

Stabilization and solidification of lead in contaminated soils

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Abstract

Lead has been identified as one of the greatest threats to human health and is one of the common contaminants in many hazardous wastes. In this study, a surplus (waste) material, i.e., sulfur, was employed as a binder to stabilize/solidify lead contaminated soils. Soil samples were collected from a battery recovery plant, which had high levels of inorganic lead contaminant. Results obtained from the study indicated that sulfur binders can be used to stabilize/solidify inorganic lead contaminated soil which may or may not contain organic compounds. However, control samples, which used portland cement to solidify the same contaminated soils, showed that portland cement was also an effective binder. The potential applications of these solidified matrixes are also discussed. Due to the excellent physical, engineering and chemical leaching characteristics, sulfur solidified wastes could be used as construction fills, such as a subbase course in road pavement construction. Under some circumstances, use of the sulfur stabilization and solidification process will be a viable choice, especially where excess sulfur, recovered from various industrial desulfurization sites, becomes a waste product which requires disposal. The excess (waste) sulfur can be used as a stabilization agent for treating lead contaminated soil locally. Thus the two waste materials can be combined and converted into an environmentally stable material for recycling without having to be deposited in a landfill site. This by itself meets the requirements for being a sustainable technology as favored by the emerging world-wide trend of the economy for the future.

Keywords: Stabilization/solidification; Recovered sulfur; Sulfur cement; Lead; Contaminated soils

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1. Introduction

Lead has been reported to affect the human nervous system, blood vessels and kidneys. It also produces adverse effects on the mental and physical development of infants and children, even at low exposure levels. Based on animal experimental evidence, lead is considered as a possible cause of human cancer [1]. The United States Environmental Protection Agency (EPA) has reported that EPA Region V alone has over 100 sites on the National Priority List (NPL) where lead contamination is found [2]. These sites include battery plants, car breaker yards, scrap metal yards, oil refinery plants, small arms firing ranges, etc. [3]. Since lead poses one of the greatest threats to human health, especially to young children and pregnant women, and is one of the common contaminants at Superfund sites across the nation, it has been selected as a model metal for use in this study.

Sulfur constitutes 0.05% of the earth's crust. Some fossil fuels, such as coal and crude oil, contain high levels of impurities of sulfur compounds. Their resulting combustion products, such as sulfur oxides (SO_x), are major air pollutants emitted from power plants, utility boilers, etc. Since the Congress enacted the 1990 Clean Air Act Amendments, the EPA has promulgated more stringent emission standards for regulating SO_x to mitigate acid rain. Elemental sulfur recovered from the purification of high sulfur coal, electric power plant operations, petroleum refineries, metal smelters and other chemical processes is commonly excessively stockpiled on industrial yards and creates disposal problems [4]. Therefore, use of the recovered sulfur to treat the soil contaminated with lead contaminants appears to warrant studies on solving the problems of lead contamination.

The use of sulfur as a construction material, as a hot-melt bonding agent mixed with aggregates to form sulfur concrete, has long been known. At room temperature, elemental sulfur exists in an orthorhombic form (S_α) which consists of 8 atoms in the form of crown-shaped rings, S_8 [5]. When the temperature is raised to about 119 °C, sulfur begins to melt and form a monoclinic modification (S_β) with more void space [6]. The main part of the sulfur melt consists of the stable and nonpolar form S_8 (more than 95%) [7]. Above a temperature of 159 °C, sulfur begins to polymerize and its viscosity increases drastically. In the temperature range of 119–159 °C, the viscosity is very low. Near the polymerization temperature, the color of liquid sulfur turns from yellow to dark red and the viscosity increases from 0.01 to 1.0 Pa s [8]. Upon lowering the temperature, sulfur again reverts to the solid S_α form. Due to this thermoplastic nature, elemental sulfur is considered to be ideal for encapsulating many contaminants in hazardous wastes, especially heavy metals [3].

However, sulfur concrete made from elemental sulfur has been found to exhibit loss of strength, and develop cracking under thermal cycling and long-term exposure [9]. The loss of strength is primarily attributed to the allotropic transformation that sulfur undergoes as it solidifies and ages. As sulfur cools below 95.5 °C, solid sulfur slowly transforms from the monoclinic (S_β) to the orthorhombic (S_α) modification. The S_α form has a higher density, therefore, the transformation of S_β to solid state S_α results approximately in 6% volume reduction along with high residual stress induced in the solid. Any process that tends to relieve the stress, such

as thermal cycling, may result in cracking and disintegration of the matrix [9]. To overcome these problems, a modified sulfur cement has been developed under US Bureau of Mines in the early 1970s [9], and also has been used to treat hazardous wastes [10, 11].

