ORGANOCLAY LABORATORY STUDY

MCCORMICK AND BAXTER CREOSOTING COMPANY PORTLAND, OREGON

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Final Report

Organoclay Laboratory Study - McCormick & Baxter

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Principal Investigator: Danny D. Reible, The University of Texas at Austin

Executive Summary

A series of experiments were conducted to assess the sorption capacity, permeability, swelling characteristics, leachability and strength of two selected organoclays (Aqua Technologies ET-1 and CETCO PM-200) when exposed to nonaqueous phase liquids (NAPLs) (FWDA-L, FWDA-D, TFA-L and TFA-DNAPLs) from the McCormick and Baxter Creosote Site, Portland, OR. Sorption capacities of the two organoclays with respect to the four NAPLs were studied in both batch and column tests. The capacity of the PM-200 is as much as 4.82 g NAPL /g organoclay and that of ET-1 1.39 g NAPL /g organoclay as measured in batch tests. Effective capacity in column tests were less than these values due to flow maldistribution and the time required to achieve maximum capacity. The capacity of the organoclays was essentially independent of the type of NAPL. The greater capacity of the PM-200 organoclay was also associated with significantly greater swelling of the organoclay matrix of the PM-200. Both organoclays showed significant reductions in strength after exposure to NAPL although neither exhibited loading related failures under conditions expected to be achieved in the field.

Both organoclays were found to provide good control of both dissolved and nonaqueous phase contaminants in column tests. The ET-1 organoclay exhibited lower capacity for NAPL than the PM-200 organoclay but swelling and the resulting decrease in permeability was much lower for the ET-1 product. Swelling reduced the effective or relative permeability of a pure layer of ET-1 organoclay to that expected of a silt or silty sand. Due to subsequent flow bypassing, the reduction of effective permeability potentially limits the ability to absorb to maximum capacity immediately over a seep. The reduction in effective permeability, however, can also aid effectiveness by encouraging lateral migration of NAPL to fresh organoclay not directly over an active

seep as long as surrounding transition zones are sufficiently large to capture diverted NAPL.   Swelling of either organoclay is associated with contact with concentrated NAPL. No significant swelling is expected with dilute aqueous emulsions of NAPL (e.g. <1% NAPL in water) if this were to be the mechanism of actual contacting at the McCormick and Baxter site.

The most effective pure organoclay configuration was found to be with ET-1 due to its smaller reductions in permeability with NAPL sorption relative to PM-200. PM-200 in a mixture of sand, however, would provide advantages due to its greater capacity relative to ET-1. Mixtures with sand of either organoclay would limit the impact of NAPL associated permeability changes and increase the effective capacity (g NAPL per g organoclay) and therefore provide a lower cost per unit NAPL absorbed.

1. Introduction

This report summarizes the results of laboratory studies of organoclays as components of an active cap designed to sorb and thereby control the migration of oily phase contamination. One of the organoclays tested was used in the McCormick and Baxter sediment cap to mitigate the migration of creosote NAPL seeps into the Willamette River.

The McCormick & Baxter site is located on the northeast shore of the Willamette River in north Portland. The legal address is 6900 North Edgewater Ave., Portland, Oregon 97203, and DEQ's Environmental Cleanup Site Information (ECSI) number for this site is 74. The site includes 43 acres of land and 23 acres of sediments beneath the Willamette River.

McCormick & Baxter Creosoting Company operated between 1944 and 1991, treating wood products with creosote, pentachlorophenol, and inorganic (arsenic, copper, chromium, and zinc) preservative solutions. Historically, process wastewaters were discharged directly to the Willamette River, and other process wastes were dumped in several areas of the site. Significant concentrations of wood-treating chemicals have been found in soil and groundwater at the site and in river sediments adjacent to the site.

The United States Environmental Protection Agency (EPA) listed the site on the National Priorities List (NPL) in June 1994 based on information collected by DEQ between September 1990 and September 1992. The EPA also designated the Oregon Department of Environmental Quality (DEQ) as the lead agency for implementing the selected remedy while funding for remedial design and construction is being provided by EPA.

The DEQ implemented a number of interim removal measures between 1992 and 1994, including plant demolition, sludge and soil removals, and extraction of creosote from the groundwater aquifers.

The Record of Decision (ROD) was issued by EPA and DEQ in April 1996 after considering public comments on the Proposed Cleanup Plan. The Remedy addressed contaminated groundwater, sediment and soil.

A component of the groundwater remedy, initiated in 1994, consisted of an automated creosote extraction and groundwater treatment system. However, due to poor product recovery and high operating costs, the automated system was discontinued in late 2000. Creosote is currently being recovered by passive and manual methods. Approximately 6,000 gallons have been recovered since 1995. A contingency groundwater remedy was implemented in the summer of 2003, with the construction of a combination steel sheet pile and soil bentonite slurry wall surrounding 18 acres. The purpose of the barrier wall is to prevent migration of creosote to the Willamette River.

