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## Activated Carbon Preconditioning to Reduce Contaminant Leaching in Cement-Based Stabilization of Soils

Renee Elizabeth Crane

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ACTIVATED CARBON PRECONDITIONING TO REDUCE CONTAMINANT  
LEACHING IN CEMENT-BASED STABILIZATION OF SOILS

by

Renee Elizabeth Crane

A thesis submitted to the Graduate College  
in partial fulfillment of the requirements  
for the degree of Master of Science  
Department of Geoscience  
Western Michigan University  
August 2013

Thesis Committee:

Daniel Cassidy, Ph.D., Chair  
Duane Hampton, Ph.D.  
David Barnes, Ph.D.

## ACTIVATED CARBON PRECONDITIONING TO REDUCE CONTAMINANT LEACHING IN CEMENT-BASED STABILIZATION OF SOILS

Renee Elizabeth Crane, M.S.

Western Michigan University, 2013

Powdered activated carbon (PAC) is often added with cement to enhance the stabilization and solidification (S/S) of materials contaminated with organic compounds. Adsorption of organic contaminants onto PAC can reduce leaching of organic contaminants. Simultaneous addition of PAC and cement reduces soil handling costs, but cement hydration reactions coat PAC with  $\text{Ca}(\text{OH})_2$  before contaminants can be adsorbed onto PAC. Laboratory studies were done on four aged, contaminated soils from manufactured gas plant sites to compare the performance of S/S treatment with simultaneous addition of PAC and cement vs. cement addition after preconditioning with PAC to enhance contaminant adsorption. Performance was evaluated by quantifying the leaching of BTEX and naphthalene with the synthetic precipitation leaching procedure, and by measuring unconfined compressive strength in amended soil samples. Ordinary (Type I) Portland cement, quicklime, and Class C fly ash were the cementing agents tested. A period of 15 to 25 weeks was required for a 1% PAC amendment to optimally reduce contaminant leaching. Adding cement after a 20-week PAC preconditioning time dramatically enhanced leaching and strength compared with adding cement and PAC simultaneously. The results from this work suggest that PAC is only effective when allowed sufficient preconditioning time before cement addition.

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Renee Elizabeth Crane

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## INTRODUCTION

### Stabilization and Solidification

Stabilization and solidification (S/S) is a site remediation method in which additives or reagents are mixed into contaminated soils, sediments and sludges to reduce physically and/or chemically the solubility, bioavailability, and mobility of the contaminants (USEPA 2009; ITRC 2011). In the last decade S/S has been increasingly used to redevelop brownfield sites contaminated with manufactured gas plant (MGP) waste. Because many of these sites have shallow contamination (i.e., less than 15 meters), S/S amendments are often added using augers or other shallow soil mixing equipment, a method known as *in situ* stabilization (ISS). The most common contaminants at these sites are polycyclic aromatic hydrocarbons (PAHs), and monoaromatics such as benzene, toluene, ethylbenzene, and xylenes, collectively referred to as BTEX. Naphthalene (a 2-ring PAH) and BTEX are volatile organic compounds (VOCs), and are the most soluble contaminants at these sites. One of the post-remedial goals of S/S treatment at these sites is to reduce the leaching of these VOCs into the water table via infiltrating precipitation.

Amendments used in S/S reduce the solubility, bioavailability, and mobility of contaminants by two primary mechanisms: (1) precipitation and/or adsorption onto solids to remove contaminants from the aqueous phase, and (2) encapsulation of contaminants in a solid medium to reduce or eliminate interaction with the pore waters. The most important measure of the effectiveness of an ISS strategy is the synthetic precipitation

leaching procedure (SPLP) using US EPA Method 1312. SPLP allows a direct measurement of the leachability of contaminants from a soil by infiltration of water following rainfall events. Amendment recipes for ISS applications vary, depending on the type and concentration of contaminants, the specific remedial goals for the site, and the intended use for the site after treatment. In addition to reducing SPLP, the amendments used in ISS should also reduce the hydraulic conductivity of the treated soil, and increase or maintain values of unconfined compressive strength (UCS) that are consistent with the intended use of the site (USEPA 2009; ITRC 2011). A minimum required UCS of 345 kPa (50 pounds/inch<sup>2</sup>) is common, and is suitable for most purposes.

Most of the research used as a foundation for S/S treatment was done before 1990 (Conner and Hoeffner, 1998). Ordinary (Type I) Portland cement (OPC) has been the most common amendment used in S/S. The CaO in OPC and other cements reacts with water to form hydrated lime, or Ca(OH)<sub>2</sub>. Hydrated lime coats soil particles, which encapsulates organic contaminants already adsorbed onto the particle surfaces. Other common cement binders include Class C fly ash (CCFA) and quicklime. Commercial quicklime is between 85%-95% CaO (by weight). The quicklime used in this study was 95% pure, and will hereafter be referred to as CaO. The average CaO content (by weight) of OPC and CCFA are approximately 65% and 25%, respectively (Shehata et al., 1999). In addition to encapsulating adsorbed contaminants, these binders are pozzolanic, and by cementing soil particles together they reduce permeability and increase UCS. However, these cementing agents do not adsorb organic contaminants, and are therefore ineffective for S/S of organic contaminants in dissolved and non-aqueous phase liquid (NAPL) form.

Moreover, it has been well-established that petroleum hydrocarbons and other organics interfere with the setting time and properties of cements use in S/S (Means et al., 1995; Jones, 1990; Conner, 1990; Zain et al., 2010; Karamalidis and Voudrias, 2007).

