of the need to improve the S/S process (EPA, 1989a).

Forslund et al. (1989) developed a physical testing program for the evaluation of 16 commercially available S/S processes for the treatment of hydroxide sludge. Generally, they found that the specimens withstood more freeze/thaw than wet/dry cycles. Several of the specimens lost much of their integrity upon saturation. No strong correlation between the physical properties tested (unconfined compressive strength, consolidation,

permeability and durability) were found. However, cement based S/S treatments tended to fail at low strain, have higher unconfined strength and were less compressible.

Frost action contributes to hydraulic pressure generated when the water volume in the pores increases upon freezing. Increase in the total porosity and change in pore size distribution observed in cadmium waste forms. El-Korci et al. (1989) used a non-destructive technique to evaluate the freeze/thaw durability of S/S cadmium wastes. They found the waste forms endure more freeze/thaw cycles than the control.

e. Leaching Models

As mentioned above, leaching is one of the most important and investigated phenomena in the use of S/S technology for hazardous waste remediation. Currently, S/S products have to pass the TCLP test in order to comply with regulations and be landfilled. It was argued that TCLP represents too harsh of conditions and simulates only a short time exposure of the waste form to an extraction fluid (Cote, 1986; Dusing et al, 1992; Ortego and Barroeta, 1991).

Development of kinetic models that described long-term leachability would improve the confidence and reliability of S/S technology. Some models use short-term leachability studies, such as TCLP, as parameters and others suggest new tests or modification to existing ones.

1. Diffusion Model

This model assumes that leaching is controlled by diffusion through the solid. Fick's first law is used to describe the flux of the species at some point in the solid. Also, it assumes a uniform initial contaminant concentration in the solid and a zero surface concentration (an immediate dissolution of the contaminant to the bulk liquid from the surface). When all other variables are known, the diffusion coefficient can be determined.

$$\left(\frac{\sum a_n}{A_0} \right) * \left(\frac{V}{S} \right) = 2 * \left(\frac{D_e}{\pi} \right)^{0.5} * t_n^{0.5}$$

Variables:

- A_n = contaminant loss during leaching period n , [mg];
- A_0 = initial amount of a contaminant present in the waste form [mg];
- V = volume of the waste form, [cm³];
- S = surface area of the waste form, [cm²];
- t_n = time to the end of leaching period n , [sec]; and,
- D_e = effective diffusion coefficient [cm²/sec].

The American Nuclear Society defined a leachability index (LX) as the negative logarithm of the diffusion coefficient.

$$LX = - \text{LOG}(D_e)$$

The index was used to compare the relative mobility of different metals under different conditions. Low LX means high mobility and high LX suggests a non-mobile species.

Brown et al, (1986) used the model to compare leaching from columns and batch tests. The results also used to predict the long-term leachability of their waste forms. The LX values for the column were higher than for the batch systems by about 0.5 units. This means a slightly lower leaching rate in the column possibly due to incomplete mixing. Cadmium was found to have the lower LX values, lead was intermediate and chromium had the highest values.

Calculation of the long-term leachability index was done for several Surface to Volume (S/V) ratios. Only very small particles and waste forms with high effective diffusion would leach significant amounts of the original metals up to hundreds of years.

Wen (1992) used the same model to compare results from batch studies. In his study the leaching of waste forms of different sizes was measured to predicted values for LX. He found the experimental results for LX to be higher than the calculated ones. The agreement of the model with the data changed as the leaching period got longer.

Chang and Bishop (1992a) used the model to prove that diffusion controlled the movement of the leaching boundary in spherical waste forms.

The effective diffusion coefficient for a given metal was used in the above publications as constant. Bishop (1988) showed that D_e is changing with time. As the alkalinity in the waste form depleted the leaching rate increased, and so the diffusion coefficient decreases.

Batchelor (1997) suggested using this model in risk assessment of groundwater contamination associated with hazardous waste landfilling. The model will produce a value for contamination concentration that can be incorporated into mass balance on the groundwater.

2. Other Models

Cheng and Bishop (1990) suggested that an "*unsteady diffusion with fast chemical reaction*" model can predict penetration diffusion in waste forms during the early time of leaching. This model takes into account the acid strength and describes the depth of acid penetration. In their model the depth of penetration and the flux of contaminant entering the extraction medium are proportional to square root of time.

Cote et al, (1986) developed a *hypothetical kinetic leaching model*. The model was based on two sets of data. First, a series of the waste form's properties that control the way water can come in contact with it (such as porosity and durability) was defined. Second, Contaminant related properties (such as solubility under different pH) were quantified. The authors presented figures to describe the concentration gradient and location in the waste form. This can be adopted for different groundwater flow regimes that can potentially come in contact with a waste form and leach contaminant out of it.

V. Summary Literature Review

S/S treatment for metal hazardous wastes is an established remediation technology. It can improve waste handling by solidification, and can reduce contaminant mobility by stabilization of the contaminant as part of the cement form or as precipitant on its grains. S/S technology has the advantage of using cement, and the wide knowledge regarding its behavior from years of experience. However, heavy metal wastes were found to alter some of the cement properties, often in a metal specific way. Commercial use of S/S must include fundamental characterization of the waste in concern, and its possible influence on the cement processes. Treatability and feasibility studies must take into account the strength and durability of the final product and the leaching potential of the contaminants in both short and long terms.

Available alkalinity is one of the important components in metals leaching. In a disposal area large waste forms, when fractured, will initially have higher acid neutralizing capacity than larger particles. These large particles, though, will leach large amount of metals over time. Testing and disposal of Stabilization/Solidification (S/S) products should be addressed by regulatory agencies.

Some of the technology limitations are:

- Contaminants are not destroyed by the treatment;
- Increase in treated material volume;
- Uniform mixing, particulate and volatile emission are problematic for in situ applications;
- Tests used in the construction field for physical properties are not always appropriate for hazardous waste treatment and disposal; and,
- Cement itself contains metals. In a field experiment, control samples made only of cement leached more chromium than the heavy metal waste forms (Kleppe, 1992).

Another problem in the field of S/S research and data collection is the extensive use of synthetic wastes and clean chemicals. Some of the phenomena and behaviors of heavy metals found in research may not be applicable to field situations. Concentration may vary, ratio of metals and competition may change, and the waste itself whether soil, slurry or sludge may impact the efficiency of the treatment.

Over the last 15 years 30% of superfund sites were treated with S/S. The number of applications declined since 1992 resembling a general slow down. It is important to improve the knowledge and understanding of the mechanisms controlling metals immobilization and to find innovative techniques to overcome the limitation of the treatment.

C. Methodology and Analytical Procedures

I. Soil Characterization

a. Physical Characterization

1. Grain Size Analysis

Size distribution of the soil particles was determined following ASTM D-1140. A pre-weighted set of sieves was used: No.4 (4.75mm); No.6 (3.36mm); No.10 (2mm); No.20 (0.85mm); No.40 (0.425mm); No.100 (0.15mm); and No.200 (0.075mm). First, the oven-dried soil was washed through No.200 sieve to separate the fine particles. The weight loss in the process is contributed to particles smaller than 0.075mm. Then the washed soil was oven dried at 60°C. After drying, the soil was sieved through the set of sieves and the weight of soil retained on each sieve was recorded. The average percent passing each sieve is reported. The fraction of soil that passes sieve #10 was further analyzed using the Hydrometer test, ASTM 422.

2. Soil Moisture

The percent of water in a soil sample was determined based on the oven dried weight of the soil. Results throughout the study are reported on dry weight basis.

3. Specific Gravity

The specific gravity (G) of the soil particles was determined at 24°C according to ASTM D-854.

4. Atterberg Limits

The liquid and plastic limits of the soil were determined according to ASTM D-4943. The liquid limit is defined as the moisture content at which 25 blows are needed to close a gap in the soil. The plastic limit is defined as the moisture content below which the soil acts more as a solid than a plastic. This is the lowest moisture content at which the

soil can be rolled out into a 1/8" thick thread. The plasticity index is the difference between the two limits.

5. Compaction Test

The relationship between water content and dry unit weight of the soil was determined. Water was added in each step to gradually increase the water content of the soil. Then, the Soil was compacted into a mold with known volume.

b. Chemical Characterization

1. Soil pH

The soil was found to be non-calcareous. The pH was determined using a Accumet Polymer-body Gel-Filled Combination Electrode with Ag/Ag/Cl reference connected to an Orion Research Expandable Ion Analyzer model EA 920. The method used based on EPA Method 9045A.

Soil pH

1. Calibrate the pH probe
2. Add 20 g of soil sample to a 50 mL beaker and add 20 mL of DI water. Stir the suspension several times over a 30 minute interval.
3. Let the soil suspension stand for about one hour to allow most of the clay to settle out from the suspension.
4. Immerse the combination electrode just below the suspension, read and record the pH. Report the pH as " pH in Soil Suspension."

2. Total Organic Carbon in Soil (TOC)

Total organic carbon content in soil samples was determined using an elemental analyzer (Perkin Elmer, Model 2400 CHN). The soil samples were pre-treated with hydrochloric acid to remove carbonate carbon. The sample was combusted in a pure oxygen environment to form the elemental gases CO₂, H₂O and N₂. The resultant combustion gases are measured quantitatively by an infrared spectroscopy.

Total Organic Carbon in Soil

1. Follow the instrument operating procedure described in the manufacturer's operating manual. Carry out an initial instrument set-up and performance check, calibrate the instrument, set the temperature program, and set up an auto sampler tray. The instrument is now ready to analyze the samples.
2. Weigh the soil samples in tin disks.

- 2.1 Take an open tin disk and, on a clean surface, fold it first in half, then in half again with the help of a forceps. Take one outside edge of the disk and gently pull it up to form a cone. Transfer the cone in the micro balance and tare the balance.
- 2.2 Remove the cone from the micro balance and, with the help of a spatula, transfer a small amount of soil sample in the cone. Fold the open end of the cone over, then roll the tin to form a 'pill.' The weight of the soil should be between 2 and 3 mg.
3. Load the tin 'pills' on the auto sampler along with the QC samples and analyze the carbon, nitrogen, and hydrogen contents of the sample.