The sediment remedy was implemented in 2004 and primarily consisted of a sand cap placed over 23 acres of contaminated sediment. An oil adsorptive material known as organoclay was used in the creosote seep areas. To protect the cap from erosion, the sand and organoclay were armored with a combination of rock and articulated concrete blocks. The sediment remedy also included the regrading and capping of the riverbank with two feet of topsoil. Revegetation of the capped riverbank with native trees and shrubs will occur in February 2006 after the soil has been stabilized with the native grasses planted in November 2004. Capping of a one acre portion of the contaminated sediments along a high pressure sewer main will be completed in September 2005.

Implementation of the soil remedy began in March 1999 with the removal of 33,000 tons of highly contaminated soil and debris. The soil remedy will be completed in September 2005 following installation of a combination impermeable/earthen cap – the impermeable portion covering the area within the subsurface barrier wall.

A primary objective of the cleanup remedy is to prevent further migration to the Willamette River from two primary areas of creosote nonaqueous phase liquid (NAPL), one from the Tank Farm Area (TFA) and the other from the Former Waste Disposal Area

(FWDA). The NAPL is predominantly creosote compounds that are present as both LNAPL and DNAPL. Prior to remedy implementation the NAPL migrated vertically to the water table (15-25 feet below ground surface [gw elevations are 5-15 ft, except right at the river]) and laterally to the river. DNAPL continued to migrate vertically and horizontally as it overcame entry pressures. Some NAPL weathering and differentiation processes may be active, such as conversion of DNAPL to LNAPL by solution of higher-density/higher-solubility LPAHs such as naphthalene relative to the lower-density/lower-solubility aliphatics. Near the beach and in the river, NAPL had been observed in seeps and sheens, predominantly at low river stage.

The ROD requires a protective cap to be placed over areas of contaminated river sediments posing an unacceptable risk to human health and the environment. To control the mobile NAPL, 1.2 million pounds of organoclay was placed in 2004 as a sediment cap component in two selected areas within the Willamette River. Organoclay is bentonite or hectorite clay that has been modified to be hydrophobic and to have an affinity for non-soluble organics. Organoclay is used in water treatment systems to reduce fouling from oil in downstream components. Because it has an affinity for organic liquids and has been used effectively in water treatment applications, organoclay was selected for placement at the NAPL seeps. The organoclay (ET-1) employed at the McCormick and Baxter Site is a product of Aqua Technologies Inc.

In order to evaluate the expected performance of this organoclay and to provide suggestions for monitoring for potential failures, the University of Texas was contracted by DEQ (IGA #005-05) to conduct laboratory studies on the selected organoclay material as well as on alternative products. The overall general objectives of the laboratory study on organoclay were:

- To expand the knowledge base on the effectiveness of organoclay as a capping material with regards to sorbing and retaining creosote nonaqueous phase liquid (NAPL) seeps for future use in remedial actions, and

- To obtain information that will shape the long-term monitoring and maintenance plan for the McCormick and Baxter organoclay cap.

Specific goals for the laboratory study include:

1. Determine sorption effectiveness of different organoclay formulations with respect to site specific NAPLs
2. Determine the effectiveness of organoclays in controlling the dissolved and non-aqueous phase contaminants
3. Determine the permeability characteristics of the different organoclays as they sorb NAPL (will reduced permeability block NAPL transport or will preferential pathways form?)
4. Determine the effect of mixing sand with the clay on NAPL capacity and swelling or other causes of reduced clay permeability
5. Determine the structural integrity and the strength characteristics of the organoclay as the clays sorb NAPL and undergo wetting and drying cycles

2. Materials and Methods

2.1 NAPL

NAPLs used in this study were collected from two areas at the McCormick and Baxter site, the Former Waste Disposal Area (FWDA) and Tank Farm Area (TFA). The NAPL is predominantly creosote compounds and its density is variable including both lighter than water NAPLs (LNAPL) and heavier than water NAPLS (DNAPL). Samples of each type were employed in the laboratory studies: FWDA-LNAPL, FWDA-DNAPL, TFA-LNAPL, and TFA-DNAPL. The physical properties of the NAPLs are shown in Table 1.

Table 1. Physical properties of NAPLs

NAPLs	FWDA-L[*]	FWDA-D	TFA-L	TFA-D
Density (g/cm^3)	0.9867, 0.9912	1.0028	0.9721	1.0919
Viscosity (cp)	22.8, 15.7	16.8	17.0	26.8
Water content (%)	11.9 (11.9-12) 1.0 (0.9-1.1)	32.8 (32.2-33.5)	45.7 (43.3-48.1)	5.3(4.3-6.3)

Note: two batches of FWDA-LNAPL were used in this study, the sampling ID are EW-15s and EW10s. EW10s was used in all slow injection experiments and EW-15s was used in all other tests.
Viscosity and density data are from PTS laboratories, water content are measured in this study using the method described in the method section.