### **Sorbents in Stabilization and Solidification**

Addition of sorbents with cementing agents is now a common practice in S/S (Paria and Yuet, 2006). Powdered activated carbon (PAC) is the most common sorbent for this purpose, but others include organically modified clays and bentonite. Coz et al. (2009) showed in laboratory S/S studies that addition of PAC with lime and other binders reduced leaching of organic and inorganic contaminants from foundry sludge. Doses of PAC used are typically 3% (i.e., weight of PAC/weight of dry soil) or less (Paria and Yuet, 2006). The combined addition of PAC and cement has the potential to achieve both adsorption and encapsulation of contaminants in S/S treatment. However, the PAC and cement are typically added at the same time to reduce soil handling and costs (Paria and Yuet, 2006; ITRC, 2011). Arafat et al. (1999) showed that the amount of phenol adsorption onto PAC decreased dramatically within the first 10 hours after cement addition because the  $\text{Ca(OH)}_2$  coating made the PAC inaccessible for adsorption. Arafat et al. (1999) also demonstrated that when phenol was allowed to adsorb onto PAC before cement addition, the amount of phenol that desorbed from the PAC was less than 2% of the amount desorbed from PAC not treated with cement. This study was not done in the presence of soil, but does suggest that preconditioning contaminated soils PAC before cement addition has the potential to enhance S/S and ISS performance.

The purpose of this work was to compare the effectiveness of preconditioning contaminated soils from MGP sites with PAC before cement addition compared with simultaneous PAC and cement addition. There is little information in the literature on the rate of adsorption of contaminants onto PAC in aged, contaminated soils. Zimmerman et al (2004) found that 6 months of contact between contaminated sediments and PAC showed lower aqueous concentrations of PCBs and PAHs compared to 1 month contact. Cho et al. (2007) showed that adsorption of PCBs in sediments onto PAC continued over a 7 month period. However, the contaminants in both of these studies have low solubility compared to BTEX and naphthalene, which were the focus in our studies. Adsorption of BTEX and naphthalene onto PAC in water systems is well understood (Walters and Luthy, 1984; Daifullah and Girgis, 2003). However, the greatest portion the mass of VOCs at MGP sites is not dissolved in pore waters, but rather is adsorbed onto soil particles and soil organic matter (SOM), or is present as a non-aqueous phase liquid (NAPL). It is therefore expected that VOC desorption and dissolution from NAPL would govern the rate of contaminant adsorption onto PAC in soil. PAC has a greater specific surface area than even clays, and adsorbs organics preferentially to soil minerals and SOM (Walters and Luthy, 1984; Jonker and Koelmans, 2002; Cornelissen et al., 2006; Brändli et al., 2008). A review by Cornelissen et al. (2005) reported that PAC has sorption coefficients for various organic contaminants 2 to 3 orders-of-magnitude higher than native organics in soils and sediments.

Four soils from different MGP sites contaminated with PAHs and BTEX were tested in this study. The doses of PAC and cements tested were 1% and 5% (weight of amendment/weight of dry soil), respectively. First, the optimal water content for UCS was determined by adding 5% doses of CaO, OPC, and CCFA to soil samples with varying water contents and measuring UCS after a 28-day cure time. Next, the total VOCs (BTEX and naphthalene) in SPLP extracts were measured over 40 weeks in samples of the four soils amended with 1% PAC at their optimal water content. This was done to evaluate the optimal time for PAC preconditioning in the soils before cement addition. Finally, the effect of PAC preconditioning on SPLP-VOCs and UCS was evaluated by measuring these two parameters in soil samples preconditioned with PAC for 20 weeks before cement addition and comparing the results with samples in which PAC and cement were added simultaneously.

## **MATERIALS AND METHODS**

### **Stabilization and Solidification Amendments**

OPC and quicklime (95% CaO) were purchased from the Cheney Lime & Cement Company (Allgood, Alabama). CCFA was obtained *gratis* from WE Energies (Milwaukee, Wisconsin). PAC was obtained *gratis* from CalgonCarbon (Pittsburgh, Pennsylvania).

### **Contaminated Soils**

Contaminated soils from four different manufactured gas plant (MGP) sites were collected and used for testing. The soils were homogenized in the field using portable cement mixers and shovels. Once in the laboratory, the soils were passed through a sieve with 2.00-mm apertures, and were then further homogenized by hand so that different batches of S/S amendments tested would be challenged with similar contaminant concentrations. The homogenized soils were kept in closed containers at 4°C, and were only opened to remove aliquots for batch S/S tests.

### **Analyses**

One sample of each homogenized soil was used to determine the relative percent clay (0.002 mm), silt (0.002 mm-0.05 mm), and sand (0.05 mm-2.00 mm) according to Gee and Bauder (1986). The percent soil organic matter (SOM) was determined by first quantifying soil organic carbon (SOC) using the Dichromate Oxidation CO<sub>2</sub> Trap Method

(Skjemstad and Baldock, 2008), and then multiplying SOC by 1.72 to obtain SOM (Tan, 2003). The water content of the soil samples was measured gravimetrically, according to Black (1965).

