

# **Report for 2005MD99B: Utilization of High Carbon Fly Ash to Remediate Groundwater-Summer Student Research**

## Publications

- There are no reported publications resulting from this project.

## Report Follows

# **Utilization of High Carbon Content Fly Ash as a Reactive Medium during the Remediation of NAPLs from Subsurface Waters**

**Summary Report**

**Submitted to:**

**Maryland Water Resources Center  
for the Summer Graduate Fellowship**

**Date: August 30, 2005**

**Mehmet M. Demirkan**

**Department of Civil and Environmental Engineering  
Geotechnical Engineering Program  
University of Maryland-College Park**

The primary goal of the proposed research was to investigate the fundamental factors affecting the reuse of fly ash as sorptive medium during groundwater

clean up. This re-use of fly ash has a potential for minimizing the movement of organic chemicals found in the soil and the groundwater. To achieve the objective, two tasks were conducted as part of this assessment: (1) evaluation of the sorption capacity of two different Maryland fly ashes in remediating the contaminated soils and contaminated groundwater, and (2) investigation of the leaching of chemicals from fly ash-soil mixed medium.

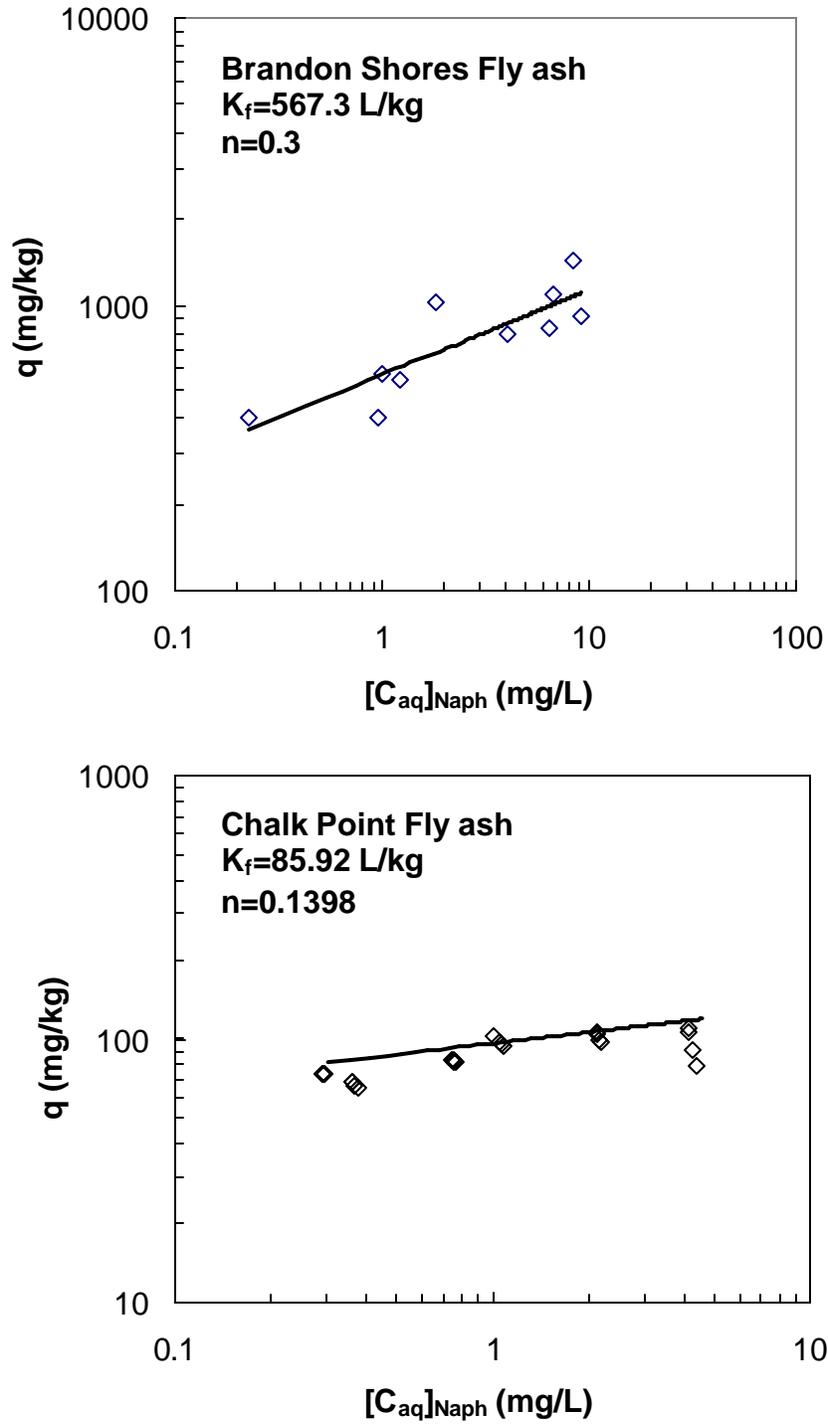
The batch adsorption technique was employed for determining adsorption isotherms and estimating partitioning coefficients of geologic materials. In the current study, batch adsorption tests were conducted on the borrow material and fly ash by following the standard procedures outlined in ASTM D5285. It was critical 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 naphthalene solution. 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 onto the ash. The fly ash and naphthalene solutions were equilibrated with end-over-end rotator shaker for 6, 12, 24 and 48 hrs and a series of batch kinetic tests were performed. The results suggested an equilibrium time of 24 hrs for future tests. These observations of a faster time for equilibrium for fly ash compared to borrow material (clayey sand) were consistent with current literature and indicated that the initial rapid sorption generally occurs by hydrogen bonding and van der Waals forces and is expected to occur instantaneously upon contact of naphthalene with fly ash. Batch adsorption tests were conducted on the Chalk Point and Brandon Shores fly ash, which has total carbon content of 2.9% and 18% respectively, to identify their naphthalene sorption characteristics.