2.2 Organoclays

Two organoclays from different sources were used in all studies: ET-1 from Aqua Technologies of Wyoming, Inc. and PM-200 from CETCO. Another organoclay from the Biomin Inc. was only employed in batch sorption tests and was found to have similar capacity to the PM-200 product, and was not used in subsequent testing.

Particle size distribution and specific gravity of the two organoclays (ET-1 and PM-200) were measured based on the standard methods (ASTM D422-63 and ASTM D 854-02). Particle size distribution was measured by sieving and hydrometer analysis. Particles greater than 75 µm (No. 200 sieve) were separated by sieving and particles smaller than

75 μm were determined by pyconometer readings in the suspension and were calculated by Stokes's Law.

Specific gravity was measured by water pycnometer. The procedure includes:

1) Measuring pycnometer mass
2) Preparing clay slurry by adding water to the organoclay in the pycnometer
3) Deairing the clay slurry by heating the slurry and removing the entrapped air of the clay
4) Filling the pycnometer with water
5) Maintaining thermal equilibrium by putting the pycnometer into the insulated contained
6) Determining the new mass of pycnometer
7) Measuring the temperature of pycnometer

Specific gravity G_t was calculated using the following equation:

$$G_t = \frac{\rho_s}{\rho_{w,t}} = \frac{M_s}{M_{\rho_{W,T}} - (M_{\rho ws,t} - M_s)}$$

Where:

ρ_s, The density of the clay solids, g/cm^3

$\rho_{w,t}$, the density of water at the test temperature (T_t), g/cm^3

M_s, the mass of the oven dry clay solids, g

$M_{\rho w,t}$, the mass of the pycnometer and water at the test temperature (T_t), g

$M_{\rho ws,t}$, the mass of pycnometer, water, and solid clay at the test temperature (T_t), g

The specific gravity of the ET-1 and PM-200 are 1.99 (1.99-1.99) and 1.73 (1.73-1.74) g/cm^3, respectively. The bulk densities of the ET-1 are 0.70-0.75 g/cm^3, corresponding to a void ratio of 0.62-0.65. The bulk densities of the PM-200 organoclay are 0.75-0.80 g/cm^3, corresponding to a void ratio of 0.54 to 0.57. For both organoclays, more than 50% of the particles are in the size between 0.85 to 2 mm. 97.8% particles are greater than 0.3 mm for ET-1 and 95.0% particles are greater than 0.3 mm for PM-200 (Figure 1).
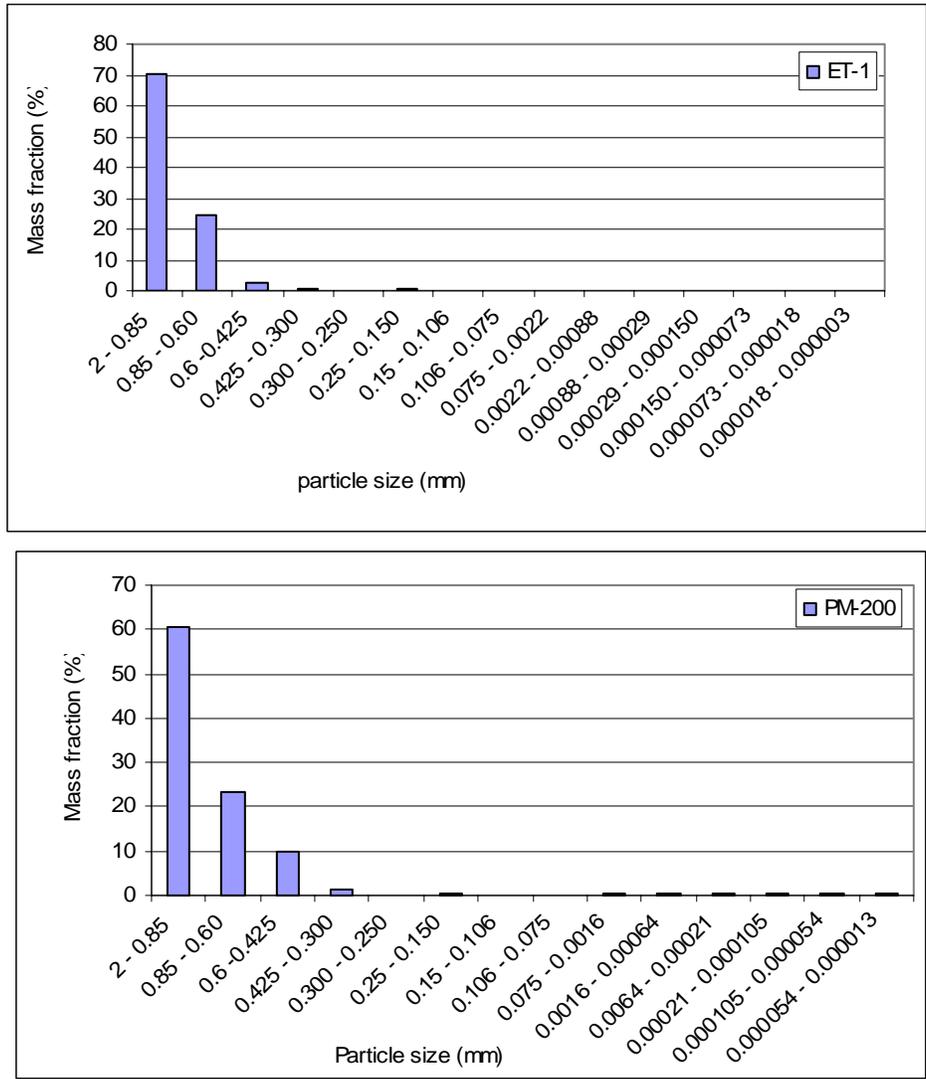
Figure 1. Particle size distributions of ET-1 and PM-200 organoclays