SPLP extractions were conducted according to EPA Method 1312, using an extraction solution with a pH of 4.2 and a liquid to solid ratio of 1:10. VOCs (BTEX and naphthalene) were quantified directly in SPLP extracts using EPA Method 8260C (GC/MS). Soil samples were analyzed for VOCs by extraction with EPA Method 5035 and then quantifying with EPA Method 8260C (GC/MS). PAHs were measured in the homogenized untreated soils by extraction with EPA Method 3545 and quantifying with EPA Method 8270C (GC/MS).

UCS was measured using a Geo-Con Model 16-T0163 pocket penetrometer (Geebung, Queensland, Australia). The UCS results in this paper represent the arithmetic mean of 6 individual measurements.

### **Amendment Testing**

One L aliquots of homogenized soil were used for all the experiments with PAC, CaO, OPC, and CCFA. The amendments were thoroughly mixed into the soil samples by hand in 3 L stainless steel bowls. Tap water was used to increase the water content of the soils and was mixed into the soil before the amendments were added. Doses of the additives were based on the mass of each amendment per mass of dry soil. After mixing, the amended samples were stored in 1 L amber glass bottles with screw tops to prevent

VOC stripping and were cured at 15°C. The bottles were only opened to take sub-samples of soil for VOC and SPLP-VOC analyses, and to measure UCS by inserting the pocket penetrometer.



## **RESULTS AND DISCUSSION**

### **The Properties of the Test Soils**

Table 1 lists the properties measured in the four contaminated soils after being homogenized. Except for the particle size distributions, all measurements were made on six sub-samples of the homogenized soils. The arithmetic means  $\pm$  the standard deviations are listed for multiple measurements. Note that the standard deviations for the contaminant analyses were all within 10% of the mean concentration, which demonstrates that the soils were well homogenized. Individual concentrations of BTEX and naphthalene are listed and the sum is the concentration of total VOCs. The discussion below will be limited to total VOC concentrations. The concentrations of total PAHs in the homogenized soils are listed in Table 1 to include all the organic contaminants in the test soils, but PAHs concentrations will not be included in the discussion below.

The four soils were selected to allow S/S testing on soils with a variety of particle size distributions, soil organic matter (SOM) contents, and contamination levels. Soils 1 and 2 are fine-grained, and have SOM contents near 5%. Soils 3 and 4 are coarse-grained and have SOM contents below detection. Soils 1 and 3 have relatively low concentrations of total VOCs and PAHs, whereas Soils 2 and 4 are more heavily contaminated. The pH is near neutral in all four soils. The background water content in Soils 1 and 2 is more than twice the values measured in Soils 3 and 4, because fine-grained soils retain more water than coarse-grained soils. The background UCS is near 60 kPa in Soils 1 and 2,

whereas as Soils 3 and 4 have zero UCS. The background UCS measurements in Table 1 are consistent with values reported for similar soil types (Reddy and Sastri, 2002).

**Table 1. Properties measured in four homogenized soils before treatment.**

<i>Analyte</i>	<i>Soil 1</i>	<i>Soil 2</i>	<i>Soil 3</i>	<i>Soil 4</i>
Clay (%)	30	27	3	2
Silt (%)	31	35	10	9
Sand (%)	39	38	87	89
SOM (%)	5.4 ± 0.9*	4.7 ± 0.7	<0.1	<0.1
pH	7.2 ± 0.6	6.9 ± 0.5	7.4 ± 0.4	6.7 ± 0.5
UCS (kPa)	63.7 ± 5.9	59.3 ± 5.1	0	0
Water content (%)	13.1 ± 0.8	12.6 ± 0.9	6.1 ± 0.4	5.6 ± 0.5
Benzene (mg/kg)	320 ± 24	5368 ± 422	275 ± 22	1892 ± 154
Toluene (mg/kg)	644 ± 57	2972 ± 171	305 ± 28	1568 ± 130
Ethylbenzene (mg/kg)	1206 ± 94	4541 ± 389	418 ± 35	2150 ± 173
Total Xylenes (mg/kg)	1049 ± 78	3859 ± 270	518 ± 39	2527 ± 222
BTEX (mg/kg)	3219 ± 250	16740 ± 1329	1516 ± 126	8137 ± 595
Naphthalene (mg/kg)	1971 ± 138	5667 ± 432	1094 ± 94	3772 ± 287
Total VOCs (mg/kg)	5190 ± 395	22407 ± 1904	2610 ± 150	11909 ± 940
Total PAHs (mg/kg)	26330 ± 2059	104650 ± 7691	19720 ± 1348	54830 ± 400

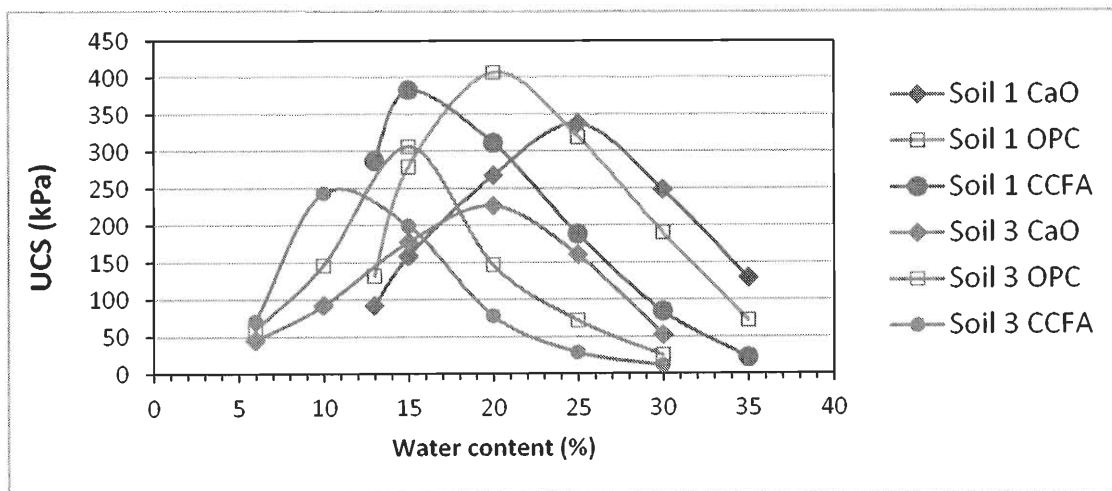
\*Arithmetic mean ± standard deviation for 6 samples.