On the other hand, sulfur extended asphalt (SEA) has been evaluated on full-scale field construction demonstration programs to encourage state highway agencies and the highway construction industry to conserve energy by utilizing SEA concrete for pavement construction [12]. Over 40 SEA pavements have been constructed to date. In these applications, sulfur is first blended with asphalt cement at high temperatures (about 135–150 °C). The amount of sulfur used in SEA ranges from 20% to 50%. Mixing of sulfur and asphalt can be done by blending molten sulfur with asphalt cement at high temperatures, by directly introducing the dry powdered sulfur into molten asphalt cement, or by directly introducing the sulfur into the asphalt-aggregate mixing chamber (pugmill). From this point on, the equipment and process used for producing the SEA mixtures and for the field construction of SEA pavements are identical to the process used for producing conventional asphalt mixtures and for the construction of conventional asphalt pavement.

The feasibility of utilizing sulfur and sulfur extended asphalt (SEA) to stabilize and solidify soil contaminated with lead contaminants has been evaluated in this study. Soil samples were collected from a battery recovery plant contaminated mainly with inorganic lead. A binder of portland cement was used as a control for comparing the relative effectiveness of sulfur and SEA binders to stabilize and solidify lead contaminated soils. For a better understanding of the effectiveness of sulfur stabilized lead contaminants, simulated soils spiked with the relevant contaminants, such as lead, were used. A sample of the real world lead contaminated soil spiked with total petroleum hydrocarbon (TPH) was also examined to understand the effect of oil in sulfur stabilization and solidification (S/S) processes.

2. Experimental procedures

2.1. Soil samples collected from a battery recovery plant

The soil sample was obtained from a battery recovery plant in Georgia. The soil contained little debris and appeared reddish in color. Moisture present in the soil sample had resulted in agglomeration of the sample. Therefore, the soil sample was first oven dried to remove free water; then the sample was ground and sieved with a #10 sieve (2 mm opening). It was determined that 66% (weight basis) passed through the sieve.

Five random samples of the soil were selected and subjected to a moisture content analysis following the ASTM D2216 procedure [13]. The moisture content of the sample was determined to be 17.0 ± 1.2 wt%.

Although there was about 34 wt% of coarse particles (i.e., greater than 2 mm), a particle size less than 2-mm was selected for preparation of the soil sample due to the constraints of physical and engineering tests. The dried, ground sample of

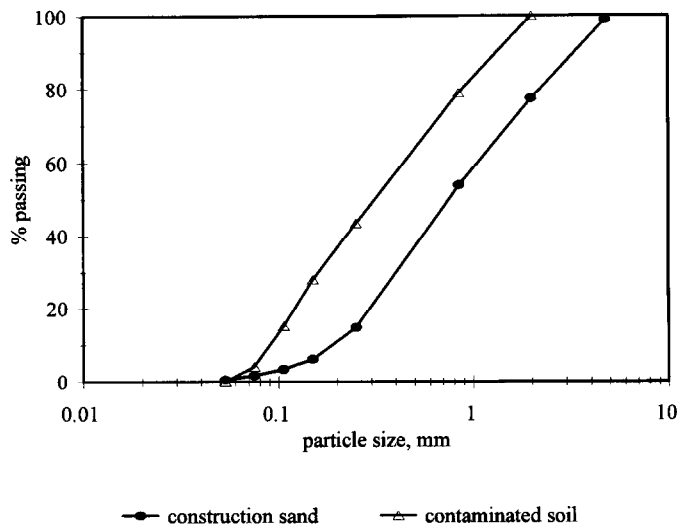


Fig. 1. Gradations of dried contaminated soil from a battery recovery plant and construction sand.

particle size less than 2 mm was subject to a sieve analysis and the results are shown in Fig. 1. The binders used in this study included portland cement (Type I), sulfur, and SEA (50/50 by wt%). Different amounts of the additive, i.e., Na_2SO_3 , were added to sulfur in the range of 0.5–4.0 wt%.

2.2. Soil sample spiked with oil

Since many lead contaminated sites also contain some degree of grease or oil, it was of interest to investigate the interference of oil during the sulfur S/S process. The soil sample from a battery recovery plant was spiked with lubricating oil up to 4 wt% to investigate the effect of total petroleum hydrocarbon (TPH) on the solidification processes of soil samples contaminated with lead. After the original soil sample was oven dried, ground, and sieved (US #4 sieve), it was spiked with Mobil SAE 30W motor oil to a final concentration of 4 wt% TPH. In order to achieve a more homogeneous distribution of the oil in the soil sample, the oil spiked soil (designated HLO) was allowed to sit for two days before any solidification processes were conducted. Portland cement, sulfur with the additive sodium sulfite (Na_2SO_3), and sulfur extended asphalt (50/50) were used as binders to solidify/stabilize this soil sample. Four different levels of binders were selected, i.e., 15, 20, 25 and 30 wt% (binder/soil sample). A 3 wt% (Na_2SO_3 /soil sample) addition of Na_2SO_3 was also added in the sulfur binder. Density, unconfined compressive strength (UCS), and the TCLP test were conducted on the solidified specimens.