Sand was employed in mixtures with organoclay for some experiments. Essentially 100% of the sand particles were between 0.3 and 0.5 mm particle size. It should be recognized that a more homogeneous sand-organoclay mixture would have likely resulted if the particle size distribution of the diluent (sand) matched the size distribution of the organoclay (i.e. coarse sand were used as the diluent).

2.3 Sorption capacity measurement

Sorption capacity of the organoclays with respect to different NAPLs were measured in both batch tests and column flow through tests.

In batch tests, the sorption capacity of organoclay was measured in the following manner:

1) Determine water content of NAPL (C_w): 10 ml NAPL was added to a 15-ml centrifuge tube, centrifuged at 8000 g for 20 minutes, the lighter phase (water or NAPL) was removed, and the water content was determined by weight difference.

2) Determine NAPL sorption capacity of organoclay:

   a. 2 g of organoclay was added to a pre-weighed glass jar (60ml) (M_{j0} pre-addition weight, M_{j1} wt after addition).

   b. The organoclay was saturated with water, any extra water was removed with a disposable glass pipette, and the jar weighed (M_{j2}).

   c. An excess volume of NAPL was added to the jar and weighed again (M_{j3}) (ratio of pure NAPL to organoclay is ~3:1 for ET-1 and ~5:1 for PM-200 and Biomin – preliminary experiments indicated that ET-1 would absorb less NAPL and a 5:1 ratio was not needed).

   d. The organoclay was allowed to absorb NAPL for a set period (24 hr for ET-1 and 48 hr for PM-200 and Biomin, preliminary experiments showed that the amount of sorption in ET-1 was stable after 24 hours whereas small amounts of sorption continued in the PM-200 and Biomin products), the free phase, including NAPL and water, was removed with a clean, pre-weighed pipette (M_{p0}), and added to a clean, pre-weighed aluminum weighing bowl (M_{v0}). After removal of the free liquid phases, the jar was weighed again (M_{j4}). The pipette and weighing bowl were also weighed (M_{p1} and M_{v1}).

   e. The jar with organoclay and NAPL, the glass pipette used to transfer NAPL, and the weighing bowl with the free liquid phase were dried at low temperature (~50 °C).

   f. After drying, all the above containers were weighed (M_{j5}, M_{p2} and M_{v2}) and the water content was determined by difference.

The NAPL sorbed by the organoclay, left on the glass pipette and in the weighing bowl should equal the NAPL added in step 3. The mass of water determined by difference in step *f* should be consistent with the original water added in step 2 and the water from the original NAPL. The material balance may not equal 100% in either case due to the difficulty in accurately determining the water content in the original NAPL in step 1 and due to NAPL losses during drying at 50 ˚C. Preliminary experiments suggested that 50 ˚C was an appropriate compromise for maximizing water loss during drying without large NAPL losses.