3. Total Metals Analysis

This method is an acid digestion procedure used to prepare soil samples for total metals analysis by Inductively Coupled Plasma (ICP) spectroscopy and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). It is based on the EPA Method 3050A (SW-846, 1992). Samples prepared by this method were analyzed for the following metals: Cd, Cr, Cu, Ni, Pb and Zn. Usually lead was analyzed on GFAA. But due to high concentration of lead in the samples they were analyzed by ICP. Otherwise dilution of the samples to the GFAA detection range (1-50ppb) would have introduced large error in the results.

Totals - EPA Method 3050A

1. Mix the soil sample thoroughly to achieve homogeneity. For each digestion procedure weigh a 1.00 to 2.00 g portion of the sample and transfer it to a beaker.
2. Add 10 mL of 1:1 HNO₃ to the beaker, mix the slurry and cover the beaker with a watch glass. Heat the sample to 95 °C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, then add five mL of concentrated HNO₃, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Allow the solution to evaporate to five mL without boiling while keeping the content of the beaker covered with the watch glass.
3. After the sample cooled, add two mL of Type II water and three mL of 30% H₂O₂. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively rigorous effervescence. Heat until the effervescence subsides and cool the beaker.
4. Continue to add 30% H₂O₂ in one mL aliquots with warming until the effervescence is minimal or the general sample appearance is unchanged. However, do not add more than a total of 10 mL of 30% H₂O₂.
5. Add five mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling.
6. After cooling, dilute the solution to 100 mL with Type II water. Particulate matter

in the digestive may clog the nebulizer and should be removed by filtration or centrifugation.

7. Filter through Whatman No. 1 filter paper or equivalent and dilute to 100 mL with Type II water. The diluted sample has an approximate acid concentration of 5% HCl and 15% HNO₃. Store at 4° C until it is ready for analysis. Analyze the sample on the ICP.
8. Calculate the total concentration of the metal in the soil:

$$\frac{\mu\text{g}}{\text{g}} = \frac{\mu\text{g}}{\text{L}} \times L \times \frac{1}{\text{g}} \times \frac{1}{\% \text{solid}}$$

4. Sequential Chemical Extraction

Sequential chemical extraction is a method to evaluate the mobility and partitioning of metals contained in a soil matrix. Each successive extraction step is stronger, so the relative binding strength of each metal is determined by the fraction removed in each step. Due to the complex nature of the soil matrix, a series of partial extraction tests have been developed to assess the availability of different elemental forms when exposed to various conditions. The sequential extraction results are viewed as semi-quantitative and are used to categorize the metals into various operationally defined geochemical fractions metals (McLean and Bledsoe 1992). The “residual fraction” is quantitative in that it is the minimum estimate of the tightly bound, unreactive concentration of the metal in the soil matrix. The exchangeable fraction gives a relative mobility of the metal associated with the soil. It is speculated that this fraction form outer-sphere complex with the soil surfaces since these complexes are less stable and dependent on ionic strength.

The procedure used in this study was a modification of the procedure developed by Asikainen and Nikolaidis (1994). The first step in the procedure uses phosphate buffer. Due to low solubility of Lead-phosphate salts the first step was changed to extraction with magnesiumchloride.

Modified Asikainen and Nikolaidis Method

Step I: Exchangeable Fraction

- 1.1 Weigh 2.0 g of the air-dried soil (< 2 mm) in a serum bottle and add 40 mL MgCl₂ 1N at pH=7. Keep the bottle on a rotary shaker for 16 hours.
- 1.2 Remove the serum bottle from the shaker and centrifuge it at 4400 rpm for one hour.
- 1.3 Cautiously draw the supernatant using a 100 mL plastic syringe/needle.
- 1.4 Attach a filter holder (containing a prewashed 0.45 μ Nylon filter) to the tip of the syringe and filter the supernatant into a plastic container. Store the filtrate at 4 °C until it is analyzed for the designated metals.

- 1.5 Add 10 mL of DI water to the residue, mix it thoroughly and centrifuge at 4400 rpm for about 25 minutes.
- 1.6 Decant the supernatant with the help of a syringe/needle and discard it.
- 1.7 Follow Step II for further treatment of the residue or store the residue until then at 4 °C.

Step II: Organic Bound Fraction

- 2.1 Add 40 mL of 0.1 M sodium pyrophosphate to the residue from Step II. Keep the bottle on a rotary shaker for 16 hours.
- 2.2 Remove the serum bottle from the shaker and centrifuge it at 4400 rpm for one hour.
- 2.3 Cautiously draw the supernatant from the serum bottle using a 100 mL plastic syringe/needle.
- 2.4 Attach a filter holder (containing a prewashed 0.45 μ Nylon filter) to the tip of the syringe and filter the supernatant into a plastic container.
- 2.5 Add 10 mL of 0.05 N HCl to the residue, mix it thoroughly for 10 minutes and centrifuge at 4400 rpm for 45 minutes.
- 2.6 Cautiously draw the supernatant from the plastic container using a 100 mL plastic syringe/needle.
- 2.7 Attach a filter holder (containing a prewashed 0.45 μ Nylon filter) to the tip of the syringe and filter the supernatant into same plastic container that has filtrate from 3.4. Store the combined filtrate at 4 °C until analyzed for the designated metals.
- 2.8 Add 10 mL of DI water to the residue, mix it thoroughly and centrifuge at 4400 rpm for about 45 minutes.
- 2.9 Decant the supernatant from the plastic container with the help of a syringe/needle and discard it.
- 2.10 Follow Step III for further treatment of the residue or store the residue at 4 °C until then.

Step III: Iron and Manganese Oxide Bound Fraction

- 3.1 Add 40 mL of 0.1 M hydroxylamine hydrochloride to the residue from Step III. Record the pH of this suspension. Heat the bottle on a hot water bath at 95 °C for six hours. Agitate the suspension periodically and make sure that the bottle is loosely covered with the cap.
- 3.2 Remove the serum bottle from the hot water bath, cool it and centrifuge at 4400 rpm for one hour.
- 3.3 Cautiously draw the supernatant from the serum bottle using a 100 mL plastic syringe/needle.
- 3.4 Attach a filter holder (containing a prewashed 0.45 μ Nylon filter) to the tip of the syringe and filter the supernatant into a plastic container. Store the filtrate at 4 °C until it is analyzed for the designated metals.
- 3.5 Add 10 mL of DI water to the residue, mix it thoroughly and centrifuge at 4400 rpm for about 45 minutes.
- 3.6 Decant the supernatant from the plastic container with the help of a syringe/needle and discard it.
- 3.7 Dry the residue in an oven at 105-110 °C for 24 hours and analyze it for residual

metals as per Step IV.

Step IV: Residuals

5.1 Perform the steps as previously discussed for the Total Metal Analysis (EPA 3050A).

II. Mobility Tests

a. Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP was designed to determine the mobility of both the organic and inorganic analytes present in liquid solid and multiphase wastes. The following standard operating procedure, based on EPA Method 1311 (U.S. EPA, 1992), was used in this study to address only inorganic analytes. The extraction fluid used for all four sites was "extraction fluid #1" made by mixing 5.7 mL of glacial acetic acid with 500 mL of DI water, add 64.3 mL of 1 N NaOH and dilute to a final volume of 1 L. The correct pH was 4.93 ± 0.05 . This extraction fluid is highly buffered at this pH.

TCLP

1. Add 100 ± 0.01 g of the sample to a 2 L Nalgene bottle and add 2 L of the appropriate extraction fluid.
2. Secure the extraction vessel into a rotary agitator and rotate at 30 ± 3 rpm for 18 ± 2 hours at ambient temperature of 23 ± 2 °C during the extraction period.
3. Prior to filtration, read and record the pH of the material in the extraction vessel.
4. Following the 18 ± 2 hours extraction, the sample is filtered through a glass fiber filter (pre-acid washed). The filtrate is defined as the TCLP extract.
5. Record the pH of the TCLP extract and preserve an aliquot (by acidified with nitric acid to a $\text{pH} < 2$) for analysis of metals.
6. The preserved sample for metals analysis must be digested by EPA method 3010A (US EPA, 1992) prior to analysis.

b. Synthetic Precipitation Leaching Procedure (SPLP)

The SPLP was designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. The following standard operating procedure, based on EPA Method 1312 (U.S. EPA, 1992), was used in this study to address only inorganic analytes. The extraction fluid used in this study was a synthetic acidic rain similar in composition to a typical acidic rain from New England region. Synthetic acidic rain was prepared by adjusting the pH of DI water to 4.2 by adding a mixture of sulfuric acid/nitric acid (60/40 by volume).

SPLP

1. Add 100 ± 0.01 g of the sample to a 2 L Nalgene bottle and add 2 L of the extraction fluid.
2. Secure the extraction vessel into a rotary agitator and rotate at 30 ± 3 rpm for 18 ± 2 hours at ambient temperature of 23 ± 2 °C during the extraction period.
3. Prior to filtration, read and record the pH of the material in the extraction vessel.
4. Following the 18 ± 2 hours extraction, the sample is filtered through a glass fiber filter (pre-acid washed). The filtrate is defined as the SPLP extract.
5. Record the pH of the SPLP extract and preserve an aliquot (by acidified with nitric acid to a $\text{pH} < 2$) for analysis of metals.
6. The preserved sample for inorganic analysis must be digested by EPA method 3010A (U.S. EPA, 1992) prior to analysis.

c. pH-Edge

This method was used for the assessment of lead mobility from the soil at different pH values. Triplicates of soil suspensions (10% w/v) were adjusted to different pH. The pH was initially adjusted with 0.1N HCl and 0.1N NaOH, to the desired value and then measured and adjusted once a day. The experiment ended when the pH in all treatments reached steady state. Due to the high concentration of lead, samples were analyzed using the ICP.

pH-Edge

1. Calibrate pH probe.
2. Weigh 20g of soil in 200mL Nalgene bottles and add 200mL of NaNO_3 0.01N.
3. Record the initial pH in each bottle.
4. By adding NaOH 0.1N or HNO_3 0.1N to each set of bottles, adjust the pH to the desired value. Record the amount added to each bottle and the final pH.
5. Place on a shaker table for 16 ± 2 hours.
6. Check and record the pH. Repeat steps 4-6 until pH is not changing.
7. Filter the samples and preserve an aliquot (by acidified with nitric acid to a $\text{pH} < 2$) for analysis of metals.
8. The preserved sample must be digested by EPA method 3010A (U.S. EPA, 1992) prior to analysis.