2.3. Studies using sulfur binder to stabilize simulated samples

Simulated samples were prepared by spiking lead sulfate into construction sand having a large nonuniformity (see Fig. 1). The moisture content of the sand was less

than 0.5 wt%. Sand was used as a simulated sample instead of a real soil sample because it presents the worst case of being able to meet the TCLP requirement. Sand has very poor adsorption for metals, therefore, the adsorption mechanism can be neglected. The level of lead sulfate added to the sand was 2000 mg Pb/kg sample. Four different levels of sulfur binder were selected, i.e., 5.3, 8.1, 11.1 and 17.6 wt%. The amount of additive, i.e., Na_2SO_3 , required for meeting TCLP tests was also investigated.

2.4. Determination of soil/binder properties

This procedure involved the development of mix proportions of the contaminated soils with binders. This allowed the soil/binder system to achieve adequate performance requirements as defined by existing regulatory criteria (e.g., 0.35 MPa) as well as to satisfy the design criteria in certain construction applications (e.g., 3.45 MPa). The mix design performed in this study was briefly described in a previous paper [14]. The following physical, engineering and chemical leaching properties, which are considered to be important characteristics determining the performance of S/S systems, have been studied in the present work.

(1) Toxicity characteristics leaching procedure (TCLP): The TCLP follows a very stringent regulatory test which determines the amounts of constituents that can be leached in a weak acid medium [15]. The samples were first crushed to a particle size smaller than 9.5 mm (passing 3/8" sieve). The crushed samples were extracted with extraction fluids and rotated at 30 ± 2 rpm for 18 ± 2 h in the extraction bottles. The extract was then filtered through a 0.7- μm glass fiber filter. The final extract was analyzed using atomic absorption spectroscopy (AAS) for lead concentrations. A Model SpectrAA-10 (Varian Co., Australia) AAS was employed. The TCLP test deprived S/S of any beneficial effects relating to micro- and macro-encapsulation, and thus yielded very conservative testing results. The TCLP test was particularly useful in comparing the effectiveness of one S/S process with another, and was, therefore, employed in this study to quantify the relative effectiveness of stabilizing lead contaminants by using sulfur and SEA binders. This test was essential for the treated samples that were considered for final disposal in sanitary landfill, recycling for construction fill materials, and other applications.

(2) Multiple extraction procedure (MEP): The MEP test is designed for simulating the leaching of contaminants under the repetitive precipitation of acid rain on sanitary landfill with improper cover materials [16]. The crushed samples underwent multiple (sequential) extractions with a synthetic acid rain solution which was prepared by mixing concentrated sulfuric acid/nitric acid of 60/40 wt% and diluting to pH 3.0 ± 0.2 . The first extraction was performed with acetic acid in accordance with the TCLP test. Then the solid residue was extracted nine times using synthetic acid rain extraction solution. Three binder/soil S/S samples which were suitable for recycling as construction materials, based on the results of EPA TCLP tests and UCS tests, were selected for MEP tests. A Model SpectrAA-10 (Varian Co., Australia) AAS was employed to determine the lead concentrations in the MEP extract.

(3) **Unconfined compressive strength:** The unconfined compressive strength (UCS) measured the compressive and/or the shear strength of a monolithic matrix without lateral confinement on the sample. For the contaminated soils solidified with portland cement, sulfur with Na_2SO_3 , and SEA, cylindrical specimens (i.e., 5 cm in diameter by 10 cm in height) were prepared. The portland cement concrete specimens were cured under standard moisture curing conditions for seven days and, then, placed on a universal testing machine to determine their UCS. For the contaminated soils solidified with elemental sulfur and SEA, cylindrical specimens were prepared and tested without curing. The unconfined compression testing was performed immediately after the samples were cooled to room temperature.

(4) **Density:** To determine the bulk density of a solidified specimen (monolithic stabilized matrix), a cast cylinder of the binder/soil specimens was weighed and measured. The bulk densities of the monolithic specimens were then calculated by dividing the mass by the volume. Bulk densities of the solidified matrixes are useful when they are applied to Superfund site remediation in the S/S processes. This measurement can be used to determine the volume of wastes to be treated, shipped off site, or returned to the site [17]. Therefore, bulk densities of portland cement, sulfur, and SEA solidified specimens were determined for all matrix samples in this study.

(5) **Permeability:** The permeability of a solidified specimen indicates its ability to permit the passage of water and to limit the loss of contaminants from the solidified specimen to the environment. Method ASCE D 5084-90 [16] was used to determine the permeabilities of two solidified specimens. One specimen of contaminated soil was solidified using 33 wt% sulfur and 2 wt% Na_2SO_3 . The other was solidified using 33.3 wt% portland cement. In this test, the cell containing the specimen was filled with water and a pressure of 13.8–27.6 Pa (2–4 psi) was applied to the system by means of compressed air. To ensure that the specimens were saturated before permeability measurements started, the in-flow and out-flow of water through the specimens were measured and were determined to be the same.

