LEACHING BEHAVIOR OF PETROLEUM CONTAMINATED SOILS STABILIZED WITH HIGH CARBON CONTENT FLY ASH

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ABSTRACT:

Utilization of recycled materials as a substitute for natural soils in engineering applications such as highway construction is an emerging application area. A research study was conducted to investigate the stabilization of petroleum-contaminated soils (PCSs) using another recycled material, high carbon content fly ash (HCCFA), and evaluate the feasibility of using the final product in highway embankment construction. A battery of laboratory tests was conducted to evaluate the environmental suitability of stabilized PCSs. The test program included batch adsorption and long-term column leaching tests. Naphthalene and o-xylene, and a tertiary model non-aqueous phase liquid were used as the pollutants in batch sorption and column tests, respectively. Batch sorption tests demonstrated a nonlinear sorption behavior for naphthalene and o-xylene onto HCCFA. Column leaching test results indicated that the naphthalene and o-xylene concentrations in the effluents collected from the stabilized PCSs columns were lower than those collected from the control columns. These laboratory test data suggest that HCCFA can be effective in remediation of PCSs; however, the level of petroleum contamination has a significant effect on the leaching properties.

INTRODUCTION

Leakage of petroleum products from improperly assembled and poorly maintained underground storage tanks (USTs) has been considered as the major source for introduction of petroleum contamination into the subsurface. According to U.S. Environmental Protection Agency (USEPA), state agencies are spending more than $1 billion annually for the clean-up of 26,000 leakage sites (USEPA 2004). In spite of the strict regulatory measures, nearly 30 % of the 700,000 USTs around the country are not equipped with leak detection and corrosion protection systems and, thus, have become a continuous source for petroleum hydrocarbon release (USEPA 2004). Petroleum products contain significant quantities of naphthalene, pyrene, benzene, toluene, and xylenes, which are listed as hazardous waste compounds by the U.S. EPA. Accordingly, remediation of petroleum-contaminated soils has increasingly been dealt with over the past several years. As a result, ex-situ treatment methods such as landspreading, thermal treatment and bioremediation, as well as in-situ
methods such as bioventing and soil vapor excavation are now being implemented (Kamnikar 2001). The difficulty encountered in remediating the petroleum-contaminated soils (PCSs) led researchers to look for alternative approaches, such as soil stabilization by addition of a binder to adsorb the pollutant(s) while maintaining the good engineering properties of the soil. Materials stabilized in such a manner could be reused in highway construction, and the most common application is their use as a borrow fill material.

Approximately 90% of the coal used in United States is burned to produce electricity. As a result, the power plants produce vast quantities of coal combustion by-products (CCBs) that present another environmental challenge. One of these CCBs, Class F fly ash, is generated in large quantities and occasionally contains significant amounts of unburned carbon (i.e., high loss on ignition). For instance, twelve power plants in Maryland that use the cyclone process to burn coal produce about 600,000 tons of high-carbon content Class F fly ash each year. This fly ash has a carbon content of 12-20% and has no value as a concrete additive, as the maximum carbon content allowed in the ASTM C618 is 6%. Recent data indicate that approximately 68% of this high-carbon content fly ash (HCCFA) is placed in landfills, thereby consuming valuable land space and creating the potential to impact aquatic resources (Petzrick 2001). Similar problems are experienced by other utilities in the United States, and the amount of HCCFA produced by power plants in the United States is expected to increase significantly in the near future due to the common use of low nitrogen oxides (NOx) burners in recent years (Hodges and Keating 1999). Therefore Class F fly ash represents an abundant solid waste for which there is a significant need to find a use.

Large-volume use of fly ash in highway applications can aid in solving this waste disposal problem as well as providing economic savings to users by replacing more costly raw materials. For example, recent investigations indicate that petroleum hydrocarbons in the soil will inhibit the cementitious reactions between the PCS and the stabilizing agent, and the pollutant will eventually emanate from the stabilized block as a result of leakage or chemical diffusion. One way to retard or limit the movement of the petroleum hydrocarbons is to provide a sorptive agent that sorbs these pollutants as they move through the soil. The organic carbon in Class F fly ashes is ideally suited for this purpose, as its adsorption of various organic contaminants such as phenols, dyes, herbicides, and polychlorinated biphenyls has been documented (Akkerman and Zardkoohi 1996, Janos et al. 2003, Konstantinou and Albanis 2000, Nollet et al. 2003). Attempts have also been made to stabilize petroleum contaminated wastes using Class F fly ash for their potential use in highway environments; however, this previous work generally included creating a monolithic medium and encapsulating the petroleum contaminants rather than adsorbing them (Tuncan et al. 2000).