III. Stabilization with Apatite

a. Equilibrium Study 1 – No pH adjustment

Soil samples were mixed with different ratios of apatite in order to find the optimal mixing ratio for the reaction. It was assumed that for soil treatment more than the stoichiometric ratio (one mole of apatite to 10 moles of lead) would be needed. The amount of lead in the samples was estimated based on the total metal analysis. Apatite was

assumed to react with all the Pb present in the soil. This is a very conservative assumption since only a portion of Pb will leach to solution and be available for the reaction. The apatite / Pb ratio was calculated using the molar as one. Soil slurries were shaken for nine days to insure completion of the reaction. The pH was recorded once a day. After nine days the samples were filtered through, digested using EPA 3010 and analyzed using GFAA.

Equilibrium Study 1

1. Weigh 20g of soil in 200mL Nalgene bottles.
2. Add the appropriate amount of apatite. Mix thoroughly.
3. Add 200mL of NaNO₃ 0.01N, mix well and record the initial pH in each bottle.
4. Place on a shaker table for 16±2 hours.
5. Check and record the pH. Repeat steps 4 and 5 until the reaction is completed.
6. Filter the samples and preserve an aliquot (by acidified with nitric acid to a pH < 2) for analysis of metals.
7. The preserved sample must be digested by EPA method 3010A (U.S. EPA, 1992) prior to analysis.

b. Equilibrium Study 2 -pH=4

In order to optimize the reaction conditions the soil was first leached in pH=4, and than reacted with apatite. This was thought to increase the amount of lead in suspension and maximize its immobilization.

Equilibrium Study 2

1. Weigh 20g of soil in 200mL Nalgene bottles. Add 200mL of NaNO₃ 0.01N, mix well and record the initial pH in each bottle.
2. By adding HNO₃ 0.1N adjust the pH to 4.
3. Place on a shaker table for 16±2 hours.
4. Repeat step 2 and 3 until the pH is stable.
5. Add the appropriate amount of apatite. Mix thoroughly.
6. Record the pH.
7. Place on a shaker table for 16±2 hours.
8. Check and record the pH. Repeat steps 7 and 8 until the reaction is completed.
9. Filter the samples and preserve an aliquot (by acidified with nitric acid to a
10. pH < 2) for analysis of metals.
11. The preserved sample must be digested by EPA method 3010A (U.S. EPA, 1992) prior to analysis.

2. Equilibrium Study 3 - Soil washing at pH=10 as a first step.

The soil was taken from a shooting range site. Literature suggests that the soil may

contain colloidal or elemental lead that does not behave the same way as ionic lead. To test the influence of colloidal lead on lead mobilization it was suggested to first leach the soil at pH=10 (colloids will be mobile in high pH due to charge reversal). Then, the soil was separated from the suspension and reacted with apatite.

Equilibrium Study 3

1. Weigh 150g of soil in a 1L beaker. Add 1.5L of NaNO₃ 0.01N. Cover the beaker, purge it with nitrogen gas and place temperature and pH probes from through the cover.
2. Measure temperature and pH constantly. By addition of NaOH 1N raise the pH to 10 and stabilize it.
3. Every half an hour sample the suspension with a syringe, centrifuge and filter the samples.
4. Analyzed the samples for Pb, using GFAA.
5. Repeat steps 2-4 for 12 hours.
6. Centrifuged the suspension.
7. Digested the eluent using EPA 3010 and the soil using EPA 3050 and analyze for Pb.
8. Dry the soil in the oven at 105°C over night.
9. Weigh 10g of soil in 200mL Nalgene bottles.
10. Add the appropriate amount of apatite. Mix thoroughly.
11. Add 100mL of NaNO₃ 0.01N, mix well and record the initial pH in each bottle.
12. Place on a shaker table for 16±2 hours.
13. Check and record the pH. Repeat steps 12 and 13 until the reaction is completed.
14. Filter the samples and preserve an aliquot (by acidified with nitric acid to a pH < 2) for analysis of metals.
15. The preserved sample must be digested by EPA method 3010A (U.S EPA, 1992) prior to analysis.

IV. Heat Treatment

a. Preparation of Heat Treated Soil

The organic fraction of the soil was eliminated by ingestion. Soil samples were placed in ovenproof ceramic dishes and placed in an oven set at 400°C for 24 hours. After the samples were cooled they were analyzed for TOC to determine whether there was a reduction in organic content.

b. Characterization Tests

The heat-treated soil was tested for total metals and sequential extraction. Total metals content was performed to ensure that no lead was lost during the heating process. In order to find out whether the lead distribution in the heat-treated soil is different from the original soil a sequential extraction analysis was performed.

c. Mobility Tests

The heat-treated soil was tested for lead mobility using TCLP, SPLP and pH-Edge tests that are described above.

V. Solidification with Portland Cement

a. Preparation of Waste Specimen

Mixtures of soil and cement were made to examine the effect of solidifying the soil on Pb mobility. Four soil to cement ratios were tested. The specimens were first mixed using a Hobart Mixer, then molded into 2"X 4" molds and cured for 7 and 28 days. Water content was the same for each ratio in order to supply sufficient amount of water to cementation and overcome competition from the fine soil's particles.

Preparation of Waste Specimen

1. Weigh soil into mixing bowl. Add the appropriate amount of cement and mix for 2 min.
2. Slowly add water and mix for 5 minutes or until paste is smooth.
3. Grease molds with mineral oil.
4. Fill about 1/3 of the mold with mixture and tap thoroughly.
5. Repeat step 4 until mold is full. Trim the top and cover with wet paper towel and plastic bag.
6. After 24 hours release the specimen from the molds. Cover the specimen with wet paper towel and seal in zip-lock bags for curing.

b. Strength Test

After the specimens cured, for 7 and 28 days, the strength of each was tested using SERTAC universal load machine. The load at which the specimen failed was recorded.

Wet/Dry Durability Test

The specimen ability to withstood wet and dry cycles was tested according to ASTM D-559. Four replicates from each soil to cement ratio were tested. One wet/dry cycle included 5 hours of soaking in water followed by 43 hours drying in an oven at 105°C. The specimen's weight and volume were recorded before each step. To represent harsher conditions samples 1 and 2 from each ratio were also subject to brushing with steel brush after oven drying. After a completion of 12 cycles the specimens were tested for strength.

c. Mobility Tests

The mixtures were tested for lead mobility using TCLP, and SPLP tests as described above. Due to interference with the GFAA and the ICP, ICP-MS was used to analyze the samples.

d. Continuous Column Leaching Study

The purpose for conducting a continuous leaching experiment was to quantify the amount of lead leached from the mixtures under continuous flow. These tests represent the actual environmental conditions better than the batch leaching experiments. Since the weathering of soils and cement consumes hydrogen ions, it was expected that the rate of weathering would increase at a pH. This increase in weathering will also result in a release of the lead immobilized by in the solidified mixture. The experimental set up is shown schematically in Fig. 1. The pH of the column effluent was recorded to determine the magnetite of weathering. The columns were wrapped in aluminum foil to prevent light penetration and growth. Inflow pH of 4.0 was used to represent acid precipitation. The flow rate of 1mL/min was chosen to allow at least 50 years of precipitation to percolate through the columns.

Continuous Column Leaching

1. Prepare one batch of eluent, with 20 L, of NaNO_3 0.01M solution. In order to provide an oxygen free environment, purge the eluent with nitrogen gas for at least 45 minutes prior to use. While purging, adjust the pH of the batch to 4 and by adding $\text{H}_2\text{SO}_4/\text{HNO}_3$ (60/40 v/v) as required.
2. The deoxygenated eluent is transferred to the columns using a peristaltic pump.
3. Prepare a set of glass columns. A typical procedure for the preparation of a glass column is described below.
4. A glass column is filled with a thin layer of glass wool that prevents the soil from escaping from the column. To avoid stratification and air entrapment during the packing, the column is first partially filled with a deoxygenated eluent and then 171g of crushed mixture are poured into the column slowly, but continuously, ensuring that the eluent level remains above the soil level. The column is gently tapped and the settling soil is manipulated with a thin glass rod to ensure tight and uniform packing. Care should be taken to minimize the exposure of the eluent and the contents of column to the atmosphere.
5. Once all the columns are ready, the eluent is passed through them through a network of Pharmed tubing. The desired flow rate is obtained by manipulating the pump. The flow rates for all the columns are monitored and adjusted (if required) at least twice a day during the first week and once a day thereafter. Periodically, eluent batch is replenished with fresh deoxygenated eluent. The experiment is carried out at ambient temperatures (20 – 25 °C)
6. The leachate from the columns were collected and measured daily in order to estimate the actual flow. The leachates from the columns were collected in 2L

conical flasks. Approximately 50 samples of 100 mL each were collected from the leachate at various time intervals during the entire leaching duration of 3 weeks. The pH was measured and the samples were acidified and analyzed for Pb.

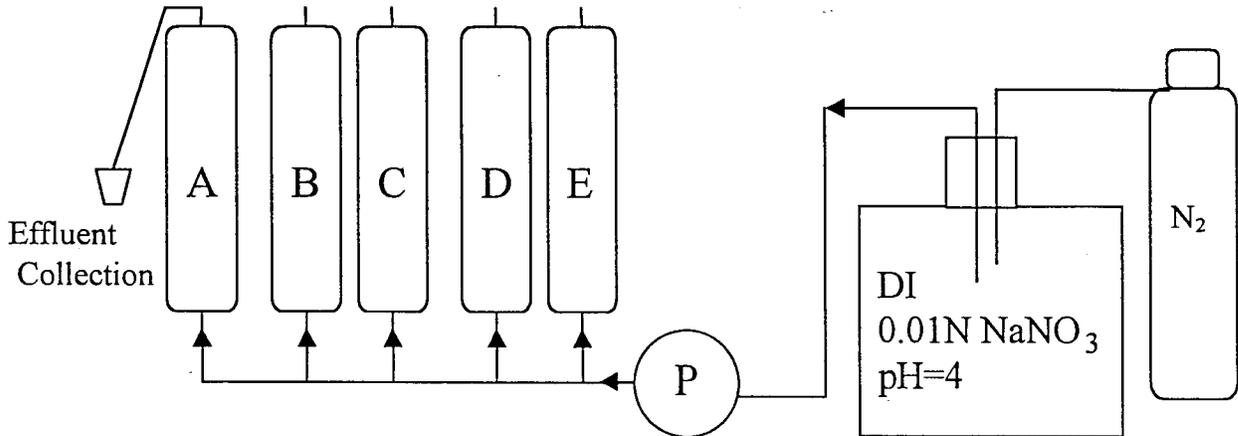


FIG. 1. – Layout of Solidified Soil Columns Study

(A=100% cement; B=50% cement 50% soil; C=25% Cement 75% soil; D=50% cement 50% heat-treated soil; E=25% cement 75% heat-treated soil).