(6) **Freeze/thaw test:** A modified ASTM D 560 method [13] was employed in the freeze/thaw test. Two solidified specimens of contaminated soils were prepared. One specimen was solidified using 33 wt% sulfur and 2 wt% Na_2SO_3 . The other sample was solidified using 33.3 wt% portland cement. The specimens were measured and their dried and water-saturated weights were obtained. A freezing cabinet was set up capable of maintaining a temperature of $-23\text{ }^\circ\text{C}$ ($-10\text{ }^\circ\text{F}$) or lower. Prior to placing the specimens into the freezing cabinet, both specimens were stored in a humidity controlled container on water-saturated pads. The specimens were then placed in the freezing cabinet for 24 h. After freezing, the specimens were placed in a covered container at a temperature of $21\text{ }^\circ\text{C}$ and a relative humidity of 100% for 23 h. The specimens were then weighed. All surface areas of the specimens were then given two firm strokes with a wire brush. After being brushed, the specimens were reweighed and turned upside down before they were replaced on the water-saturated pads and then returned to the freezing cabinet. Twelve cycles of the above described procedures were required to complete a freeze/thaw test.

3. Results

3.1. Soil samples collected from a battery recovery plant

Bulk densities of the solidified specimens were determined by weighing the specimens and dividing the weight by the calculated volume of the specimen. The results showed that the densities of solidified specimens increased slightly with increasing binder content (see Table 1). This was because the binder content filled the void space of solidified specimens and increased the densities of solidified specimens. The results of the unconfined compressive strength of solidified specimens are also shown in Table 1. It was found that sulfur solidified specimens had almost an order of magnitude greater unconfined compressive strength than those solidified by the other two binders. The UCS of solidified specimens also increased with increasing binder content.

The permeability of sulfur solidified specimens was between 2.6×10^{-9} and 2.8×10^{-9} m/s. The sulfur solidified specimen prepared for this test had a density of 2.25 g/cm^3 . After seven days saturation, volume expansion of the sulfur solidified specimen was about 6.5%. It had a reasonable hydrostability. The specimen solidified by portland cement had a density of 1.93 g/cm^3 . The permeability of this specimen was 2.6×10^{-9} m/s. After seven days saturation, volume expansion was negligible for the portland cement solidified specimen. Due to the satisfactory permeability properties of these two solidified specimens, they could be applied in pavement construction for subbase layers.

Results of the freezing and thawing tests indicated that the weight loss of sulfur solidified specimen was zero or negligible. Similar results were obtained for the portland cement solidified specimen. It was observed that the weights of the sulfur solidified specimen increased slightly during the freeze and thaw test. One plausible reason is capillary action of water in the pore spaces of the specimen. Since sulfur

Table 1
Densities and UCS of contaminated soils solidified by portland cement, sulfur and SEA binders

Binder contents	Density (g/cm^3)	UCS (MPa) ^a
<i>Portland cement</i>		
17.6 wt% portland cement	1.936	1.54
25.0 wt% portland cement	2.082	4.06
33.3 wt% portland cement	2.120	4.40
<i>Sulfur</i>		
28.6 wt% sulfur	2.204	17.02
31.5 wt% sulfur + 0.5 wt% Na_2SO_3	2.299	24.06
34.5 wt% sulfur + 0.5 wt% Na_2SO_3	2.353	42.39
<i>Sulfur extended asphalt</i>		
17.6 wt% 50/50 SEA	1.845	2.64
21.2 wt% 50/50 SEA	2.054	7.47
25.0 wt% 50/50 SEA	2.122	6.59

^a 1 MPa = 144.8 psi.

Table 2

The results of EPA TCLP tests of contaminated soils from a battery plant solidified by portland cement, sulfur and SEA binders

Components	Lead concentration (mg/l)
Untreated soil sample	40.65 ± 0.12
<i>Portland cement</i>	
17.6 wt% portland cement	0.38 ± 0.06
25.0 wt% portland cement	0.38 ± 0.01
33.3 wt% portland cement	0.23 ± 0.01
<i>Sulfur</i>	
28.6 wt% sulfur	14.03 ± 2.34
31.5 wt% sulfur + 0.5 wt% Na ₂ SO ₃	13.75 ± 1.62
34.5 wt% sulfur + 0.5 wt% Na ₂ SO ₃	11.81 ± 1.88
33.0 wt% sulfur + 2.0 wt% Na ₂ SO ₃	1.24 ± 0.09
<i>Sulfur extended asphalt</i>	
17.6 wt% SEA (50/50)	6.35 ± 0.38
21.2 wt% SEA (50/50)	5.82 ± 0.02
25.0 wt% SEA (50/50)	3.07 ± 0.08

is immiscible with water, the well compacted specimen leaves small pores for water-saturation. However, the freezing and thawing procedures could force some pores open which then absorbed water during the test.

Samples of the original soil as well as the solidified samples were tested for chemical leaching characteristics using the TCLP test. The lead concentration in the TCLP extract of untreated raw soil sample was 40.65 ± 0.12 mg/l. After the soil was solidified by different binders, the results of the TCLP tests showed that the sulfur binder, alone, could not satisfactorily stabilize lead contaminants in this contaminated soil (see Table 2). Therefore, an additive of Na₂SO₃ was investigated to improve the sulfur S/S process. It was found that 2 wt% Na₂SO₃ was required along with 33 wt% sulfur in order to reach 1.24 mg Pb/l in the TCLP extract. For the soil samples stabilized by portland cement, the lead concentrations in the TCLP extract were very low (see Table 2). These results showed that the portland cement process was able to stabilize inorganic lead in the contaminated soil. For the soil samples stabilized by 50/50 SEA, the lead concentrations in the TCLP extract decreased as the SEA content increased. Unlike sulfur binder, SEA stabilized soil could meet the TCLP lead concentration requirement of less than 5 mg Pb/l with 25 wt% SEA.