Based on the literature and the experimental data, the Freundlich isotherm was selected to model adsorption behavior of the fly ash. The equation used to describe the isotherm is:

$$q_i = K_f [C_{aq}]_{NAPTH}^{(1/n)} \quad (1)$$

where  $q_i$  is the concentration sorbed onto the solid phase (mg/kg),  $[C_{aq}]_{NAPTH}$  is the concentration of naphthalene in aqueous solution after sorption (mg/L),  $K_f$  is Freundlich equilibrium isotherm constant (L/kg), and  $n$  is a dimensionless empirical constant that indicates a nonlinear relationship between the organic contaminant and the sorbent (fly ash). This phenomenon is directly related to the properties of the surfaces that are available for adsorption. The results shown in Figure 1 indicate that the Freundlich isotherm constant for Brandon Shores fly ash for naphthalene is 567.3 L/kg with a  $n$  value of 0.3. The same parameters are 85.92 L/kg and 0.14, respectively, for the Chalk Point fly ash. The high sorption capacity of the Brandon Shores fly ash is evident from Figure 1. The test results also indicate that the Chalk Point has sorptive capacity that is less

than Brandon Shores fly ash, accordingly related to the unburned carbon content.

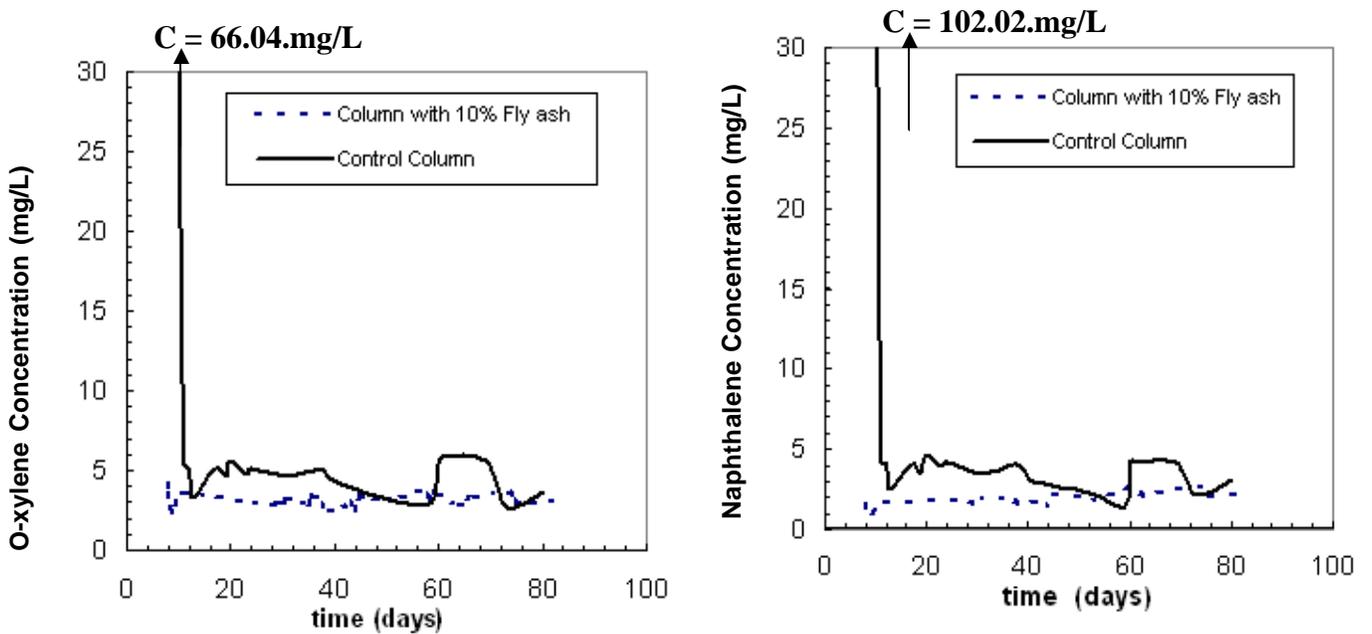


**FIGURE 1** Freundlich sorption isotherms for the Chalk Point and Brandon Shores Fly ash

Column leaching tests performed during Summer 2005 consisted of the continuous flow of liquid through a solid matrix (petroleum contaminated soil herein). Naphthalene and o-xylene concentrations were measured in the samples collected from the effluent sampling ports of the columns. The diameter and height of the test specimen were 101.6 mm and 114.3 mm, respectively. A clayey sand which is labeled as borrow material by the highway engineers, was used as main soil medium. The borrow material and borrow material/fly ash mixture specimens were spiked with model NAPL before compacting them using standard Proctor energy. One of the two columns included contaminated borrow material only and was noted as the control column. The other column included 10% fly ash. The height of the stainless steel column was 177.8 mm, and the upper 63.5 mm-section of the column was devoted to influent collection, i.e. used as an influent reservoir. A supply (influent) tank was placed above the columns, and used to apply the hydraulic gradient of 4 to 5, which was selected based on the flow rate. 