The objectives of the current study were: (1) to evaluate the capacity of HCCFA in remediating petroleum residues, and (2) to investigate the leaching performance of stabilized soils originally contaminated by petroleum residues. To meet these objectives, simulated petroleum-contaminated soils were stabilized with a high carbon content Class F fly ash. A series of laboratory tests that included batch
adsorption and column leaching tests were performed on the fly ash and soil-fly ash mixtures to evaluate the effectiveness of the stabilization process.

**MATERIALS**

To simulate petroleum contaminated soils, a borrow material that is commonly used in embankment construction in Maryland was spiked with petroleum residues. The borrow material was classified as clayey sand (SC) according to the Unified Soil Classification System (USCS) and A-2-4 according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System. Grain size analyses indicated that the soil had approximately 34% particles passing through the U.S. No. 200 sieve, and 10% particles that were smaller than 2 µm in diameter. The standard Proctor compaction tests conducted following the procedures outlined in the ASTM D 698 indicated that the maximum dry unit weight and optimum water content of the soil were 20.1 kN/m³ and 10%, respectively. Based on an analysis performed using a SHIMADZU 500 carbon analyzer, the borrow material had a total organic content (TOC) of about 0.5% by weight. The cation exchange capacity (CEC) and pH of the material were 2.9 meq/100g and 7.2, respectively.

The fly ash used in the current study was obtained from the Brandon Shores Power Plant located in Baltimore, Maryland. It was produced as a result of burning pulverized bituminous coal and classified as Class F fly ash according to ASTM C 610. Atterberg limit tests conducted on the fly ash indicated that material did not exhibit any plasticity. Approximately 92% of the particles were finer than the U.S. No. 200 sieve size. Physicochemical properties for the fly ash are summarized in Table 1.

**TABLE 1 The physiochemical properties of the fly ash used in the current study**

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Chemical Constituents</th>
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<tbody>
<tr>
<td>D₁₀ (mm)</td>
<td>SiO₂ (%)</td>
</tr>
<tr>
<td>D₃₀ (mm)</td>
<td>Al₂O₃ (%)</td>
</tr>
<tr>
<td>D₆₀ (mm)</td>
<td>Fe₂O₃ (%)</td>
</tr>
<tr>
<td>Fines content (%)</td>
<td>TiO₂ (%)</td>
</tr>
<tr>
<td>Cu</td>
<td>CaO (%)</td>
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<tr>
<td>Ce</td>
<td>MgO (%)</td>
</tr>
<tr>
<td>pH</td>
<td>K₂O (%)</td>
</tr>
<tr>
<td>SSA(¹)(m²/g)</td>
<td>Na₂O (%)</td>
</tr>
<tr>
<td>TOC(²)(%)</td>
<td>SO₃ (%)</td>
</tr>
<tr>
<td>LOI(³)(%)</td>
<td>LOI (%)</td>
</tr>
</tbody>
</table>

Notes: (1) SSA= Specific surface area (2) TOC= Total organic content (3) LOI=Loss on ignition, i.e., unburned carbon content

**Contaminants**

Petroleum products such as diesel fuel have very complex nature and typically consist of more than 100 compounds (Lee et al. 1992). The chemical composition can be variable and is highly dependent on the source of the crude oil and the degree of
chemical modification. This chemical complexity makes analysis challenging, therefore, naphthalene, a polycyclic aromatic hydrocarbon (PAH), and o-xylene, a compound from the benzene-toluene-ethylbenzene-xylene (BTEX) group, were selected as the target model contaminants for the batch adsorption tests. A PAH was chosen as one of the target compounds in this study primarily for three reasons. First, aromatic hydrocarbons, including PAHs, represent a significant fraction of the hydrocarbons in diesel fuels (Lee et al., 1992). Second, PAHs have relatively low solubility, high sorption, and low volatility which facilitate sorption and leaching studies. Furthermore, naphthalene is one of the pollutants listed on the U.S. EPA priority list. O-xylene was included in the testing because the BTEX group compounds are commonly encountered subsurface pollutants and are also included in the U.S. EPA’s priority pollutant list.