Three binder/soil mixtures, which were suitable for recycling as construction materials based on the results of TCLP tests and UCS tests, were selected for MEP test, i.e., 33.3 wt% portland cement (PC-3), 33.0 wt% sulfur + 2.0 wt% Na₂SO₃ (S-4), and 25.0 wt% SEA (SEA-3). After the first extraction of the TCLP test, lead concentrations of these three specimens were 0.526, 1.016 and 3.503 mg/l, respectively. Then the residues from the TCLP tests went through nine sequential extractions of the MEP test. The results of the MEP tests are shown in Fig. 2. All three specimens passed the MEP test.

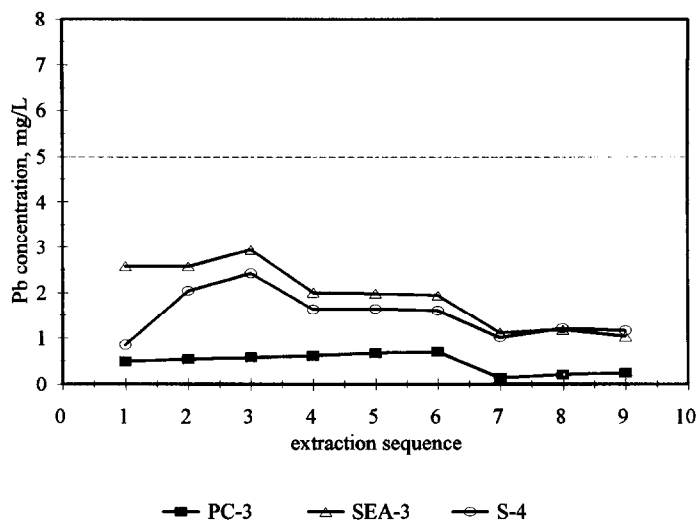


Fig. 2. Results of MEP tests of solidified specimens.

Table 3

Density and UCS data of the oil spiked contaminated soil solidified by portland cement, sulfur and SEA binders

Specimen	Binder content (wt%) ^a	Density (g/cm ³)	UCS (MPa)
<i>Portland cement</i> ^b			
HLO-PC-15	15	2.11	4.78
HLO-PC-20	20	2.11	7.47
HLO-PC-25	25	2.11	8.74
HLO-PC-30	30	2.11	10.00
<i>Sulfur + Na₂SO₃</i> ^c			
HLO-SEA-15	15	1.94	3.08
HLO-SEA-20	20	1.98	3.14
HLO-SEA-25	25	1.98	15.39
HLO-SEA-30	30	2.02	15.72
<i>SEA (50/50)</i>			
HLO-S-15	15	1.91	2.75
HLO-S-20	20	1.99	3.08
HLO-S-25	25	2.09	3.14
HLO-S-30	30	2.14	5.21

^a Binder content, wt% = (binder weight)/(soil sample weight) × 100.

^b For portland cement solidified specimens, moisture content = 13.5% H₂O; density = dry density (pre-determined).

^c For sulfur solidified specimens, binder content, wt% = (sulfur weight)/(soil sample weight) × 100; Na₂SO₃ content = 3 wt% (Na₂SO₃/soil sample).

3.2. Soil sample spiked with oil

The density and UCS data of the solidified specimens spiked with oil are tabulated in Table 3. For the portland cement solidified specimens, adequate strength

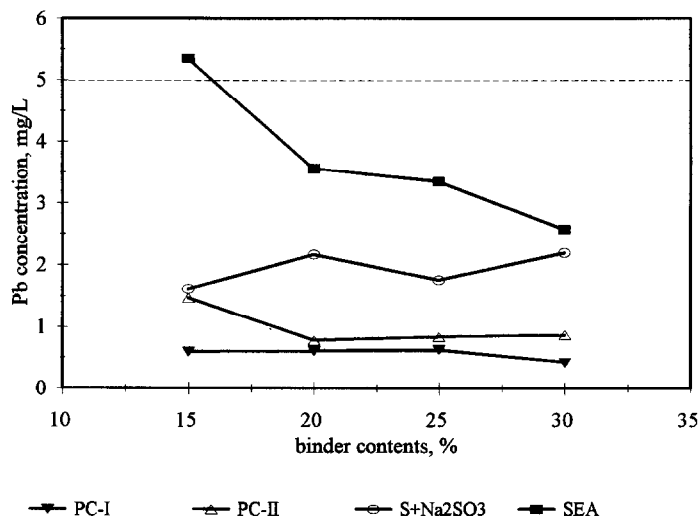


Fig. 3. Results of EPA TCLP tests of oil spiked soil samples solidified by portland cement, sulfur and SEA binders. PC-I represents that the samples were solidified by portland cement and TCLP extraction fluid #1 was used. PC-II is that the sample were solidified by portland cement and TCLP extraction fluid #2 was used. S + Na₂SO₃ represents that the binder contained elemental sulfur and 3 wt% of Na₂SO₃. SEA means that the binder contained 50/50 by weight of sulfur/asphalt.