D. Results and Discussion

A summary of the results and a discussion of the main point is presented below. Appendix D presents a detailed listing of the results of each experiment.

I. Physical-Chemical

Table 1 summarizes the physical-chemical characteristics of the soil. The soil type was determined based on the Uniform Soil Classification System (Lamb, 1969) and found to be silty sand. The soil sample can be classified as non-plastic, with 30% of the particles smaller than 0.075 mm. Total metal concentrations on the soil ranged from 420 ppm for lead to 10 ppm for cadmium, and did not exceed the Connecticut standards for direct exposure in residential and industrial areas.

Sequential chemical extraction analysis indicated that 15.7% of lead was bound to the exchangeable fraction, 25.1% to the organic fraction, 21.9% to the oxide fraction and 37.3% was in the residual fraction.

TABLE 1 - PHYSICAL AND CHEMICAL SOIL CHARACTERISTICS

Soil Type	Silty sand				
Moisture Content [%]	11.5±0.05				
Particle Size Distribution [mm]	D _{50%} = 0.257 D _{30%} = 0.075				
Atterberg Limit [plasticity index]	3.2				
pH [1:1 w/w]	5.0				
Total Organic Carbon [%]	2.7±0.3				
TOTAL METALS CONTENT [µg/g]					
Zn	Pb	Cd	Ni	Cr	Cu
69±3	420±22	10±0.4	16±1	25±3	42±6
SEQUENTIAL EXTRACTION [% OF LEAD]					
Exchangeable	Organic	Iron Oxide	Residual		
24±1	35±3	9±2	32±1		

II. Lead Mobility

The soil underwent TCLP and SPLP mobility testing. Table 2 presents the TCLP and SPLP results and compares them to the Connecticut RSRs. In this soil, only lead exceeded the Connecticut RSRs for both TCLP and SPLP. As expected, the TCLP results were higher than the SPLP results due to the difference in extraction fluids. The suspension pH did not change during the TCLP test and increased only slightly during the SPLP test. The lead is so leachable because most of it is on exchangeable or organic sites

TABLE 2 – MOBILITY SOIL CHARACTERISTICS

[µg/L]	TCLP	SPLP	CT RSRs
Initial pH	4.9	4.6	---
Final pH	4.8	5.0	---
Zn	141±11	56±0.3	5000
Pb	3523±309	182±57	15
Cd	<20	<20	5
Ni	<20	<20	100
Cr	<30	<30	50
Cu	28±2	16±0.6	1300

The equilibrium study (pH-Edge) showed the amphoteric nature of Pb with high mobility at low pHs (3-4), minimum around pH 6 and increasing at pH above 7 (Fig. 2). On a µg/g basis, the amount leached in the SPLP test was equivalent to the amount leached at the pH-Edge at pH=5. The results suggested that acid rain (pH of 4) could mobilize significant amounts of Pb, leach it to the groundwater and cause an environmental risk.

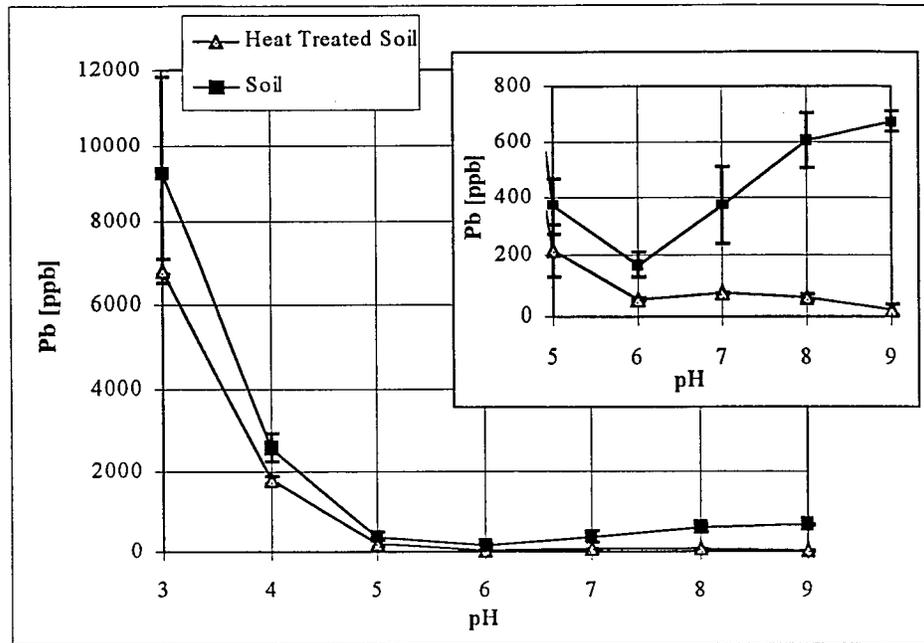
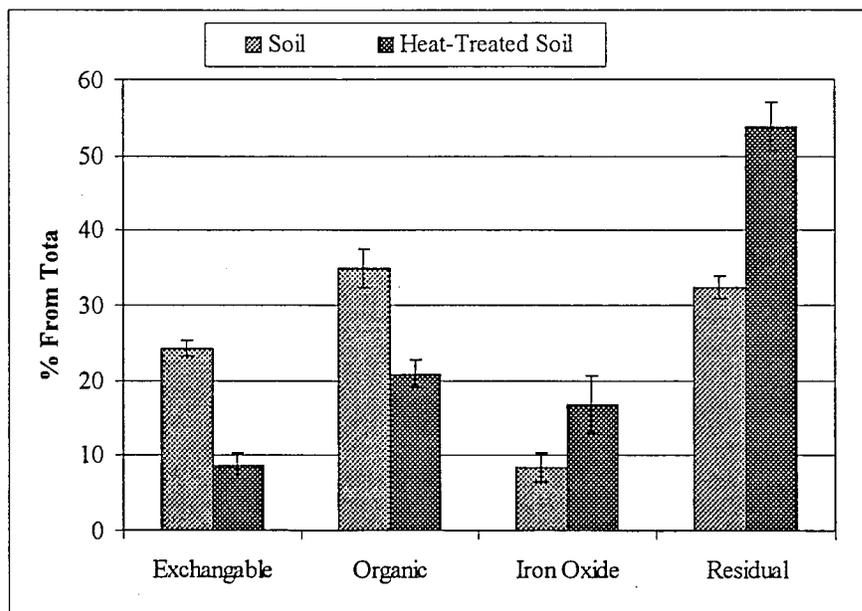


FIG. 2.- pH-EDGE FOR THE SOIL AND THE HEAT-TREATED SOIL.

About 25% of the total Pb are bound to the organic fraction (Fig. 3). This fraction can be soluble in high pH, so it was postulated that the high mobility of Pb at pH higher than 7 was due to its association with the organic matter. Those results are consistent with the work of Nikolaidis et al., (1998) that showed higher leaching concentration of metals such as lead and copper from the soil associated with organic matter at pHs greater



than 7 compared with pH of 6.

FIG. 3. - SEQUENTIAL EXTRACTION OF THE SOIL AND THE HEAT-TREATED SOIL.

III. Apatite Stabilized Soil

The results showed that apatite does not affect Pb mobility for this soil (Table 3). This is in contrast to the finding of previous studies with other soils (Ma et al., 1993; 1994a; 1994b; 1995; 1996; and Laperch et al., 1996) that showed decrease in dissolved Pb after an addition of apatite or phosphate rock. The difference may be a result of the different sources and contamination levels of Pb removed by apatite in former studies. Ma et al., (1993) used 2100 mg-Pb/Kg from an abandoned lead battery processing/recycling facility; Ma et al., (1995) used 2560 mg-Pb/Kg from insecticide applications; Laperche et al., (1996) used 37026 mg-Pb/Kg from paint residues; and Ma et al., 1994a; 1994b; and 1996 used $PbNO_{3(aq)}$ as a source for aqueous Pb. Shooting range soils may contain Pb in different forms, than Pb in the above soils, such as colloidal Pb, metallic Pb and Pb bound to different fractions of the soil.

TABLE 3 – STABILIZED SOIL

FIRST STUDY							
Sample	1	2	3	4	5	6	7
Apatite/Pb ratio	0	0.9	5	10.5	15	21	103
Pb [ppb]	34±0.4	49±5	51±6	41±4	42±5	44±8	43±7
SECOND STUDY							
Sample	1		2		3		4
Apatite/Pb ratio	0		2.1		10.1		101.4
Pb [ppb]	565±32		427±38		202±7		41±10
THIRD STUDY							
Sample	1	2		3		4	
Apatite/Pb ratio	0	1.4		5.1		9.7	
Pb [ppb]	795±60	949±19		976±80		1163±146	

Based on the pH-Edge results, the soil in the second study was placed in suspension that was adjusted to pH 4. This was thought to increase Pb mobility making it more available for the reaction with apatite. In all apatite to Pb ratios, the residual amount of Pb in suspension was high (Table 3). This is probably due to initial Pb leaching in pH 4 and little or no reaction with apatite in later steps. T-Test results showed that except for samples 1 and 2 all samples were statistically different. Since only very high apatite to Pb ratio showed reduction in Pb mobilization we concluded that the treatment with apatite is not feasible for this soil even after performing a soil washing step at pH 4. To test the possibility of colloidal Pb the third study involved soil that was washed at high pH. After washing the soil in pH 10 and separating the aqueous phase the washed soil leached more Pb to the suspension than in the previous studies (Table 3). All samples were found to be statistically different and higher than sample 1 (no apatite added). This can be due to leaching of organic matter that was complexing Pb (the aqueous phase's color was very dark and it separated after acid addition). It may also be a result of cation exchange between the soil and apatite.

Stabilization of soil with apatite was thought to be a first step in S/S process. Since

the addition of apatite did not seem to reduce Pb mobility, with and without pH adjustments, further testing of soil solidification was conducted with addition of cement alone.