### **Optimal Water Content for Unconfined Compressive Strength**

PAC does not absorb water or change UCS. However, CaO-containing cementing agents do both. The UCS achieved with cement-based S/S is highly dependent on the water content of the soil (USEPA 2009; ITRC 2011). In order to evaluate PAC preconditioning at water contents that would achieve maximum UCS, initial studies were done to determine the optimal water content for UCS with the three cements. Each of the 4 test soils were amended with 5% CaO, 5% OPC, and 5% CCFA at different water contents. The lowest water content tested in each soil was the background value (see

Table 1). Water contents were increased in 5% intervals up to a maximum of 30% for the sandy soils (Soils 3 and 4) and to 40% for the two fine-grained soils (Soils 1 and 2). The UCS was measured after a 28-day cure time for each water content.

Figure 1 illustrates the variations in UCS with water content for Soil 1 and Soil 3, and shows that the water content of the soils has a significant impact on UCS for all three cements tested. It is also clear from Figure 1 that the optimal water content was lowest with CCFA and highest with CaO (quicklime). This general pattern is predictable and can be explained by CaO content of the cements. CaO reacts with water to form  $\text{Ca(OH)}_2$ , which consumes water. The quicklime used in these studies was 95% CaO while the CaO content of OPC and CCFA are approximately 65% and 25%, respectively (Shehata et al., 1999). The drying effect of CaO makes quicklime preferable for stabilization of sediments and waste streams with high water content.



**Figure 1. Variations in UCS with water content on samples of Soil 1 and Soil 3 treated with 5% doses of the three cements tested. Note, in both soils the optimal water content was greatest for quicklime (CaO) and lowest for CCFA.**

Table 2 lists the optimal water content for UCS in the soils with each cementing agent. The optimal water contents listed in Table 2 are consistent with those reported in the S/S literature for other coarse-grained and fine-grained soils (Horpibulsuk et al., 2004; Horpibulsuk et al., 2009; Horpibulsuk et al., 2010). In each soil the optimal water content was highest for CaO (quicklime) and lowest for CCFA, due to the differences in CaO content. The optimal water contents for any cement mixture were higher in the two fine-grained soils (Soils 1 and 2) than in the two coarse-grained soils (Soils 3 and 4). This observation is common in S/S (Horpibulsuk et al., 2004; Horpibulsuk et al., 2010). The reason is that fine-grained soils hold water under greater capillary forces than coarse-grained soils, making the water less available for reaction with CaO.

**Table 2. The optimal water content (in weight percent) determined for amendment of each soil with the three cements tested.**

<i>Cement</i>	<i>Soil 1</i>	<i>Soil 2</i>	<i>Soil 3</i>	<i>Soil 4</i>
CaO	25	25	20	20
OPC	20	20	15	15
CCFA	15	15	10	10

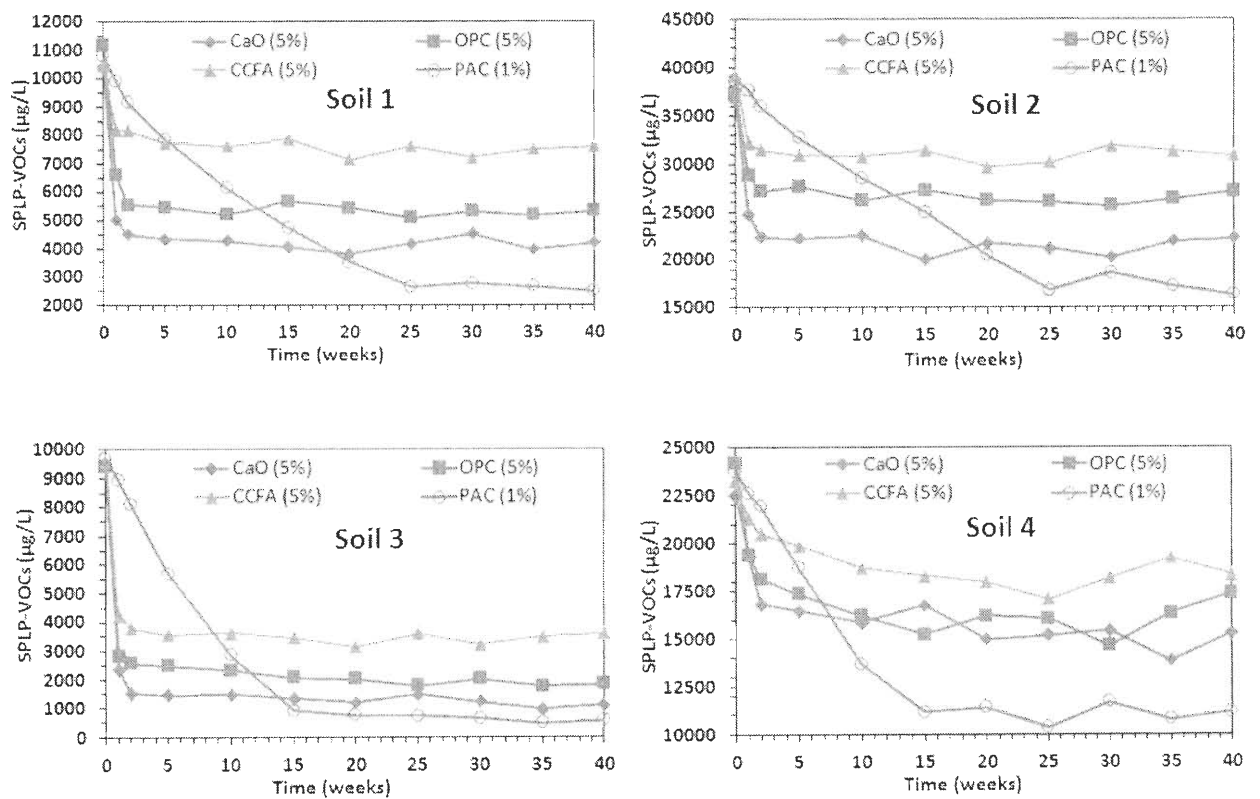
### **Synthetic Precipitation Leaching Procedure Changes with Time**