(UCS > 3.45 MPa) was obtained for the cement content equal to or greater than 15%. For the sulfur solidified specimens, the results show that at low sulfur content (15 and 20%), weak specimens were obtained due to insufficient binder to create a well-blended mixture. However, at higher sulfur content (25 and 30%), the solidified specimens had adequate strength in that the UCS values were well above 3.45 MPa (500 psi) and even surpassed those of the cement solidified specimens at the same binder contents. For the SEA solidified specimens, low UCS values were obtained for the chosen SEA content range compared to those of the cement and sulfur solidified specimens. It is known that oil can reduce the viscosity of asphalt and thus affect the strength and stability of the asphalt/soil mixtures.

Fig. 3 shows the results of the TCLP tests of the solidified specimens using different binders. For the raw sample, the lead concentration in the TCLP extract was 35.99 ± 0.43 mg/l. Due to the concern for the buffer capacity of cement solidified specimens, both TCLP extraction fluids, #1 (having nominal pH value of 5) and #2 (nominal pH = 3) were used for the portland cement solidified specimens. Results indicated that no matter which extraction fluid was used, the portland cement could satisfactorily stabilize the lead contaminated soil in the presence of 4 wt% TPH. Sulfur and SEA could also successfully stabilize the lead contaminated soil to meet the regulatory criterion for the selected content range except for the lowest SEA content (15 wt%) specimen which was on the borderline (see Fig. 3). The higher the SEA content, the lower the concentration of lead detected in the TCLP extracts. For the sulfur solidified specimens, the TCLP lead concentration appeared to be independent of the sulfur content which might indicate that the resistance of the solidified

specimens to leaching was not a function of the sulfur content as long as sufficient Na_2SO_3 was provided. Increasing sulfur content increased the strength as discussed in the previous section but had little effect on the stabilizing ability. These results are comparable to those of the same soil sample which was not spiked with oil. It may be concluded that the presence of up to 4 wt% TPH had little effect on the solidification/stabilization of the inorganic lead contaminated soil sample no matter which binder was used.

3.3. Studies using sulfur binder to stabilize simulated samples

Fig. 4 shows the results of the bulk densities of sulfur solidified simulated specimens. It was found that the bulk densities of the solidified specimens increased with increasing sulfur content. The reason for such an increase could be a gradual reduction in void volume in the solidified specimen with increasing amount of elemental sulfur added. The unconfined compressive strengths of four solidified simulated samples with different sulfur contents are also shown in Fig. 4. The greater is the sulfur content, the higher the unconfined compressive strength yields, which increases linearly within the range of sulfur contents studied.

The results of the TCLP test in this case again showed that the sulfur binder alone could not satisfactorily stabilize lead in the simulated samples. The lead concentration in the TCLP extract of untreated simulated samples was 77.76 ± 3.86 mg/l. The lead concentration of a simulated sample solidified by 17.6 wt% sulfur was 31.88 ± 1.59 mg/l. This showed that the use of sulfur alone could not stabilize lead compounds in the simulated sample satisfactorily. Four different levels of Na_2SO_3 were added to the sulfur binder in order to improve the stabilization process. As can be seen from Fig. 5, the amount of sulfur added has very little effect on the TCLP results. However, a critical level of additive (greater than 0.08 wt%) appears to be adequate to properly stabilize lead at the concentration used. When more additive was used, a lower lead concentration in the TCLP extract resulted, even at low weight percent of sulfur employed.

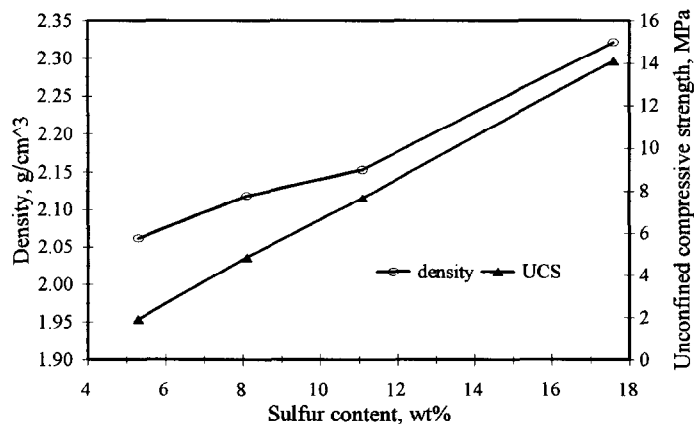


Fig. 4. Densities and unconfined compressive strength of sulfur solidified simulated soil samples.