Petroleum contamination was simulated with a tertiary, model nonaqueous phase liquid (NAPL) during the column leaching tests. The model NAPL consisted of naphthalene and o-xylene dissolved in dodecane. These three compounds represented the PAH, BTEX, and n-alkane groups, respectively. The NAPL mixture was designed to give nominal aqueous equilibrium concentrations of 5 mg/L and 10 mg/L for naphthalene and o-xylene, respectively. The former value is higher than the reported aqueous equilibrium concentration of naphthalene in diesel fuel (Lee et al., 1992), but was selected mainly due to analytical and experimental constraints. The aqueous solubilities of naphthalene, o-xylene and dodecane at 25°C were 31 mg/L, 170 mg/L and 0.0037 mg/L, respectively.

**METHODS**

**Laboratory Preparation of Contaminated Soils**

During the laboratory preparation of the column leaching specimens, borrow material was spiked with tertiary NAPL at levels of 2% and 0.5% by weight. These percentages were selected because soils exhibiting higher concentrations, e.g., greater than 3% by weight, are accepted as hazardous waste and are generally disposed of in hazardous waste landfills (Kamnikar, 2001). The model NAPL was introduced into the borrow material (soil) by following the “spiking” procedure of Doick et al. (2003), in order to prepare homogenous and reproducible soil-contaminant mixtures. As part of the methodology, 3500 g of soil (borrow material) was hydrated by adding 3% water by dry weight. A 700 g sample of this hydrated soil was then placed into a stainless steel bowl and appropriate mass of NAPL was added subsequently. All mixtures were blended by hand using a stainless steel spoon for 90 seconds. The remaining 2800 g of hydrated soil was divided into four aliquots equal in weight. Each aliquot was spiked and blended for about 90 seconds. The spiked soil samples were then placed into 2 L amber glass jars with no headspace.

Previous research has indicated that the contact time between soil and contaminant has a significant effect on the laboratory test results. This effect of contact time is often referred to as aging and is defined as the diffusion of organic contaminants into the micro- and nano-scale pores of the soil. As a result of aging, physical entrapment and partitioning into soil organic matter or its organic carbon
fraction occurs (Doick et al. 2003). The NAPL-spiked borrow materials were aged before fly ash addition at 4 °C for four-week(s), following the suggestions of Reid et al. (1998) and Northcott and Jones (2000). The fly ash was added to the aged NAPL-spiked specimens at ratios of 5 and 10% by weight. These ratios fall in the range of those used in previous studies (Tuncan 2000). The fly ash–amended contaminated soil specimens (i.e., stabilized soils) were then placed in amber glass containers and cured at 4 °C for 2 days to allow for equilibrium to occur before starting the tests.

**Batch Adsorption Tests**

The batch adsorption technique is one of the most commonly used laboratory test methods for determining adsorption isotherms and estimating partitioning coefficients of geologic materials (USEPA 1999). This test method is generally listed under the category of screening tests and is applicable to a large group of pollutants and geomaterials (Kim et al. 2001, Headley et al. 2001, Lee and Benson 2004). In the current study, batch adsorption tests were conducted on the borrow material and fly ash by following the standard procedures outlined in ASTM D 5285. A critical step in this procedure is to determine the solid-to-solution ratio for the materials tested, i.e., the ratio of the weight of the solid to the volume of the test solution (USEPA 1999). ASTM D 5285 recommends a solid-to-solution ratio that would result in 20 to 80% sorption of the contaminant. After a series of preliminary tests conducted at different solid-to-solution ratios, a mass ratio of 1/120 was selected for fly ash which resulted in 50% sorption of naphthalene and o-xylene onto the ash. Batch kinetic test results suggested an equilibrium time of 24 hrs was appropriate for testing of both naphthalene and o-xylene. The observed trends are meaningful as the initial sorption generally occurs by hydrogen bonding and van der Waals forces, and is expected to occur instantaneously upon contact of the nonpolar organic chemical with fly ash (Semple et al. 2003).