One of the goals of this study was to determine the effect of adding PAC on the leachability of VOCs, which were the most soluble contaminants in the test soils, and therefore most susceptible to leaching. To this end, VOC concentrations in SPLP extracts were monitored over a 40-week period in soil samples amended with 1% PAC. For comparison, SPLP-VOCs were also measured in soil samples amended with 5% CaO, 5% OPC, and 5% CCFA. The time profiles of SPLP-VOCs are shown in Figure 2. All of the

amendments reduced VOC leaching significantly. The reductions in SPLP-VOCs with CaO, OPC, and CCFA occurred mostly within the first week, after which concentrations remained nearly constant. The rapid decrease in SPLP can be attributed to stabilization by encapsulation of VOCs adsorbed to the soil. The hydration of CaO in cements coats all surfaces with  $\text{Ca(OH)}_2$ , which encapsulates adsorbed contaminants (USEPA 2009; ITRC 2011). The hydration reactions and resulting encapsulation take place immediately upon addition of cementing agents. In all four test soils, CaO resulted in the lowest final concentrations of SPLP-VOCs among the cements, and CCFA resulted in the highest concentrations. It is therefore reasonable to attribute the trend observed in SPLP reductions in Figure 2 to the CaO content of the cements. Quicklime (CaO) achieved the greatest encapsulation of VOCs due to its high CaO content. Similarly, CCFA showed the least degree of encapsulation because it has the lowest CaO content among the three cements.

Amendment with 1%PAC resulted in lower final SPLP-VOC concentrations than a 5% dose of any of the cements. However, the rate at which PAC reduced SPLP-VOCs was much lower than the reductions observed with the cements. SPLP-VOCs in PAC amended soils decreased in a linear fashion for between 15 to 25 weeks, after which an abrupt change occurred and concentrations remained relatively constant. The two fine-grained soils, Soils 1 and 2, required 25 days to achieve minimum SPLP-VOC concentrations, whereas this change occurred after only 15 days in the two coarse-grained soils (Soils 3 and 4). Although adsorption of VOCs onto PAC in the soils was not directly measured, it can be reasonably concluded that adsorption is the mechanism by which

PAC reduced the SPLP-VOC concentrations. This adsorption is irreversible under the conditions in SPLP extraction; otherwise the VOCs would be extracted and measured. It is not known why less time was required for SPLP-VOCs to attain their minimum value in the coarse-grained soils than the fine-grained soils. But, this can perhaps be attributed to slower desorption of VOCs from the clay- and silt-sized particles in Soils 1 and 2.



**Figure 2. VOC concentrations in SPLP extracts over a 40-week period for the four soils amended with 1% PAC, 5% CaO, 5% OPC, and 5% CCFA.**

Table 3 lists the concentrations of VOCs measured in the soils 40 weeks after amendment with 1% PAC, 5% CaO, 5% OPC, and 5% CCFA. The VOC concentrations are somewhat less than the background concentrations provided in Table 1. Also listed in

Table 3 is the percent recovery of the VOCs after 40 weeks (i.e., the percent of the total mass of BTEX and naphthalene remaining in the stabilized soils compared with the mass before the amendments were added). The percent recovery of the VOCs was greater than 90% for all amendment scenarios in all four soils, including PAC. Clearly, the solvent extraction required for measuring VOC concentrations in soil was able to recover BTEX and naphthalene from PAC that the SPLP extraction solution could not. The soil VOC concentrations in Table 3 allow a mass balance to be completed on these S/S reactions, and demonstrate that the reduced leachability of VOCs observed in Figure 2 was not due to volatile losses of VOCs, or other loss mechanisms.