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. From the sampling port attached to the base of column, the effluent was 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. The liquid-to-liquid extraction and GC analysis procedures used in the batch-sorption tests were followed for analysis of the effluent samples collected from the columns. The temporal variations in o-xylene and naphthalene concentrations that were measured in the collected effluent samples are shown in Figure 2. For both organic compounds, the concentrations released from the control column are generally higher than the concentrations released from the columns with fly ash-amended borrow material. The fluctuations in the concentrations after sampling are attributed to the changes in water head due to refilling of the influent tank. Under the applied hydraulic gradients (4 to 5), mobilization of o-xylene and naphthalene from the borrow material (clayey sand) was extremely slow. Hence, the fluctuations in the applied hydraulic gradient are believed to have a very limited effect on NAPL mobilization.

Figure 2 shows that there is an 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, and dropped to about 5 mg/L within 8 days. The low sorptive capacity of the borrow material is believed to have caused this effect. The fly ash, on the other hand, limited this release and immobilized the contaminants due to its high sorptive capacity. The initial effluent concentrations from the fly ash-amended specimens are quite low as compared to those measured in the effluent collected from the borrow material. The o-xylene and naphthalene concentrations are 4.17 mg/L and 1.58 mg/L, respectively, for the column with 10% fly ash. The profound difference between control and fly ash-amended columns and high control concentrations indicate there was an initial release of NAPL in the control column. The results

suggest that the high carbon content in the fly ash is suitable for immobilization of organic constituents in soils contaminated with petroleum residues.



**FIGURE 2 O-xylene and naphthalene concentrations measured in the effluents collected from the two columns.**

To conclude, we observed that the results of the batch-scale adsorption tests conducted on the fly ashes revealed that the unburned carbon content of the fly ash controlled the sorption capacity and Brandon Shores fly ash had very good naphthalene sorption properties due to the presence of high carbon content in its structure.

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 limited the initial release of the contaminants from the specimen, compared to a longer release observed for the control column.