IV. Heat-treated Soil

More than 30% of the soil's lead is bond to the organic fraction. In order to tests the influence of these bonds on lead mobility, we heat the soil and removed the entire organic fraction. After heating the soil at 400°C for 24 hours the soil's color changed from dark brown to red and the TOC content was reduced from 2.656% to 0.024% without changing the total lead concentration in the soil. Lead mobility in the heat-treated soil was lower in both TCLP and SPLP tests (Table 4). The average Pb concentration leached in the SPLP test was below CT standards and proved the treatment successful. An equilibrium study (pH-Edge) showed lower concentrations throughout the pH range (3 to 9) comparing with the soil and no Pb mobilization at pH higher than 7 (Fig. 2).

TABLE 4 – HEAT-TREATED SOIL CHARACTERISTICS

TOTAL METALS CONTENT [$\mu\text{g/g}$]					
Zn	Pb	Cd	Ni	Cr	Cu
79 \pm 3					
	488 \pm 18	11 \pm 0.5	17 \pm 1	26 \pm 1	35 \pm 1
MOBILITY [$\mu\text{g/L}$]					
		TCLP		SPLP	
	Initial pH	4.9		5.5	
	Final pH	4.9		6.4	
	Pb	2474 \pm 116		13 \pm 5.22	

The heat treatment did not change the total amount of Pb but changed the fractionation of Pb (Fig. 3). Sequential extraction on the heat-treated soil showed that 8.5% of the total Pb were in the exchangeable fraction, 20.9% in the organic fraction, 16.8% in the iron-oxide fraction and 53.8% in the residual fraction. T-Test for means showed that the sum of all fractions in the soil and the heat-treated soil was statistically the same, proving that no Pb was lost during the heat treatment. A statistical difference was found between the soil and the heat-treated soil in each fraction suggesting a shift in Pb distribution as a result of the heat treatment. The relatively high percentage of lead that remained bound to the organic fraction can be explained as an artifact of the test or as a result of very strong bonds to the organic fraction left after heating.

V. Solidified Soil

This study consisted of mixing different ratios of soil and heat-treated soil with cement. Curing time was 7 and 28 days for the soil mixtures and 28 days for mixtures

with heat-treated soil. To prevent competition for water, between the cement and the fine soil particles, the water content was constant (200 mL water : 1000 g mix). The strength of the mixtures decreased with increasing soil to cement ratio. Mixtures with heat-treated soil were stronger than the original soil mixtures after 28 days. Curing usually results in stronger samples (Kosmatke and Panarese, 1990) and this was the result for the 50% soil mixtures but not for the 75% soil mixtures. After 12 cycles of wetting and drying the strength of the mixtures containing 25% cement decreased. The change in strength was not statistically significant when comparing mixtures with 50% cement (Fig. 4).

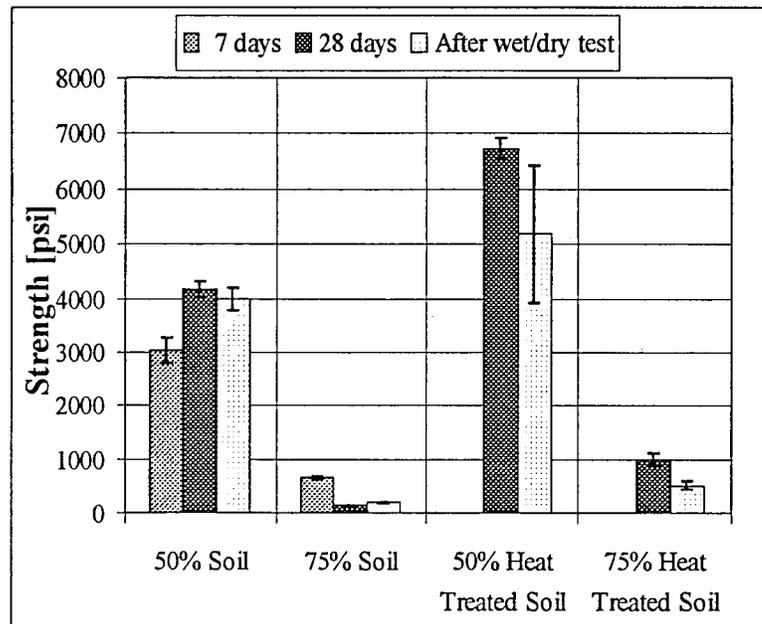


FIG. 4. – STRENGTH OF SOLIDIFIED SOIL AND HEAT-TREATED SOIL AFTER 7 AND 28 DAYS OF CURING AND AFTER WET/DRY DURABILITY TEST.

The strength of the mixtures remained above the requirement of 50psi (Tables 5 and 6). Table 5 also shows the weight loss during wet/dry cycles, mixtures with more cement resisted the treatment better.

During the mobility tests, the suspension pH changed rapidly after addition of the crushed solidified mixtures with the larger change in the unbuffered SPLP test (Table 7). The final pH was about 12 for both tests.

TABLE 5 – SOLIDIFIED SOIL, 7 DAYS CURING

% Cement	35	30	25
Strength [psi]	2171±248	897±3	652±29
Mobility [µg/L]		TCLP	
initial pH	4.4	4.4	4.2
final pH	12.1	12	12.1
Pb	20±12	<5	7±2
Cu	134±64	146±7	193±12
		SPLP	
initial pH	11.5	11.2	11.4
final pH	12.4	13	12.3
Pb	110±65	74±40	39±5
Cu	103±46	102±2	131±2

TABLE 6 – STRENGTH AND DURABILITY - SOLIDIFIED MIXTURES, 28 DAY CURING

% Cement	Soil		Heat-treated Soil	
	50	25	50	25
Strength [psi]	4168±153	149±15	6717±191	988±116
After wet/dry test [psi]	3990±217	197±20	5173±516	1248±70
Weight loss [%]	16±0.1	26±4	14±0.2	22±4

A sample of cured cement was tested for total Pb, TCLP and SPLP. The cement contained 172 µgPb/g and it leached less than 5 ppb in both tests. All cement mixtures passed the TCLP test and failed the SPLP test. Lead mobility in TCLP test was reduced for all treatments compared to the original soil and heat-treated soil and was below the Connecticut RSR's. This was also found by Hanscom and Richards (1998) who solidified, on site, soil from a shooting range in Massachusetts that contained up to 1630 mg/Kg Pb. They used the product as a cap for a nearby landfill and reported a reduction in lead TCLP from 39.1 mg/L to below 0.1 mg/L.

Previous work (Lackovic et al, 1997) showed higher TCLP values compared to SPLP. This was explained as a result of the buffer effect of the TCLP extraction fluid.

TABLE 7– MOBILITY AND CONTINUOUS FLOW, SOLIDIFIED MIXTURES, 28 DAYS CURING

% Cement	Cement	Soil		Heat-treated Soil	
	100	50	25	50	25
initial pH	4.15	4.61	4.19	4.36	4.58
final pH	12.09	12.05	11.50	12.02	11.62
Pb [ppb]	<5	<5	<5	7±1	<5
initial pH	11.66	12.13	11.57	11.96	11.93
final pH	12.38	12.51	12.44	12.51	12.57

Pb [ppb]	<5	103±153	37±27	281±199	168±194
			Columns Study		
Pb Removal [µg/g]	0.36	1.68	1.41	1.74	2.41
ACC3.42 [µg/L]	4	36	35	49	82
Acid Flux [eq/day]	9.55E-14	9.28E-14	1.83E-13	1.04E-13	2.53E-13

Unexpectedly in this study, SPLP results were higher than TCLP and the variations within triplicate were very high. The test was repeated and the same trend was found. Since the pure cement did not leach lead in both TCLP and SPLP tests we assume that the higher values and increased leaching in the SPLP test had to do with soil and the soil-cement behavior. The variation within SPLP results is also unexplained at this point. Tickanen and Turpin (1996) also reported an increase in SPLP lead mobility compared to TCLP results for soil stabilized with Portland cement. Further studies of the effect of high suspension pH on leaching from soil/cement may provide an explanation. However, it is clear that SPLP is not an appropriate mobility test for cement stabilized soil.

An increase in leached copper (Cu) was observed in the soil mixtures and can be attributed to the high pH and copper's amphoteric nature. However mixtures with heat-treated soil immobilized copper completely.

The inconclusive results of the mobility tests suggested that a further study of the solidified mixtures' mobility is needed. Continuous leaching experiment can quantify the amount of lead leaching from the mixtures and the pH change as a function of time. The environmental conditions are represented better in this type of experiment than in the batch leaching tests. During the column study, the flow rate was steady at 1ml/min, allowing 490 pore volumes to percolate through the columns. Due to the presence of cement in all columns an effluent with a high pH was collected throughout the duration of the experiment. The change in pH shows lower acid flux for columns containing 100% cement and 50% cement compared to 25% cement (Table 7). In all five columns a sharp decrease in Pb concentration occurred in the first 30 pore volumes (Fig. 5 and 6).

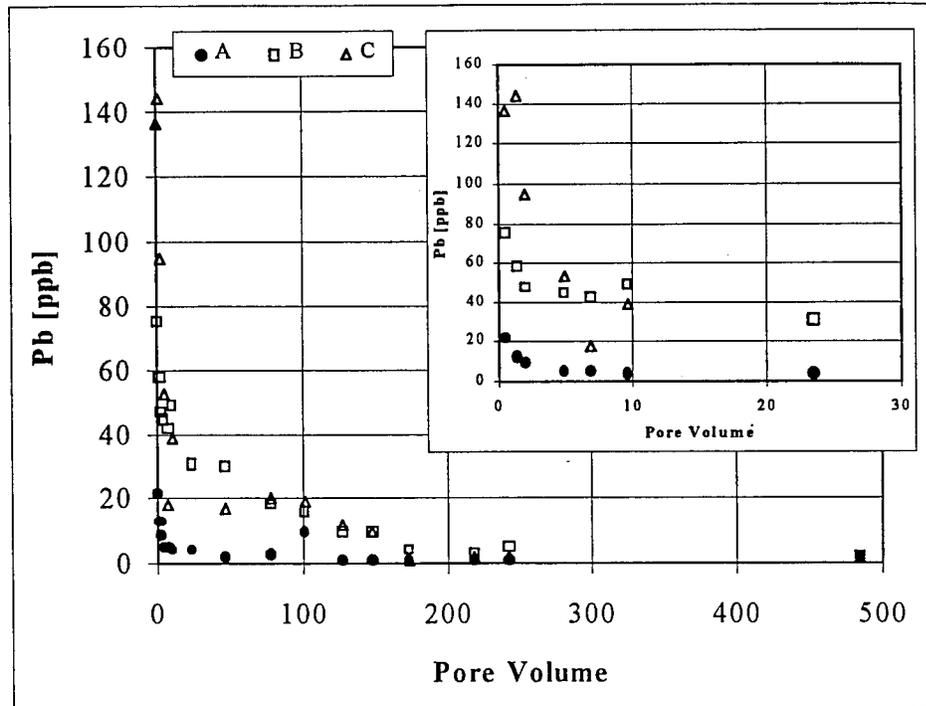


FIG. 5 - COLUMN STUDY - EFFLUENT Pb
 (A=100% CEMENT; B=50%CEMENT/50%SOIL; C=25%CEMENT/75%SOIL).