For determination of the adsorption capacity of fly ash, three 0.5 g-fly ash specimens were placed in 60 mL centrifuge tubes, after which the contaminant solution prepared 24 hrs before the test was added to the tubes so as to leave no headspace. Two control specimens (containing contaminant solution only) were prepared as well. The centrifuge tubes were sealed with Teflon caps and were rotated for 24 hrs using an end-over-end rotator. The agitated samples were then separated by centrifuge at 3000 rpm for 15 min and the supernatant was transferred to a clean vial for analysis.

**Column Leaching Tests**

Soils contaminated with petroleum hydrocarbons can be remediated by using binders with significant sorptive capacity; however, the long-term leaching of undesired constituents from the stabilized end-product should be studied. Column tests have been used to determine the transport of PAH’s through compacted clay liners (Kim et al. 2001), and TCE and pesticides through foundry sand (Lee et al. 2004, Lee and Benson 2004), and similar techniques were selected for this study.
Column leaching tests were performed in this study by applying a continuous flow of deionized water through a solid matrix (petroleum contaminated soil herein). To prepare the solid matrix, the borrow material and borrow material/fly ash mixture specimens were spiked with model 0.5% or 2% by weight NAPL, as discussed above, before compacting them in the stainless steel column using the standard Proctor effort. The resulting diameter and height of the test specimen were 101.6 mm and 114.3 mm, respectively. The height of the stainless steel column was 177.8 mm, with the upper 63.5 mm-section of the column used as an influent reservoir. A supply (influent) tank was placed above the columns, and used to apply a hydraulic gradient of 4 to 5, which was selected based on the desired flow rate. The specimen was underlined by a glass fiber filter and a stainless steel screen. An effluent reservoir was located between the bottom of the specimen and lower base of the column. The effluent leaving the specimen was collected in Teflon® effluent bags. All the tubings were Teflon® and the fittings were Teflon® or brass. Inert (nitrile) o-rings were used to provide isolation for the seal between the column and upper and lower plates. Using a sampling port attached to the base of column, the effluent was also monitored daily for the first two months of the tests. Due to relatively stabilized flow rates, weekly monitoring was adopted after two months. Tests were terminated after ensuring the stabilization of the flow and steady-state concentration of the contaminants. As part of the current research study, a total of seven column leaching tests were conducted. Three of the columns included contaminated borrow material only and were noted as the control column. The remaining columns included 5% or 10% Brandon Shores fly ash by weight.

**Analytical Methods**

A Shimadzu 5301 Fluorescence Spectrophotometer was generally utilized to measure the final contaminant concentrations in the fly ash specimens from the batch adsorption tests. The excitation and emission wavelengths for naphthalene and o-xylene in aqueous solution were 273 and 336 nm, and 267 and 289 nm, respectively. Preliminary investigations indicated that the detection limit of the equipment for naphthalene and o-xylene were 0.0165 mg/L and 1.273 mg/L, respectively. Thus, the specimens with any of the tested initial naphthalene concentration and o-xylene concentrations greater than 2 mg/L could be accurately determined using the spectrophotometer.

Due to relatively high detection limits of o-xylene in fluorescence method, low concentrations (<2mg/L) of o-xylene in the batch adsorption tests were determined using a gas chromatograph (GC). In addition, the concentrations of the contaminants from the column leaching tests were also measured using the GC. Before measuring the concentrations, a liquid-liquid extraction procedure was performed using hexane, with acenaphthene as an internal standard. Analysis of the contaminants in the hexane extracts was performed using a Hewlett Packard (HP) Model 6980 gas chromatograph equipped with a flame ionization detector (FID). The GC analysis of o-xylene, naphthalene, dodecane and acenaphthene were performed as follows: the oven temperature was kept at 40 °C for 4 minutes after injection of 1 µL.
of extracted sample in hexane, and then the temperature was increased 40 °C/min up to 220 °C.