Balance Equations

NAPL sorption:

$$M_{NAPL} = M_{j5} - M_{j1}$$

Sorption capacity of organoclay:

$$F = M_{NAPL}/M_{clay} = (M_{j5} - M_{j1})/(M_{j1} - M_{j0})$$

NAPL balance after adjusting water content in NAPL

$$(M_{j5} - M_{j1}) + (M_{p2} - M_{p0}) + (M_{v2} - M_{v0}) = (M_{j3} - M_{j2})*(1-Cw)$$

Water balance after adjusting water content in NAPL

$$(M_{j4} - M_{j5}) + (M_{p1} - M_{p2}) + (M_{v1} - M_{v2}) = (M_{j2} - M_{j1}) + (M_{j3} - M_{j2})*Cw$$

Sorption capacity of the organoclay for NAPLs in the column testing (described below) was determined from the rate of progression of NAPL in the column compared to the rate of NAPL injection. If NAPL has progressed a length L up the column of cross-sectional area A in a time Δt, the sorption capacity of the organoclay for the NAPL, X (in g NAPL/g organoclay) is

$$X = \frac{Q_{NAPL}\rho_{NAPL}\Delta t}{\rho_{OC}AL}$$

where Q_{NAPL} is the NAPL flow rate, and ρ_{NAPL} and ρ_{OC} are the bulk densities of the NAPL and organoclay.

Effective sorption capacity of organoclay for NAPLs was calculated based on the total NAPL injected until visual observation of breakthrough and the total mass of organoclay in the column.

$$X_{eff} = \frac{M_{NAPL}}{M_{clay}}$$

Where M_{NAPL} and M_{clay} are the mass of total NAPL injected and the total organoclay packed in the column.

2.4 Column Testing Procedures

Column testing was used to determine NAPL migration and sorption characteristics under flow conditions. Figure 2 shows a schematic of the experimental arrangement. Column testing was conducted initially in a long column (4.8 x 60 cm) and subsequent testing was conducted in shorter (4.8 x 15 cm) columns because there were no significant behavioral changes with column length. Initial tests were conducted in which FWDA-LNAPL was injected at a rate equivalent to a superficial column velocity (Darcy velocity) of 0.28 cm/min for a period of hours followed by a waiting period to allow NAPL sorption-related swelling of organoclay. These tests were used to determine organoclay permeability when first exposed to NAPL and to identify organoclay behavioral changes with swelling. Initial testing continued until the column was completely saturated with NAPL to evaluate near saturation migration of NAPL and dissolved phase PAHs. A final methodology for column testing was devised on the basis of these preliminary tests and subsequent testing was accomplished with slow continuous injection of NAPL at a rate equivalent to a Darcy velocity of 1 cm/day. At this rate, NAPL penetration into the organoclay matrix was taking place at a rate comparable to the rate of swelling.
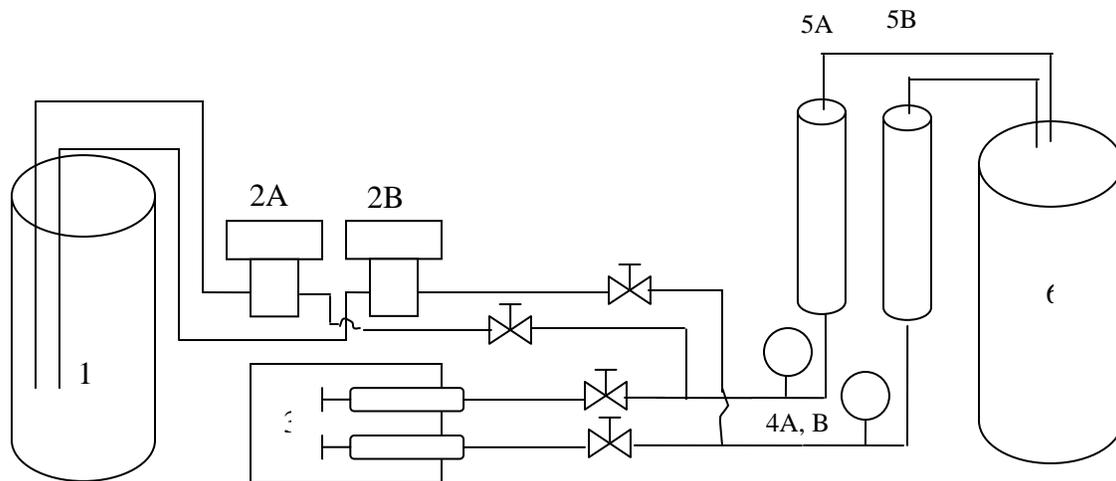
Figure 2. Schematic diagram of column testing. 1 water tank, 2 water pump, 3 syringe pump for NAPLs, 4 pressure gauge, 5 column, 6 waste tank

The initial testing with ET-1 was conducted in the following steps:

1) Column was packed with mild vibration to ensure column uniformity.

2) Water was pumped through the column using a metering pump (Fluid metering, Inc., NY, USA) to saturate organoclay followed by dyed water with approximately 200 ppm NaCl. The NaCl was used as a tracer for measurement of hydraulic residence time in the column. Also the dye in the water with NaCl was used to indicate any flow non-uniformity in the column.