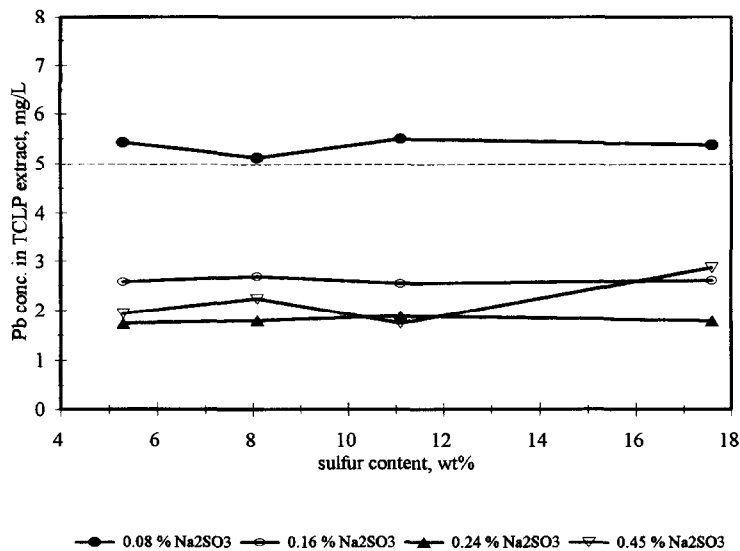


Fig. 5. Results of EPA TCLP tests of sulfur stabilized simulated soil samples.

4. Discussions

Two soil samples were tested in this study. One was a real world contaminated soil from a battery plant, and the other was a construction sand spiked with lead compounds and used as a simulated soil sample. Two gradation analyses of these samples showed that the soil from the real world contaminated site had more fine particles than the simulated sample (see Fig. 1). The major mechanisms involved in the sulfur S/S process have been reported to be the encapsulation of contaminants with some chemical reactions of lead ion and polysulfide [3]. Therefore, the surface area of the soil will be the most important factor in determining the amount of binder required. Since the contaminated soil from the battery recovery plant had more small particles, more sulfur binder was needed to solidify the lead contaminants. The same held true for the SEA binder. More SEA binder content was needed to solidify the real world contaminated soil.

From the physical and engineering studies, it was found that both bulk density and UCS of sulfur solidified specimens increased as the sulfur binder content increased. Since sulfur is a liquid and has very low viscosity within the range of the operating temperature (i.e., 120–140 °C), sulfur binder easily wets the particles and contaminants. More the sulfur binder added, more void spaces were filled. Therefore, the bulk density of sulfur solidified specimens increased as the sulfur content increased. The same held true for the other two binders. On the other hand, after the particles and contaminants have been wetted, more sulfur binder will increase the binding force of the particles. The UCS, therefore, increased as the sulfur binder increased. They increased in linear relationships which could allow the development of a simple field test using density to estimate UCS. However, more data is required to substantiate this. From Table 1, it can be seen that the UCS decreased slightly

as SEA increased to 25 wt% of binder content. Asphalt cement and SEA are viscous materials at room temperature. The use of higher binder content than the optimum amount increased the film thickness of binders which coated the aggregates and resulted in the loss of compressive strength of solidified matrixes.

The permeability of sulfur solidified specimens was determined as 2.7×10^{-9} m/s while the bulk density was 2.25 g/cm^3 . The permeability would have been smaller if the specimen had been more compacted. However, this permeability was sufficient to consider recycling of this material as a subbase course of road pavement. It was also found that there was little expansion of sulfur solidified specimen when they were saturated with water. The volume expansion was so small that it could be negligible in field applications. The result of freeze/thaw tests showed that the sulfur solidified specimens remained intact after twelve cycles of testing. Although there is no direct relation between this test and the sulfur S/S process, it is believed that the durability of sulfur solidified specimen could last for long-term application.

The results of EPA TCLP tests showed that the use of elemental sulfur as a binder alone could not stabilize contaminated soil satisfactorily. The lead concentrations in the TCLP extract were higher than the EPA criterion of 5.0 mg/l. Even when elemental sulfur was modified by adding 0.5 wt% of Na_2SO_3 , the results were still unsatisfactory. However, the construction sand (simulated soil) samples, solidified by sulfur binder, passed EPA TCLP tests when elemental sulfur was modified by adding a small amount of Na_2SO_3 (e.g., 0.16 wt%). The coarse particles and poor adsorption property made the lead contaminants easier to be encapsulated in this simulated soil. For the actual contaminated soil, the small particles and complicated soil properties made it difficult to be stabilized by sulfur binder. Two wt% of Na_2SO_3 was required to stabilize and solidify the lead contaminated soil. For SEA as a binder, the asphalt cement helped to encapsulate lead contaminated soils due to its polymeric properties. At low SEA content, it could not stabilize and solidify lead contaminants. Twenty-five wt% of SEA binder was required. For portland cement as a binder, all specimens passed EPA TCLP tests.