The starting point was different for each column with higher concentrations leaching out of the heat-treated columns and the lowest from the cement column. Overall, the five columns leached less than one percent of their total Pb. Lackovic et al., (1997) compared column results with batch tests using the Average Cumulative Concentration (ACC) at the point where the soil to effluent ratio was the same as in TCLP/SPLP tests (1g/20ml). In our setting the same ratio occurred at 3.42 L so the ACC3.42 was used for evaluating the results (Table 7). For all columns the ACC3.42 was higher than the TCLP suggesting that the batch test significantly underpredicted the leaching that will occur in natural environments.

Due to the high variability in SPLP results, it is not possible to compare it with the column results.

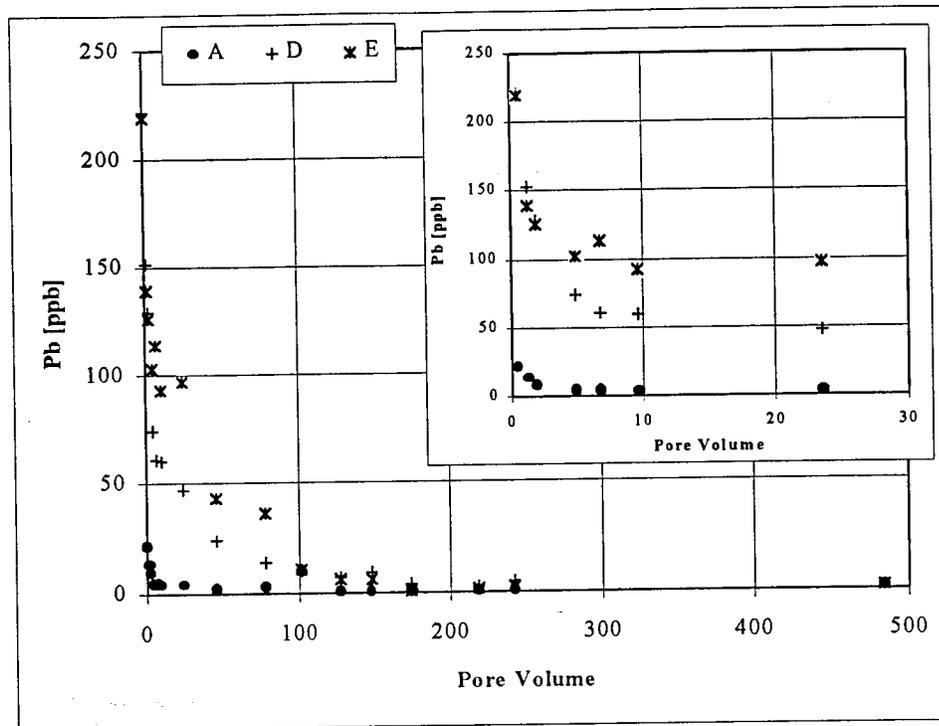


FIG. 6 – COLUMN STUDY - EFFLUENT Pb
 (A=100% CEMENT; D=50%CEMENT/50% HEAT-TREATED SOIL;
 E=25%CEMENT/75% HEAT-TREATED SOIL).

E. Conclusions

1. Lead contaminated soils from shooting ranges can pose significant environment risks.
2. Lead's mobility makes it a risk to surface and groundwater.
3. The exchangeable and the organic components contain over 40% of the total lead in the original soil and only 30% in the heat-treated soil.
4. Heat treatment reduces the amount of leachable Pb over a wide pH range, and in TCLP and SPLP mobility tests.
5. Apatite did not reduce Pb mobility in shooting range soil under natural pH conditions or after soil washing in pH 4 or 10.
6. Although S/S process are widely used for remediation of metal contaminated soils it may not be applicable to some shooting range soils due to lead mobility at high pH's. Remediation programs must consider site-specific conditions.
7. When testing S/S products for mobility, batch leaching tests (such as TCLP and SPLP) may not predict the real environmental risks.

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APPENDIX -A

DATA

Soil Characterization

Physical Characterization

TABLE 1C – GRAIN SIZE ANALYSIS - SIEVE ANALYSIS [% PASSING]

Sample Replicate	D [mm]					
	3.360	2.000	0.850	0.425	0.150	0.075
1	96.706	90.402	77.765	64.232	42.787	31.803
2	95.452	86.738	71.290	58.713	40.135	30.337
3	96.134	87.096	68.416	52.717	33.276	24.022
AVG.	96.097	88.079	72.490	58.554	38.733	28.721
STD	0.628	2.020	4.788	5.759	4.908	4.135

TABLE 2C – GRAIN SIZE ANALYSIS - HYDROMETER ANALYSIS [% PASSING]

Sample Replicate	D [mm]							
	0.033	0.021	0.012	0.009	0.006	0.003	0.002	0.001
1	37.622	32.715	29.443	26.172	24.536	22.082	19.629	17.993
2	35.921	32.655	31.022	26.124	24.491	22.042	19.593	17.993
3	39.219	32.682	27.780	26.146	25.329	22.878	19.609	17.993
AVG.	37.587	32.684	29.415	26.147	24.785	22.334	19.610	17.993
STD	1.649	0.030	1.621	0.024	0.471	0.471	0.018	0.000

TABLE 3C – MOISTURE CONTENT [%]

Sample Replicate	Wet Weight	Dry Weight	Water Weight	% Moisture
1	19.920	17.840	2.080	11.659
2	22.430	20.090	2.340	11.648
3	20.940	18.740	2.200	11.740
AVG.				11.682
STD				0.050

TABLE 4C – SPECIFIC GRAVITY [G], AT 24°C [g/cm³]

Sample Replicate	G
1	2.623
2	2.582
3	2.619
AVG.	2.608
STD	0.022

TABLE 5C – ATTERBERG LIMITS

% Moisture	No. of Blows
41.301	5.000
36.416	8.000
35.460	14.000
34.311	22.000
33.427	28.000
31.190	42.000

Liquid Limit 33.482
 Plastic Limit 30.282
 Plasticity Index 3.200

TABLE 6C – COMPACTION TEST

% water	Soil Weight [lb.]	Moist Density	Dry Density [lb/f ³]
3.111	3.140	94.200	91.357
5.880	3.310	99.300	93.785
8.387	3.450	103.500	95.491
11.645	3.630	108.900	97.542
15.166	3.840	115.200	100.029
18.041	4.020	120.600	102.168
21.090	4.010	120.300	99.347
24.358	3.980	119.400	96.013

Chemical Characterization

TABLE 7C – SOIL PH IN SUSPENSION [1:1 W/W]

Sample Replicate	pH	[H ⁺]
1	4.97	1.07E-05
2	5.00	1.00E-05
3	5.05	8.91E-06
AVG.	5.01	9.88E-06
STD		9.08E-07

TABLE 8C – TOTAL ORGANIC CARBON [%]

Sample Replicate	TOC
1	2.795
2	3.010
3	2.256
4	2.564
AVG.	2.656
STD	0.323

TABLE 9C – TOTAL METALS IN SOIL [µg/g]

Sample Replicate	Zn	Pb	Cd	Ni	Cr	Cu
1	71.01	445.12	10.49	16.18	24.97	36.55
2	71.54	393.98	10.59	15.34	28.40	34.73
3	68.42	17294.94	10.13	15.29	23.14	48.17
4	65.91	13834.87	9.81	15.17	22.10	48.27
5	74.93	431.24		17.82	29.03	40.02
6	72.65	431.57		16.99	26.31	36.91
AVG.^a	70.74	425.48	10.25	16.13	25.81	40.78
STD	3.18	21.97	0.35	1.08	2.57	6.01

^a – Samples 3 and 4 were excluded from the average and standard deviation for Pb.

TABLE 10C – SEQUENTIAL EXTRACTION [%]

Sample Replicate	Exchangeable	Organic	Iron Oxide	Residual	<u>Recovery</u>
1	24.325	36.112	5.823	33.740	156.047
2	25.471	31.190	9.793	33.545	144.180
3	22.832	35.650	9.709	31.810	134.088
4	1.645	11.256	1.818	85.281	
5	24.407	36.782	8.191	30.620	148.819
AVG.^a	24.259	34.934	8.379	32.429	145.784
STD	1.085	2.539	1.856	1.486	9.200

^a – Sample 4 was excluded from the average and standard deviation.