RESULTS

Batch Adsorption Tests on HCCFA and Borrow Material

In analyzing batch adsorption test data, it is common to relate the mass of sorbed contaminant per mass of sorbent \( q_i \) (mg/kg) to the final aqueous equilibrium concentration of the contaminant in solution \( C_f \) (mg/L) by using sorption isotherm models. The adsorption test data in this study were analyzed using a nonlinear regression analysis. Specifically, isotherm models were fit to the collected experimental data using a model calibration software, ISOFIT, which employs an equal data-weighting scheme (Matott 2004). The best fit was determined through observing the highest value of \( R^2 \) and the lowest standard error of the regression. The best fit adsorption isotherm models are presented in Figure 1.

Based on the results of the nonlinear regression analysis, sorption of naphthalene to the Brandon Shores fly ash is best described by the Freundlich isotherm, as evidenced by the relatively high \( R^2 \) values and low standard errors of regression. Similarly, the Freundlich isotherm was found by Accordin-Day and Gschwend (2002) to provide best model fit to the experimental data during testing of sediments with PAHs. The equation used to describe the Freundlich isotherm is:

\[
q_i = K_F [C_f]^n
\]

where \( K_F \) is the Freundlich equilibrium isotherm constant (L/kg), \( n \) is a dimensionless empirical constant that describes the nonlinear relationship between the organic contaminant and the sorbent (fly ash), and \( C_f \) is the final concentration of naphthalene (mg/L). These parameters are directly related to the properties of the surfaces that are available for adsorption. A Freundlich isotherm essentially indicates that the interaction between the naphthalene and fly ash exhibits a nonlinear behavior, and the low “\( n \)” value of 0.2335 for naphthalene adsorption indicates a strong nonlinearity. Such nonlinearity was also reported by Luthy et al. (1997) during sorption testing of natural soils and sediments. The highly heterogeneous structure and uneven distribution of the unburned carbon present in the fly ash (i.e., presence of different carbon forms at different amounts in a given fly ash) may be responsible for this observed behavior.

The data for Brandon Shores fly ash with o-xylene suggested a Langmuir type isotherm is the best model for describing the data (Figure 1). The Langmuir sorption isotherm is generally the preferred model for describing the sorption of chemicals on a solid surface that contains a fixed number of identical active sorption sites. The equation for Langmuir isotherm is:
FIG. 1 Adsorption isotherms of naphthalene and \textit{o}-xylene and HCCFA (s=standard error of regression analysis)

\[
q_i = \frac{Q_{max}K_L C_f}{1+K_L C_f}
\]

where \( q_i \) is the sorbed concentration (mg/kg), \( Q_{max} \) is the sorption capacity of particular solid (mg/kg), \( K_L \) is the Langmuir isotherm coefficient (L/kg) and \( C_f \) is the equilibrium (final) concentration (mg/L). One conceptual difficulty associated with the Langmuir isotherm is that, in some cases, the estimated sorption capacity greatly exceeds the theoretically allowed monolayer coverage on solid surface (Xia and Ball 1999). Similar observations were made by Bartelt-Hunt et al. (2005) when benzene and \textit{o}-xylene were tested with organophilic clays. Organophilic clays are clayey soils modified with hydrophobic surfactants and, as a result, exhibit very high hydrophobic (sorptive) chemical structure. Even though the chemistry of sorption in organophilic clays and HCCFA are different, the trends in sorption are noteworthy.

A series of batch adsorption tests were also performed on the unmodified borrow material, using the same procedure used for the fly ash. The best fit isotherm model for the experimental data was a linear isotherm for both naphthalene and \textit{o}-xylene data (Figure 2). The partition coefficients for the linear isotherm were determined to be 27.45 L/kg and 20.43 L/kg for naphthalene and \textit{o}-xylene, respectively.
Column Leaching Tests

The concentrations of naphthalene and \( o \)-xylene were measured by collecting effluent samples from the seven test columns. Sample collection began once the full saturation of the column specimens occurred, which took about 8 to 10 days due to low hydraulic gradient applied during testing. The temporal variations in the measured \( o \)-xylene and naphthalene concentrations in the effluents collected from the 2\% NAPL contaminated columns are shown in Figure 3.