3) 60 ml NAPL was continually pumped into the column using a syringe pump (Coleparmer Inc., IL, USA) at a flow rate of 5 ml/min(0.28 cm/min, darcy velocity).

4) The pump was shutdown and then restarted after a 2.5 hr wait time. The NAPL injection was continued until almost all organoclay was wetted by NAPL or just before breakthrough.

5) The pump was shutdown again and then restarted after a 5 day waiting period until breakthrough.

6) Water was pumped through the column and dissolved PAH concentration in the outlet was measured to test desorption or leaching of the sorbed NAPL. These initial measurements were not useful due to the contamination of the tubing with the NAPL after breakthrough.

For the PM-200, similar testing was conducted but modifications in procedure were necessary due to the fast and significant swelling and correspondingly significant reduction in permeability of this organoclay. In one experiment, the PM-200 was mixed with sand at a ratio of 2:1.   Other experiments were conducted with both organoclays at various sand/organoclay mixtures up to 10:1 sand:organoclay.

In the experiments with continuous injection at a slow flow of 1 cm/day darcy velocity, NAPL sorption capacity, effective permeability with respect to NAPL (determined by measurement of the pressure gradient across the column) and dissolved PAH concentrations in the effluent (except TFA-DNAPL) were monitored over time. For ET-1, all four NAPLs were injected until breakthrough. After NAPL breakthrough, water was pumped to the column and PAH concentrations in the effluent were measured to test the leaching of the sorbed NAPL and desorption of the sorbed organic contaminants. One experiment for FWDA-LNAPL was conducted with site water to identify potential changes in conditions associated with site water. Dry-wet cycling was conducted to explore the potential effect of tidal exposure of the organoclay cap. NAPL (FWDA-LNAPL) and water saturated organoclay was allowed to drain and then rewetted to test the potential for NAPL mobilization by this mechanism.

Similar testing was conducted on PM-200, however, the low permeability of the rapidly swelling PM-200 organoclay required high injection pressures within 24 hours to overcome an effective permeability reduced by both swelling and partial saturation (relative permeability). Experiments were halted if the required pumping pressures exceeded 60 psi. To ensure testing of the PM-200 organoclay to breakthrough, some columns were packed with only a 2 cm layer of the media and filled with glass beads. Two NAPLs (FWDA-LNAPL and TFA- DNAPL) were used for testing. Each NAPL

was continuously injected until breakthrough. Also, the PM-200 was mixed with sand at a ratio of 10:1, two NAPLs (FWDA- LNAPL and TFA- DNAPL) were pumped through until breakthrough with measurement of the permeability associated with the sand/PM-200 mixture. A similar experiment was conducted with one NAPL (FWDA-LNAPL) and a sand/ET-1 mixture to test the ability to retain some sorption capacity while having a minimal impact on permeability. CETCO has recently incorporated organoclay into laminated mats as used in the Anacostia active capping demonstration project (www.hsrc-ssw.org). These mats provide a mean of placing a thin layer of organoclay for specific applications and have been employed as a temporary measure to control NAPL release as a result of gas movement from sediments at the McCormick and Baxter site. Studies similar to those conducted herein on the effectiveness and operational limitations of these laminated mats could provide valuable information in considering the use of organoclay in sediment cap applications.

2.5 Sampling and Chemical Analysis

The effluent from the column was monitored for breakthrough of PAH compounds. Hexane was introduced into the collection vial prior to effluent collection to minimize loss of any volatile compounds. The solvent was then exchanged with acetonitrile before analysis on a high performance liquid chromatography (HPLC, Waters 2690) with both UV-Diode array and fluorescence detectors. In high flow experiments, water samples could be collected without significant loss and were directly analyzed on HPLC. Detection limits were limited by the small volume of sample collected (1 mL or less) Detection limits of PAHs by HPLC were measured based on the method provided by Rong (2002) by measuring the standard deviation in measured concentrations of prepared standards.

$MDL = SD * t_{0.99}$

MDL, method detection limit

SD, standard deviation

$t_{0.99}$, t-distribution table value for 99% confidence with the degree of freedom (n-1).

The method detection limits of several PAHs for the fluorescence detector are listed in the following table.

Table 2. Method detection limits of selected PAHs

Compounds	Naphthalene	Phenanthrene	BkF	BaP	B[ghi]P
Detection limit(μg/L)	1.37	0.34	0.036	0.046	0.085

BkF: benzo[k]fluoranthene; B[a]P: benzo[a]pyrene; B[ghi]P: benzo[ghi]perylene

For most samples, only two PAHs, naphthalene and phenanthrene, were identified with high confidence. Although the detection limits of the other compounds were much lower, their presence in lower concentrations in the site NAPL and greater hydrophobicity (stronger sorption and lower rates of migration) resulted no measurable breakthrough of these compounds.