**Table 3. Concentrations of total VOCs in the soils and the percent recovery of the background concentrations 40 weeks after amending with PAC, CaO, PC, and FA.**

<i>Parameter</i>	<i>Soil 1</i>	<i>Soil 2</i>	<i>Soil 3</i>	<i>Soil 4</i>
<i>PAC</i>				
Total VOCs (mg/kg)	4973	21658	2527	11391
% Recovery	95.8	96.7	96.8	95.7
<i>CaO</i>				
Total VOCs (mg/kg)	4652	20388	2379	10537
% Recovery	89.6	91.0	91.1	88.5
<i>OPC</i>				
Total VOCs (mg/kg)	4842	21185	2494	10870
% Recovery	93.3	94.6	95.6	91.3
<i>CCFA</i>				
Total VOCs (mg/kg)	4803	20835	2456	11031
% Recovery	92.5	93.0	94.1	92.7

No previous studies have been found in the literature on rates of adsorption of VOCs in contaminated soils onto PAC. Studies in contaminated sediments show PCBs and PAHs continue to adsorb onto PAC for periods of 6 to 7 months (Zimmerman et al.,

2004; Cho et al., 2007). Although adsorption onto PAC was not measured directly in these experiments, it can be concluded from the results in Figure 2 and Table 3 that during the first 15 to 25 weeks, VOCs preferentially adsorbed onto PAC surfaces and that this adsorption was responsible for reducing VOC leaching. After this period, no further reductions in VOC leaching were observed, either because the PAC surface became saturated and/or because some of VOCs were unable to desorb from the soils because of irreversible adsorption of onto minerals and SOM. It has also been shown that native organics adsorb onto PAC reducing its capacity to adsorb contaminants (Kwon and Pignatello, 2005; Cornelissen and Gustafsson, 2006; Brändli et al., 2008). This may have played a role in Soils 1 and 2, which had SOM contents near 5%. These results suggest that 15 to 25 weeks was a suitable time for preconditioning the four contaminated soils with PAC before addition of cementing agents.

#### **Powdered Activated Carbon Preconditioning vs. Simultaneous Addition of Powdered Activated Carbon and Cement**

Experiments were conducted to compare S/S treatment using simultaneous addition of cement and PAC vs. preconditioning soils with PAC before adding the cements. Samples of the four soils were amended with 1% PAC for 20 weeks prior to cement addition. After preconditioning, these samples were amended with 5% CaO, 5% OPC, and 5% CCFA. Measurements of UCS were made over an 8-week period, after which the soils were SPLP-extracted to measure total VOCs. The same UCS and SPLP-VOC measurements were made in soil samples amended simultaneously with 1% PAC and 5% of the three cements. Finally, a set of soil samples was amended with 5% doses



of the three cements alone (no PAC) for comparison with the other amendment scenarios.

Table 4 lists the SPLP-VOCs concentrations measured 8 weeks after cement addition.

Figure 3 shows time profiles of UCS measurements over the 8-week period for the OPC-amended samples with PAC preconditioning and simultaneous PAC and cement addition.

Table 5 lists the UCS measurements for all the cement amendment scenarios after 8 weeks of curing time.

**Table 4. Concentrations of total VOCs ( $\mu\text{g/L}$ ) in SPLP extracts with cement alone, simultaneous cement and PAC addition, and cement addition after 20 weeks of PAC preconditioning.**

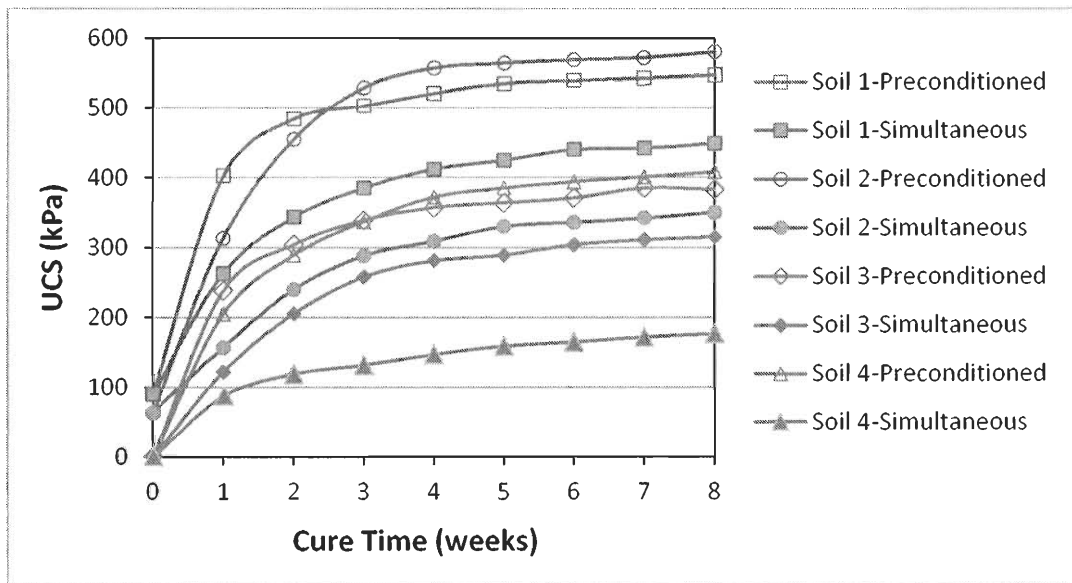
<i>Cement</i>	<i>Soil 1</i>	<i>Soil 2</i>	<i>Soil 3</i>	<i>Soil 4</i>
<i>Alone</i>				
CaO	4061	21443	1532	15426
OPC	4972	26297	1874	16233
CCFA	7383	29748	3575	18476
<i>Added simultaneously with PAC</i>				
CaO	3887	19558	1484	13992
OPC	4546	24838	1831	15451
CCFA	7044	28370	3294	16956
<i>Added 20 weeks after PAC</i>				
CaO	667	4073	239	3238
OPC	825	5117	287	3768
CCFA	954	6443	304	4229
<i>% Reduction with PAC preconditioning</i>				
CaO	82.8%	79.2%	83.9%	76.9%
OPC	81.9%	79.4%	84.3%	75.6%
CCFA	86.5%	77.3%	90.8%	75.1%