For both organic compounds, the concentrations measured in the control column are generally higher than the concentrations measured in the columns with fly ash-amended borrow material. The fluctuations in the concentrations observed in Figure 3 for the control and fly ash amended columns are attributed to the changes in the applied hydraulic head due to refilling of the influent tank. Such changes affected the average pore water velocity and, possibly in turn, the rates of mass transfer from sorbed of NAPL contaminants into aqueous phase. However, under the applied hydraulic gradients (4 to 5), mobilization of \( o \)-xylene and naphthalene from the borrow material (clayey sand) was expected to be extremely slow (Mercer and Cohen 1990). Hence, the fluctuations in the applied hydraulic gradient are believed to have a very limited effect on NAPL mobilization.

Nevertheless, the data in Figure 3 also reveal that there was a large initial release of \( o \)-xylene and naphthalene in the control columns. The initial concentrations were measured as 66.04 mg/L and 102.02 mg/L for \( o \)-xylene and naphthalene, respectively, before dropping to about 5 mg/L within 8 days, and are sufficiently high that they can only be explained as being due to an initial release of NAPL contamination. This explanation is consistent with the observation of dodecane in the column effluent. The low sorptive capacity of the borrow material may have caused
FIG. 3 O-xylene and naphthalene concentrations measured in the effluents collected from the 2% NAPL columns.

this effect. The HCCFA, on the other hand, apparently limited this NAPL release and immobilized the contaminants due to its high sorptive capacity. As a result, the initial concentrations from the fly ash-amended specimens are quite low as effluent compared to those measured in the effluent collected from the borrow material. The
concentrations of \( o \)-xylene and naphthalene in the first collected effluent samples were 4.17 mg/L and 1.58 mg/L, respectively, for the column with 10% fly ash, and 4.2 mg/L and 4.3 mg/L, respectively, for the column with 5% fly ash.

![Graph showing O-xylene and naphthalene concentrations](image)

**FIG. 4** \( o \)-xylene and naphthalene concentrations measured in the effluents collected from the 0.5 % NAPL columns.
The effluent concentrations of naphthalene and o-xylene for the 5% and 10% fly ash-amended columns contaminated with 0.5% NAPL loading are shown in Figure 4. One important effect of lowering the contamination level was that no initial NAPL release was observed in any of 0.5% NAPL columns, based on the low naphthalene and o-xylene concentrations and lack of dodecane observed in the effluent collected from the 0.5% NAPL columns (not shown herein). It should be noted that the two control columns are still running as stabilization of flow and concentration has not yet occurred. Figure 4 also shows that the naphthalene and o-xylene concentrations in the effluents collected from the 10% and 5% fly ash-amended columns were consistently lower than those collected from the control columns. These observations suggest that the addition of fly ash remediates the contaminated soil by immobilizing the organic pollutants and reducing their final concentrations in the effluent.

CONCLUSIONS

A laboratory study was conducted to remediate petroleum residues in soil using high-carbon content fly ash. A battery of laboratory tests that included batch-sorption and column leaching tests were performed on the mixtures to evaluate the effectiveness of the stabilization process. The results of the batch-scale adsorption tests conducted on the fly ash revealed that the ash had very good naphthalene and o-xylene sorption properties due to the presence of high carbon content in its structure. The adsorption behavior of fly ashes onto naphthalene and o-xylene is highly nonlinear probably due to heterogeneous structure and uneven distribution of the unburned carbon present in the fly ash.

Column leaching tests were performed on the fly ash stabilized specimens and borrow material originally contaminated with a synthetic NAPL. The results indicated that the naphthalene and o-xylene concentrations in the effluents collected from the fly ash stabilized specimens were lower than those collected from the control specimen (i.e., borrow material). Moreover, addition of fly ash apparently limited the initial release of the contaminants from the specimen, compared to a larger release observed in the control columns.

The findings indicate that the high-carbon content fly ash can be a good sorptive agent for remediation of petroleum contaminated soils due to its low cost and presence of high carbon content. However, caution should be exercised when extending these laboratory results to field conditions, because the level of contamination may have a significant effect on leaching properties.

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