2.6 Organoclay Strength Measurement

Structure integrity of the organoclay after sorbing NAPL was assessed by comparing the strength of the organoclay before and after sorbing NAPL. The strength of organoclay was measured using an unconsolidated-undrained (UU) triaxial compression test. The UU test models the response of soils to loads applied over short periods of time such as days or weeks such that there is inadequate time for drainage to occur.   Here it is designed to simulate the response of the organoclay to loading with the overlying cap and armoring materials before and after NAPL sorption. This test is essentially that described in ASTM T296-95. Organoclay was first compacted into cylinder form in a consistent manner to achieve similar bulk densities in the samples.   The diameter and length of the test specimen were 1.49 by 3.10 inches. The specimen was placed in the triaxial test chamber and sealed inside a rubber membrane. The chamber was then filled with water and the confining pressure was adjusted to 10 psi to simulate the baseline loading of the organoclay. A 1% axial strain per minute was then applied maintaining a constant confining pressure of 10 psi until the clay failed under the increasing axial loads. The

applied load, displacement of the specimen (strain), and volume change of the specimen were recorded.

If the sample is saturated and undrained, there will be no change in volume during the test. Assuming the sample remains a right cylinder, the corrected cross sectional area (A) at a given axial strain is:

$$A = \frac{A_0}{1 - (\varepsilon_a / 100)}$$

Where A_0 is the average, initial cross sectional area and ε_a is the axial strain in percent. If the sample is unsaturated, the clay will change volume when sheared and the area will be calculated after correcting this volume change. Volume changes of all samples in this test were less than 5%, therefore, volume change was not corrected in the area correction. The stress is computed from the measured force (F) as indicated by the applied load and the corrected sectional area at each point in the test:

$$\sigma_1 - \sigma_3 = \frac{F}{A}$$

The total axial stress (σ_1) is the confining pressure (σ_3) plus the applied pressure.

Failure of the sample is defined as the peak recorded stress (Type 1) . For some samples, the stress increased rapidly to a near-peak value but then continued to increase slightly as the strain was continued at 1%/minute (Type 2). For these cases, failure was defined as the stresses at 20% axial strain which is in the region of near constant stress. The selected locations (dotted line) are shown conceptually in Figure 3.
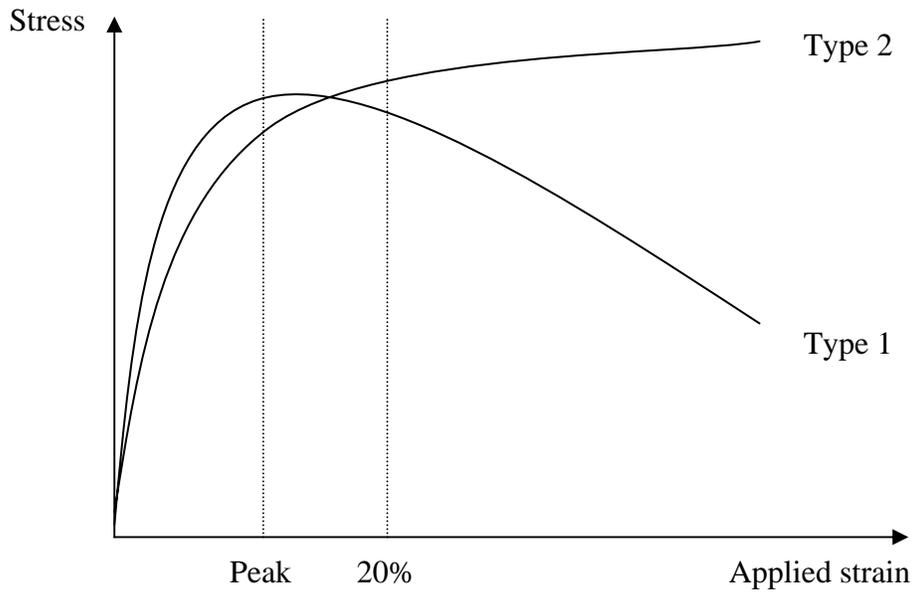
Figure 3. Observed stress versus strain curves during strength testing

Different compacting conditions will influence the measured stresses of the specimen; therefore, two replicates were applied for each organoclay treatment. Strength of water saturated ET-1 and PM-200 and NAPL saturated ET-1 was measured. For PM-200, insufficient NAPL saturated organoclay was available and a specimen was prepared composed half of NAPL saturated PM-200 and half of water saturated PM-200.