Mobility Tests

TABLE 11C – TCLP FOR SOIL [$\mu\text{g/L}$]

Sample Replicate	pH initial	pH final	Zn	Pb	Cu
1	4.88	4.82	153	3879	27
2	4.88	4.80	131	3375	26
3	4.87	4.83	140	3316	30
AVG.	4.88	4.82	141.33	3523.33	27.67
STD			11.06	309.43	2.08

TABLE 12C – SPLP FOR SOIL [$\mu\text{g/L}$]

Soil Replicate	pH initial	pH final	Pb
1	4.76	5.00	130
2	4.45	5.02	137
3	4.51	5.02	272
4	4.63	5.00	192
5	4.60	5.02	180
AVG.	4.58	5.01	182.20
STD			56.86

TABLE 13C – PH-EDGE FOR SOIL [$\mu\text{g/L}$]

Sample Replicate	pH							
	3.0	4.0	4.9	5.0	6.0	7.0	8.0	9.0
1	12184	2203	325	260		263	517	682
2	8360	2783	343	415	139	335	586	634
3	7276	2760	716	440	199	526	715	706
AVG.	9273.3	2582.0	461.3	371.7	169.0	374.7	606.0	674.0
STD	2578.3	328.4	220.7	97.5	42.4	135.9	100.5	36.7

Stabilization with Apatite

Equilibrium Study 1 - No pH adjustment

TABLE 14C - STABILIZATION STUDY 1 - Pb [$\mu\text{g/L}$]

Sample Replicate	Apatite/Pb						
	0.0	0.9	5.0	10.5	15.1	20.7	103.2
1	34.0	51.0	50.6	40.7	37.3	52.1	138.0
2	33.4	43.6	44.7	44.7	46.4	36.6	38.0
3	250.0	52.4	56.6	37.4	43.5	42.7	48.0
AVG.	33.7^a	49.0	50.6	40.9	42.4	43.8	43.0^b
STD	0.4	4.7	6.00	3.7	4.7	7.8	7.1

^a - Sample 3 was excluded from the average and standard deviation

^b - Sample 1 was excluded from the average and standard deviation

TABLE 15C - STABILIZATION STUDY 1, T-TEST

Apatite/Pb	0.0	103.2	0.9	5.0	10.5	15.1	20.7	Blank
0.0		1.86	5.57	4.91	3.39	3.22	2.24	43.50
103.2	(2)		1.05	1.26	0.38	0.11	0.12	7.04
0.9	(3)	(3)		0.37	2.34	1.72	0.99	14.90
5.0	(3)	(3)	(4)		2.41	1.89	1.21	12.39
10.5	(3)	(3)	(4)	(4)		0.43	0.58	15.34
15.1	(3)	(3)	(4)	(4)	(4)		0.27	12.73
20.7	(3)	(3)	(4)	(4)	(4)	(4)		7.98
Blank	(3)	(3)	(4)	(4)	(4)	(4)	(4)	
T (df=2, 95%)	4.30							
T (df=3, 95%)	3.18							
T (df=4, 95%)	2.78							

df - Degree of freedom

bold - Statistical difference was found

Equilibrium Study 2 – pH=4

TABLE 16C – STABILIZATION STUDY 2, Pb [$\mu\text{g/L}$]

Sample Replicate	Apatite/Pb			
	0	2.1	10.1	101.4
1	587	453	207	51
2	1290	400	197	32
3	542	2599	779	39
AVG.	564.5^a	426.5^b	202.0	40.7
STD	31.8	37.5	7.1	9.6

^a – Sample 2 was excluded from the average and standard deviation

^b – Sample 3 was excluded from the average and standard deviation

TABLE 17C – STABILIZATION STUDY 2, T-TEST

Apatite/Pb	0	2.1	10.1	101.4	Blank
0.0		3.97	15.73	22.6	25.01
2.1	(2)		8.32	14.25	16.03
10.1	(2)	(2)		21.6	40.04
101.4	(3)	(3)	(3)		7.02
Blank	(3)	(3)	(3)	(4)	
T (df=2, 95%)	4.30				
T (df=3, 95%)	3.18				
T (df=4, 95%)	2.78				

() – Degree of freedom

bold – Statistical difference was found

Equilibrium Study 3 – Soil washing at pH=10 as a first step.

TABLE 18C – TOTAL Pb BEFORE AND AFTER LEACHING AT PH=10 [$\mu\text{g/g}$]

Sample Replicate	Soil Before	Soil After
1	612.188	578.486
2	555.405	498.321
3	533.498	501.029
AVG	567.031	525.945
STD	40.613	45.521

NO SIGNIFICANCE WITH T T-TEST (1.16)

TABLE 19C – STABILIZATION STUDY 3, Pb [$\mu\text{g/L}$]

Sample Replicate	Apatite/Pb			
	0.0	1.4	5.1	9.7
1	773	946	939	995
2	862	970	1068	1255
3	750	932	921	1241
AVG.	795.0	949.3	976.0	1163.7
STD	59.2	19.2	80.2	146.2

TABLE 20C – STABILIZATION STUDY 3, T-TEST

Apatite/Pb	0.0	1.4	5.1	9.7	Blank
0.0		4.30	3.15	4.05	19.43
1.4	(4)		0.56	2.52	65.26
5.1	(4)	(4)		1.95	18.31
9.7	(4)	(4)	(4)		12.32
Blank	(4)	(4)	(4)	(4)	
T (df=4, 95%)	2.78				

df – Degree of freedom

bold – Statistical difference was found

Solidification with Portland Cement

Strength and Durability Tests

TABLE 21C – STRENGTH OF SOIL MIXTURES AFTER 7 DAYS CURING [psi]

Sample Replicate	Soil		
	65%	70%	75%
1	1886	900	648
2	2295	896	626
3	2332	895	683
AVG.	2171	897	652.3
STD	247.5	2.6	28.7

TABLE 22C – STRENGTH OF SOIL AND HEAT-TREATED SOIL MIXTURES AFTER 28 DAYS
CURING [psi]

Sample Replicate	Soil		Heat-treated Soil	
	50%	75%	50%	75%
1	4079.62	165.605	6624.2	1085.99
2	4343.95	136.943	6589.17	859.873
3	4079.62	143.312	6936.31	1019.11
AVG.	4167.73	148.62	6716.56	988.323
STD	152.612	15.0504	191.109	116.158

TABLE 23C – STRENGTH OF SOIL AND HEAT-TREATED SOIL MIXTURES AFTER 12 WET/DRY
CYCLES [psi]

Sample Replicate	Soil		Heat-treated Soil	
	50%	75%	50%	75%
1	3837.58	175.159	5044.59	1267.52
2	3773.89	222.93	5735.67	1207.01
3	4136.94	197.452	4525.48	1337.58
4	4213.38	194.268	5385.35	1181.53
AVG.	3990.45	197.452	5172.77	1248.41
STD	217.122	19.6319	515.579	69.5309

TABLE 24C – TOTAL WEIGHT LOSS OF CEMENT MIXTURES AFTER 12 WET/DRY CYCLES
[%]

Sample Replicate	Soil		Heat-treated Soil	
	50%	75%	50%	75%
1	15.55	29.80	14.19	25.65
2	15.63	28.19	14.07	25.17
AVG.	15.59	29.00	14.13	25.41
STD	0.06	1.14	0.09	0.34
3	15.33	22.24	13.76	17.98
4	15.58	21.83	13.97	17.80
AVG.	15.46	22.03	13.86	17.89
STD	0.18	0.29	0.15	0.12
Loss Due to Brushing	0.14	6.96	0.27	7.52

Note: samples 1 and 2 were brushed with a wire scratch brush after each drying cycle.

Mobility Tests

TABLE 25C – CEMENT MIXTURES IN COLUMNS STUDY

	A	B	C	D	E
% Cement	100	50	25	50	25
% Soil		50	75		
% Heat-treated Soil				50	75

TABLE 26C – pH TCLP FOR CEMENT MIXTURES

Sample Replicate	1		2		3	
	initial pH	final pH	initial pH	final pH	initial pH	final pH
A	4.49	12.10	4.02	12.11	4.07	12.06
B	4.52	12.01	4.75	12.06	4.60	12.07
C	4.17	11.46	4.18	11.51	4.22	11.52
D	4.29	11.98	4.33	12.03	4.47	12.04
E	4.54	11.62	4.66	11.63	4.56	11.60

TABLE 27C – Pb TCLP FOR CEMENT MIXTURES [$\mu\text{g/L}$]

	A	B	C	D	E
Sample Replicate					
1	<5	<5	<5	6.01	<5
2	<5	<5	<5	<5	<5
3	<5	<5	<5	7.62	<5
AVG.	<5	<5	<5		<5
STD					

TABLE 28C – pH SPLP FOR CEMENT MIXTURES

Sample Replicate	1		2		3	
	initial pH	final pH	initial pH	final pH	initial pH	final pH
A	11.71	12.35	11.60	12.37	11.67	12.43
B	12.08	12.50	12.16	12.50	12.15	12.52
C	11.46	12.41	11.66	12.45	11.60	12.46
D	11.89	12.49	11.95	12.50	12.06	12.54
E	11.92	12.56	11.97	12.58	11.91	12.56

TABLE 29C - Pb SPLP FOR CEMENT MIXTURES [$\mu\text{g/L}$]

Sample Replicate	A	B	C	D	E
1	<5	115.8	18.9	227	126.9
2	<5	10.6	66.5	26	37.1
3	<5	10	11.4	275.6	30.6
AVG.	<5	45.47	32.27	176.20	64.87
STD		60.91	29.88	132.33	53.82
4	<5	28.42	23.85	219.6	130.176
5	<5	221.7	26.17	59.25	131.453
6	<5	353.2	75.09	98.39	551.403
AVG.	<5	206.86	41.70	125.75	271.01
STD		154.29	28.94	83.60	242.83

Continuous Column Study

TABLE 30C - FLOW RATE [ml/min]

Time [min]	Pore Volumes	A	B	C	D	E	AVG.	STD
45	0.73				0.87		0.87	
80	1.29	0.90					0.90	
100	1.61		0.98		1.05		1.01	0.05
120	1.94			1.10			1.10	
180	2.90	1.08	1.00			1.02	1.03	0.04
240	3.87				1.05		1.05	
300	4.84			1.00		1.02	1.01	0.01
360	5.81	1.07	1.02				1.04	0.04
420	6.77			1.08	1.03		1.05	0.03
480	7.74	1.05				1.00	1.03	0.04
540	8.71		1.00	1.07			1.03	0.05
600	9.68				1.05	1.00	1.03	0.04
863	13.91	1.10	1.02	1.09	1.06	1.02	1.06	0.04
1355	21.85	1.04	0.99	1.05	1.03	0.98	1.02	0.03
1455	23.47	1.04	1.01		1.03	1.00		0.02
2085	33.63	1.03	0.97	1.03	1.01	0.97	1.00	0.03
2775	44.76	1.10		1.02	1.07	1.02		0.04
2835	45.73	1.07	1.00	1.05	1.03	1.00	1.03	0.03
3503	56.49	1.03	0.86	0.68	0.99	0.92	0.90	0.14
4230	68.23	1.05	0.98	1.02	1.00	0.98	1.01	0.03
4850	78.23	1.02	0.96	1.02	1.00	0.96	0.99	0.03
4795	77.34	1.00	1.07	1.04	1.00	1.00	1.02	0.03
6269	101.10	1.02	1.09	1.06	1.02	1.02	1.04	0.03
6359	102.56	1.09	1.02	1.07	1.05	1.02	1.05	0.03
7102	114.54	0.98	0.92	0.98	0.96	0.92	0.95	0.03