In order to simulate the worst case of acid rain leaching, the best solidified specimen (based on TCLP and UCS data) from each binder group was selected for MEP tests. The results indicated that lead concentrations in the MEP extract could meet EPA criterion for all three specimens. All these specimens could be considered for recycling and used as a subbase course of road pavement.

Since many lead contaminated sites also contain some degree of grease or oil, it was important to investigate the effect of total petroleum hydrocarbon (TPH). In the literature review, there were many unsuccessful cases using portland cement as a binder because of the inhibition of the cement hydration by some organics [18, 19]. In this study, it was found that sulfur solidified specimens at 25 wt% of sulfur binder had highest UCS. Because of this good engineering property, sulfur solidified soils could be considered for recycling as construction materials. From EPA TCLP tests, the lead concentrations of sulfur solidified specimens could meet EPA criterion, even when contaminated with 4 wt% oil. This result showed that the oil did not influence the sulfur S/S process. However, oil could influence the hydration process in the portland cement process.

The major incentive for the use of sulfur as a binder material for the S/S of hazardous wastes is in fact its favorable economics. Sulfur is normally recovered as a waste material from many industrial desulfurization processes. The average price of recovered sulfur is in the range of \$8–\$12/long ton [20]. This compares favorably with portland cement which has a market price range of between \$80–\$120/long ton. In addition, the recovered sulfur is normally unsuitable for use as industrial grade sulfur without further refining because of its impurity contents. Therefore, the use of an otherwise waste sulfur as a binder material for the S/S of another hazardous waste, e.g., lead contaminated soils, which in turn has the potential of being recycled as construction materials, indeed meets all the criteria of developing a sustainable technology [14].

5. Conclusions

The effectiveness of using portland cement, sulfur and SEA to solidify and stabilize inorganic lead contaminated soils has been investigated. For portland cement solidified specimens, lead concentrations in both TCLP and MEP extracts could meet EPA criterion of 5.0 mg/l. The SEA S/S system could reduce the Pb concentration to 3.07 ± 0.08 mg/l at 25 wt% SEA content. Even being processed at elevated temperature, elemental sulfur could not completely encapsulate all of the lead compounds in inorganic lead contaminated soil and simulated samples spiked with PbSO₄ during TCLP leaching tests. However, the use of a modifier, e.g., Na₂SO₃, in the sulfur binder could reduce the Pb leaching to less than 5.0 mg/l. It was also found that the amounts of modifiers greatly affected the stabilization of lead compounds. However, no influence was found due to the variation of binder contents. The amounts of sulfur binder and the modifier used to achieve optimum performance and economics are dependant upon the intended means of disposal or recycling of the S/S wastes.

From the results of physical and engineering properties reported here, the bulk density of sulfur solidified specimens could be related to the UCS of the same specimen. If so, a simple density test can be readily used in the field for quality control purposes instead of relying on more complicated UCS tests in the laboratory. It was also found that the UCS of sulfur solidified specimens was much higher than those solidified by portland cement. Because of this high UCS, as well as its good properties of permeability and durability, the lead contaminated soil solidified by sulfur binder could be considered for recycling as the subbase course in the road pavement.

The results of two spiked soil samples solidified by different binders showed that 4 wt% lubricating oil did not interfere substantially with the performance of portland cement, sulfur, or SEA S/S processes. From the UCS results of this study, all solidified specimens had greater than 0.34 MPa of UCS. The best UCS in this study was a soil sample solidified by 25 wt% of sulfur binder. This was very important for the applications of the solidified matrix as a construction material. From the EPA TCLP data, all solidified specimens could meet the EPA criterion for lead. These results support the use of sulfur to solidify and stabilize inorganic lead/TPH contaminated soils.

Results obtained from this study indicated that sulfur binder can be used to stabilize and solidify inorganic lead contaminated soil which may or may not contain organic compounds (TPH). However, control samples which used portland cement to stabilize and solidify the same contaminated soils showed that the use of portland cement was also effective. However, based on the same amount of sulfur binder used with the soil samples studied herein, the UCS is almost an order of magnitude higher (see Table 2) than for those solidified with portland cement. This renders the sulfur solidified soil attractive for recycling as a construction material. Also there are circumstances where portland cement is ineffective in stabilizing and solidifying some soils. It is well known that certain chemicals can inhibit the hydration process of portland cement. Therefore, if those chemicals are present in contaminated soils, the use of portland cement may be ineffective to treat those types of contaminated soils.

Other circumstances where the use of sulfur S/S process could be a viable choice depends on whether excess elemental sulfur is being produced from various industrial desulfurization sites and becomes a waste product requiring disposal. The excess (waste) sulfur could then be used as the stabilization agent for treating contaminated soils locally, such as the inorganic lead contaminated soils investigated in this study. Thus two waste materials could be combined and converted into an environmentally stable material for recycling as construction materials rather than disposal in a landfill site. This would also provide the added incentive of savings on transportation and tipping fees for the ultimate disposal of solidified wastes. Further, the technology of using surplus sulfur to solidify contaminated soils for recycling as road subbase and other construction materials meets all the requirements for developing a sustainable engineering system.

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