The results in Table 4 show that adding PAC simultaneously with each cement resulted in slightly lower SPLP-VOC concentrations than amendment with the cement alone. This is true for all the cements in all four soils. However, comparing the SPLP-

VOC concentrations for simultaneous PAC and cement addition vs. those for cement addition after PAC preconditioning show that PAC preconditioning achieved markedly lower SPLP-VOC concentrations. The percent reduction in VOC leaching with PAC preconditioning ranged between approximately 75% and 91% of the leaching observed with simultaneous addition of PAC and cement. The greatest percent reductions achieved with PAC preconditioning were observed for Soils 1 and 3; the two soils with the lowest initial contaminant concentrations (see Table 1).

The most likely mechanism for the enhanced reduction in leaching achieved with PAC preconditioning is that the VOCs adsorbed onto the PAC during 20 weeks of contact time was then encapsulated by hydration reactions after the cements were added. The adsorption of VOCs by PAC takes place relatively slowly over a period of 15-25 weeks (see Figure 2). Cement hydration reactions coat both soil and PAC surfaces within hours to days (USEPA 2009; ITRC 2011). Simultaneous addition of cement and PAC results in the coating of PAC surfaces with  $\text{Ca}(\text{OH})_2$  before they are able to adsorb a significant amount of VOCs. This renders the coated surfaces unavailable for adsorption and undermines the desired impact of PAC amendment. Arafat et al. (1999) showed that after 10 hours of cement hydration reactions, the mass of phenol adsorbed by PAC was reduced to 4% of the mass adsorbed on PAC not coated by cement. This study also demonstrated that when phenol was allowed to adsorb onto PAC before cement addition, the amount of phenol that desorbed from the PAC after cement addition was less than 2% of the amount that desorbed from PAC not treated with cement. The results of these studies clearly show that simultaneous addition of PAC with cement in the four soils

tested did not allow sufficient time for PAC to adsorb VOCs. In fact, simultaneous addition of cement with PAC resulted in very modest improvements relative to adding cement alone. These results call into question the efficacy of adding PAC at the same time as cement.



**Figure 3. UCS measurements over 8 weeks made in the four soils amended with 5% OPC after 20 weeks of PAC preconditioning vs. simultaneous addition of cement and PAC.**

The results in Figure 3 and Table 5 show that UCS was also enhanced by PAC preconditioning. Time profiles of UCS measurements in OPC-amended soils showed PAC preconditioning improved the rates of increase in UCS and significantly increased the final UCS achieved after 8 weeks of cure time. Time profiles of UCS with the other cements showed a similar pattern. Table 5 lists UCS measurements after 8 weeks for all the cement amendment scenarios, including adding cement alone. Simultaneous addition of the cements with PAC resulted in UCS values that were slightly greater than adding

the cement alone, except for OPC amendment in Soil 4. However, PAC preconditioning resulted in significantly higher UCS measurements than did simultaneous addition of PAC and cement. The percent increase achieved with PAC preconditioning vs. simultaneous addition is listed at the bottom of Table 5, and the numbers show that PAC preconditioning enhanced UCS between approximately 20% and 150% relative to simultaneous addition. The greatest UCS enhancements resulting from PAC preconditioning were observed in Soils 2 and 4, which had the highest initial contaminant concentrations (see Table 1). Increased UCS with PAC preconditioning can be attributed to the time allowed for PAC to adsorb BTEX, naphthalene and other PAHs in the soils.

**Table 5. UCS measurements (kPa) with cement alone, simultaneous cement and PAC addition, and cement addition after 20 weeks of PAC preconditioning. Also listed are the percent increases in UCS resulting from PAC preconditioning.**

<i>Cement</i>	<i>Soil 1</i>	<i>Soil 2</i>	<i>Soil 3</i>	<i>Soil 4</i>
<i>Alone</i>				
CaO	246	178	178	87
OPC	439	336	303	182
CCFA	442	369	298	164
<i>Added simultaneously with PAC</i>				
CaO	336	271	233	139
OPC	449	350	315	177
CCFA	429	372	304	169
<i>Added 20 weeks after PAC</i>				
CaO	468	452	312	318
OPC	548	581	383	408
CCFA	559	593	392	419
<i>% Increase resulting from PAC Preconditioning</i>				
CaO	39%	67%	34%	129%
OPC	22%	66%	22%	131%
CCFA	30%	59%	29%	148%

Petroleum hydrocarbons are known to retard cement hydration reactions, reduce the final strength, and increase the porosity of soils and sludges amended with cement.

Hydrocarbons and other organics interference with cement hydration by adsorbing onto incipient cement surfaces (Conner, 1990; Means et al., 1995; Zain et al., 2010; Karamalidis and Voudrias, 2007) and complex aluminate, ferrite and silicate, which delaying the formation of hydration products (Jones, 1990).