7898	127.39	1.02	0.93	1.02	1.00	0.93	0.98	0.05
8499	137.07	1.00	0.95	1.05	0.98	0.95	0.99	0.04
9159	147.73	1.05	0.98	1.05	0.00	1.00	0.82	0.46
9927	160.10	1.06	1.00	1.06	1.04	1.00	1.03	0.03
10754	173.45	1.05	1.02	1.05	1.03	1.00	1.03	0.02
11442	184.54	1.03	0.97	1.03	1.00	0.96	1.00	0.03
12189	196.60	1.08	1.02	1.08	1.07	1.02	1.05	0.03
12850	207.26	1.01	0.95	1.01	0.98	0.95	0.98	0.03
13554	218.61	1.09	1.05	1.07	1.07	1.05	1.07	0.02
14259	229.98	1.06	1.00	1.06	1.04	0.99	1.03	0.03
15645	252.34	1.07	1.01	1.08	1.05	1.01	1.04	0.03
17084	275.54	1.03	0.95	0.91	1.01	0.97	0.97	0.05
18621	300.34	1.02	0.97	1.03	1.01	0.97	1.00	0.03
20031	323.08	1.03	0.97	1.03	1.01	0.97	1.00	0.03
21291	343.40	1.04	0.99	1.04	1.02	0.98	1.02	0.03
22566	363.97	1.04	0.98	1.04	1.02	0.98	1.01	0.03
24024	387.48	1.14	1.09	1.15	1.13	1.08	1.12	0.03
28559	460.62	1.03	1.02	1.08	1.06	1.02	1.04	0.03
29956	483.16	1.01	0.99		1.04	0.99	1.01	0.02

TABLE 31C - PH

Time [min]	Pore Volumes	A	B	C	D	E
15	0.24	13.10	12.83	12.65	13.05	12.95
30	0.48	13.02	12.86	12.60	13.00	12.90
45	0.73	13.00	12.84	12.59	12.96	12.82
60	0.97	12.89	12.81	12.58	12.92	12.75
80	1.29	12.91	12.81	12.55	12.86	12.67
100	1.61	12.84	12.76	12.53	12.79	12.58
120	1.94	12.80	12.74	12.48	12.73	12.52
180	2.90	12.71	12.67	12.46	12.64	12.50
240	3.87	12.55	12.41	12.33	12.46	12.40
300	4.84	12.49	12.34	12.29	12.39	12.38
360	5.81	12.57	12.52	12.35	12.51	12.46
420	6.77	12.45	12.34	12.24	12.38	12.35
480	7.74	12.43	12.29	12.23	12.35	12.32
540	8.71	12.42	12.36	12.21	12.30	12.30
600	9.68	12.31	12.28	12.19	12.34	12.31
863	13.91	12.27	12.17	12.02	12.22	12.22
1197	19.31	12.24	12.18	12.02	12.22	12.17
1255	20.24	12.28	12.20	12.05	12.25	12.25

1355	21.85	12.34	12.25	12.12	12.27	12.29
1455	23.47	12.30	12.23		12.29	12.29
2085	33.63	12.33	12.28	12.09	12.22	12.26
2775	44.76	12.29	12.30	12.08	12.21	12.21
2835	45.73	12.35	12.30	12.04	12.22	12.18
3503	56.49	12.28	12.27	12.02	12.17	12.14
4230	68.23	12.24	12.27	12.11	12.11	12.10
4850	78.23	12.25	12.20	12.03	12.03	11.99
4795	77.34	11.94	11.95	11.77	11.90	11.79
6269	101.10	12.15	12.14	12.05	12.02	11.92
6359	102.56	12.15	12.13	12.04	11.99	11.88
7102	114.54	12.15	12.13	12.04	11.99	11.85
7898	127.39	12.13	12.11	12.03	11.96	11.83
9159	147.73	12.10	12.08	11.98	11.91	11.74
10754	173.45	11.94	11.92	11.78	11.81	11.53
12189	196.60	11.94	11.93	11.75	11.79	11.52
13554	218.61	11.88	11.87	11.61	11.73	11.50
15024	242.32	11.89	11.88	11.65	11.74	11.53
25561	412.27	11.73	11.77	11.52	11.66	11.34
30016	484.13	11.60	11.58	11.34	11.49	11.18

TABLE 32C - Pb [$\mu\text{g/L}$]

Time [min]	Pore Volumes	A	B	C	D	E
30	0.48	22	75	136	221	219
80	1.29	13	58	144	152	139
120	1.94	9	47	95	129	126
300	4.84	5	45	53	74	103
420	6.77	5	42	18	61	114
600	9.68	4	49	39	60	93
1455	23.47	4	31		47	97
2835	45.73	2	30	17	24	43
4850	78.23	3	18	20	14	36
6269	101.10	10	16	19	10	11
7898	127.39	1	10	12	7	6
9159	147.73	1	10	10	9	6
10754	173.45	1	4	1	4	1
13554	218.61	1	3	2	2	2
15024	242.32	1	5	2	5	2
30016	484.13	2	2	1	2	1

TABLE 33C – COLUMNS DATA

	A	B	C	D	E
Total Pb [µg]	29412	50616	61218	56430	69939
Pb leached [µg/g]	61.38	288.24	242.54	298.82	414.32
Pb Leached [%]	0.21	0.57	0.40	0.53	0.59
ACC3.42 [µg/L]	12.85	121.83	118.92	168.24	279.94
Acid flux [eq/day]	9.55E-14	9.28E-14	1.83E-13	1.04E-13	2.53E-13

Heat Treatment

Chemical Characteristics

TABLE 34C – TOTAL METALS IN HEAT-TREATED SOIL [µg/g]

Sample Replicate	Zn	Pb	Cd	Ni	Cr	Cu
1	74.68	481.92	10.30	16.29	25.22	34.35
2	80.95	513.88	11.08	16.47	27.55	35.54
3	74.69	477.30	10.56	15.83	26.79	33.96
4	75.12	477.70	11.39	18.48	26.17	36.66
AVG.	76.36	487.70	10.83	16.77	26.43	35.13
STD	3.07	17.58	0.49	1.17	0.99	1.22

TABLE 35C – SEQUENTIAL EXTRACTION OF THE HEAT-TREATED SOIL [%]

Sample Replicate	Exchangeable	Organic	Iron Oxide	Residual	Recovery
1	7.983	21.545	16.368	54.104	115.488
2	8.296	20.765	20.466	50.473	117.428
3	9.624	23.345	15.599	51.432	105.243
4	6.085	18.291	20.275	55.349	144.014
5	10.597	20.308	11.067	58.027	103.036
AVG.	8.517	20.851	16.755	53.877	117.042
STD	1.718	1.841	3.873	3.042	16.320

Mobility Tests

TABLE 36C – TCLP FOR HEAT-TREATED SOIL [µg/L]

Sample Replicate	pH initial	pH final	Zn	Pb	Cu
1	4.90	4.86	470	2395	35
2	4.89	4.86	450	2419	36
3	4.89	4.88	441	12125	38
AVG.	4.89	4.86	453.67	5646.33	36.33
STD			14.84	5610.70	1.53

TABLE 37C – SPLP FOR HEAT-TREATED SOIL [$\mu\text{g/L}$]

Soil Replicate	pH initial	pH final	Pb
1	5.32	6.23	5.20
2	5.48	6.32	14.00
3	5.51	6.44	17.70
4	5.58	6.46	17.20
5	5.51	6.39	10.30
AVG.	5.47	6.36	12.88
STD			5.22

TABLE 38C – pH-EDGE FOR HEAT-TREATED SOIL [$\mu\text{g/L}$]

Sample Replicate	pH						
	3.0	4.0	5.0	6.0	7.0	8.0	9.0
1	7072	1716	187	48	74	77	35
2	6492	1817	316	55	80	54	31
3	6823	1863	149	58	74	55	
AVG.	6795.7	1798.7	217.3	53.7	76.0	62.0	22.0
STD	290.9	75.2	87.5	5.1	3.5	13.0	2.8

APPENDIX - B

QUALITY ASSURANCE/ QUALITY CONTROL (QA/QC)

In order to ensure a high quality of the data that was generated in this study, an elaborate QA/QC program was followed.

Sample Replicates

All tests and analyses were performed on three sub-samples or more. The average and standard deviation were calculated for each set of results.

Procedure and Preparation Blank

For each analytical batch of samples, a blank (Type II water and reagents) was carried through the entire analytical process (procedure blank). This was useful to determine if the process was contributing contaminants to the samples.

For all aqueous digestions (EPA 3010) a blank (Type II water and reagents) was added to verify that no contamination was added to the samples in this process (preparation blank).

In all cases the procedure and the preparation blanks were found to be below the detection limit of the ICP or the GFAA.

Duplicates

One duplicate sample must be analyzed from every group of samples of a similar matrix type. The Relative Percent Difference (RPD) for each component are calculated as follows:

$$RPD = \frac{2 |S - D|}{(S+D)} \times 100$$

Where: **S** = First sample value (original), **D** = Second sample value (duplicate)

A control limit of 20% for the RPD shall be used for original and duplicate samples. Duplicate samples were processed on a routine basis (one in 20 samples).

TABLE 1D - DUPLICATES

SAMPLE	RESULT 1	RESULT 2	RPD
TCLP Soil	2395	2067	15
SPLP Soil	130	131	1
PH-Edge Soil	8360	8452	1
TCLP Solidification	<5	<5	0
SPLP Solidification	10	9.4	6

Spike

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added prior to digestion and at least one spike sample analysis must be performed on each group of similar sample matrix types. If the sample analysis is performed on the same sample that is chosen for duplicate sample analysis, the spike calculation must be performed on the sample designated as the "original sample". The average of duplicate analysis cannot be used for the calculation of percent recovery. The Percent Recovery (% Recovery) for each component are calculated as follows:

$$\% \text{ Recovery} = \frac{(S - O)}{SV} * 100$$

Where: S = spiked sample value, O = original sample value (duplicate), and SV = spiked value.

If the spike recovery is not within the limits of 75-125%, the data of all the samples was not accepted.

TABLE 2D - SPIKES

SAMPLE	SPIKED SAMPLE	ORIGINAL SAMPLE	SPIKE VALUE	RECOVERY [%]
pH-Edge Soil	807	317	500	98
Eq Study 3	1945	955	1000	99
SPLP Soil	13.6	5.2	10	84
TCLP Solidification	420	<5	500	84
SPLP Solidification	119.1	10	100	109