### **Summary**

Amending the four test soils with 1% PAC over a period of 15 to 25 weeks reduced the leaching of BTEX and naphthalene (VOCs) measured with the synthetic precipitation leaching protocol (SPLP), after which no further reduction was observed. Allowing a 20-week PAC preconditioning time in the four test soils significantly enhanced the ability of added quicklime, Portland cement, and Class C fly ash to reduce contaminant leaching and to increase unconfined compressive strength compared with simultaneous addition of PAC. Adding PAC and cement at the same time showed only modest improvements in leaching and strength compared with adding cement without PAC.

### **Conclusion**

A time period on the order of months is required for PAC to adsorb VOCs in soils from MGP sites with aged contamination. When combining PAC with CaO-based cementing agents in stabilization and solidification (S/S) or in situ stabilization (ISS)

applications, adding the cements before allowing a sufficient PAC preconditioning time can severely limit the adsorption of contaminants onto PAC by coating the PAC surfaces with  $\text{Ca(OH)}_2$  and inhibiting contaminant adsorption. PAC preconditioning times can be determined by measuring the reduction in leaching of the contaminants of concern over time in samples amended with PAC. The optimal PAC preconditioning time can be considered to be the time when contaminant leaching ceases to be reduced by the PAC.

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## APPENDIX

Variations in UCS with water content on samples of Soil 1 and Soil 3 treated with 5% doses of the three cements tested.

UCS vs. WC	Water Content (WC) (%)	Soil 1 CaO	Soil 1 OPC	Soil 1 CCFA	Soil 3 CaO	Soil 3 OPC	Soil 3 CCFA
	6				45	60	71
	10				92	146	243
	13	92	132	287			
	15	158	279	382	177	306	199
	20	267	406	311	226	147	78
	25	337	319	188	160	72	29
	30	248	190	84	52	25	11
	35	129	72	22			

Data for UCS measurements over 8 weeks made in the four soils amended with 5% OPC after 20 weeks of PAC preconditioning vs. simultaneous addition of cement and PAC.

OPC Only	Time (weeks)	Soil 1 Pre conditioned	Soil 1- Simultaneous	Soil 2 Pre conditioned	Soil 2- Simultaneous	Soil 3 Pre conditioned	Soil 3- Simultaneous	Soil 4 Pre conditioned	Soil 4- Simultaneous
	0	90	90	64	64	0	0	0	0
	1	402	263	313	157	238	122	205	87
	2	484	343	455	240	304	205	289	119
	3	503	385	529	288	339	258	337	132
	4	521	412	557	309	357	281	372	147
	5	535	425	564	330	364	289	385	159
	6	539	440	569	336	371	304	394	165
	7	543	442	572	342	385	311	401	172
	8	548	449	581	350	383	315	408	177

Data for VOC concentrations in SPLP extracts over a 40-week period for the four soils amended with 1% PAC, 5% CaO, 5% OPC, and 5% CCFA.

<b>Soil 1</b>	<b>Time (weeks)</b>	<b>CaO (5%)</b>	<b>OPC (5%)</b>	<b>CCFA (5%)</b>	<b>PAC (1%)</b>
	0	10400	11200	10500	10800
	1	5070	6637	8230	9930
	2	4540	5587	8190	9180
	5	4360	5490	7750	7895
	10	4290	5220	7630	6150
	15	4060	5670	7850	4740
	20	3820	5430	7140	3540
	25	4190	5100	7600	2660
	30	4540	5320	7200	2790
	35	3980	5170	7490	2683
	40	4210	5330	7590	2480
				ug sorbed	<b>8320</b>
				g/kg	2.6

<b>Soil 2</b>	<b>Time (weeks)</b>	<b>CaO (5%)</b>	<b>OPC (5%)</b>	<b>CCFA (5%)</b>	<b>PAC (1%)</b>
	0	36700	37200	39200	38600
	1	24840	28850	32230	37660
	2	22400	27140	31430	35940
	5	22250	27600	30890	32730
	10	22560	26200	30700	28480
	15	20060	27230	31300	24980
	20	21770	26190	29560	20430
	25	21230	26050	30060	16890
	30	20330	25630	31770	18700
	35	21980	26330	31230	17300
	40	22250	27050	30790	16450
				ug sorbed	<b>22150</b>
				g/kg	6.921875

<b>Soil 3</b>	Time (weeks)	CaO (5%)	OPC (5%)	CCFA (5%)	PAC (1%)
	0	9500	9400	9600	9700
	1	2370	2837	4230	8950
	2	1540	2587	3790	8130
	5	1460	2490	3550	5700
	10	1490	2320	3630	2860
	15	1360	2070	3450	940
	20	1220	2030	3140	770
	25	1490	1800	3600	740
	30	1240	2020	3200	650
	35	980	1770	3490	500
	40	1110	1830	3590	580
				ug sorbed	<b>9120</b>
				g/kg	2.85

<b>Soil 4</b>	Time (weeks)	CaO (5%)	OPC (5%)	CCFA (5%)	PAC (1%)
	0	22530	24200	23300	23790
	1	19340	19400	21230	22660
	2	16830	18140	20490	21940
	5	16480	17330	19890	18730
	10	15850	16250	18700	13680
	15	16770	15230	18300	11180
	20	14990	16190	17960	11430
	25	15200	16050	17060	10390
	30	15440	14630	18170	11700
	35	13860	16330	19230	10800
	40	15300	17380	18340	11180
				ug sorbed	<b>12610</b>
				g/kg	3.940625