2.7 Data Analysis

During all testing, the pressure difference across the column and the migration length of NAPL was used to estimate the effective hydraulic conductivity. The effective hydraulic conductivity of organoclay was estimated using the pressure gradient defined by the pressure difference across the column divided by the wetted length of organoclay. For water or NAPL saturated conditions, this was the entire column length. For partially NAPL saturated conditions, this presumes that the pressure gradient is much higher in the NAPL saturated region. The effective hydraulic conductivity, K_{eff}, was calculated based on Darcy's law.

$$K_{eff} = \frac{Q}{A}\left(\frac{\Delta h}{\Delta l}\right)^{-1}$$

Where Q/A is the volumetric flow rate of the injected fluid, cm^3/min, divided by flow area, cm^2, or darcy velocity in cm/min, Δl is the height of organoclay wetted with liquid, cm, and Δh is the pressure difference across the wetted column as defined by the head difference in the flowing fluid, cm. The effective permeability of the medium is then given by

$$k_{eff} = \frac{K_{eff}\,\mu}{\rho g}$$

Here ρ is density of water or NAPL, g/cm^3, and μ is the viscosity, cp. k_{eff} is the effective permeability cm^2. The measured effective permeability with NAPL is reduced over that of fresh water saturated organoclay as a result of partial saturation (the effect of relative permeability) and the swelling and pore size reduction associated with NAPL sorption. For convenience the effective permeability is evaluated in darcy, 1 darcy=10^{-8} cm^2.

3. Qualitative Experimental Observations

3.1 Batch testing

In batch tests with ET-1, little swelling of the organoclay was noted with exposure to NAPL and apparent particle integrity was little changed. The free liquid phase of NAPL and water was easily separated from the organoclay. With the PM-200, significantly greater sorption of NAPL was noted, coupled with extensive swelling and apparent loss of particle integrity. Organoclay and NAPL were not easily separated after two days sorption, the clay and the swollen aggregate could be broken during shaking. The free liquid was more viscous than the original NAPL, which was likely due to the presence of very fine organoclay particles of clay in the liquid phase. The capacity of the PM-200 with respect to NAPL, however, was significantly greater than for ET-1. In this study, sorption capacity of organoclay with respect to NAPL is defined as the quantity of NAPL that can not flow freely from the organoclay although it may represent simple NAPL entrapment in the swollen organoclay matrix as well as sorption. When mixing with

NAPL, the Biomin organoclay behaved very similarly to the PM-200 organoclay except that the clay phase retained more water.

3.2 Column test

3.2.1 Initial testing- rapid intermittent injection of NAPL

A) ET-1 organoclay

Figure 4a-c shows the migration of FWDA-LNAPL in the ET-1 organoclay. NAPL was introduced continuously until approximately half of the column length contained NAPL as shown in Figure 4a. The NAPL wetting front was approximately horizontal with little or no evidence of flow heterogeneity or fingering. Pressure measurements during this period were used to estimate the effective permeability as discussed below. Pausing for 2.5 hours before continuing the introduction of NAPL led to a small increase in the required pumping pressure due to slight organoclay swelling. Pumping of NAPL was continued until just before breakthrough in the column. The lower zone of organoclay had been in contact with NAPL for the longest period and had sorbed more NAPL than the upper zone, as shown in Figure 4b. Before continuing injection of NAPL beyond that shown in Figure 4b, the experiment was delayed for 5 days to ensure complete swelling of the organoclay. Subsequent NAPL injection required significantly higher pressures and the flow rate was reduced to that equivalent to a Darcy velocity of 0.33 cm/hr. As shown by the darker column in Figure 4c, the subsequent injection of NAPL led to increased NAPL sorption throughout the column before breakthrough occurred.

Figure 4. Intermittent pumping of FWDA-LNAPL through the 15 cm column with ET-1.
(a) first 60 ml NAPL (b) more NAPL after 2.5 hr-waiting period just before breakthrough
(c) more NAPL after 5 d-waiting period until breakthrough.

B) PM-200 organoclay

Following the same experimental procedure as described above, the PM-200 organoclay
exhibited significant swelling after the 2.5 hr-waiting period. Initiating NAPL injection
after this period quickly led to a rapid increase in pressure required to maintain the flow
rate due to swelling of the organoclay.   With an applied pressure of 60 psi (at which
point the experiment was shutdown) the newly injected NAPL had only migrated 1.3 cm
into the old NAPL layer (Figure 5 a-b) and had not progressed into virgin organoclay at
the top of the column. The dark layer at the bottom of the column in Figure 5b shows the
increased saturation in this layer. In one experiment, the pressure required to pump
NAPL into the swollen organoclay was sufficient to lift the bed as shown in Figure 5c.
Experiments with a 2:1 mixture of sand and the PM-200 organoclay that had
approximately the same potential capacity as pure ET-1 organoclay allowed continuation
of NAPL injection after the first 2.5 hr waiting period (Figure 5d). Continued swelling
after the 5 day pause, however, also led to >60 psi pressures required to maintain flow
rate and the experiment was shutdown.

(a)	(b)	(c)	(d)
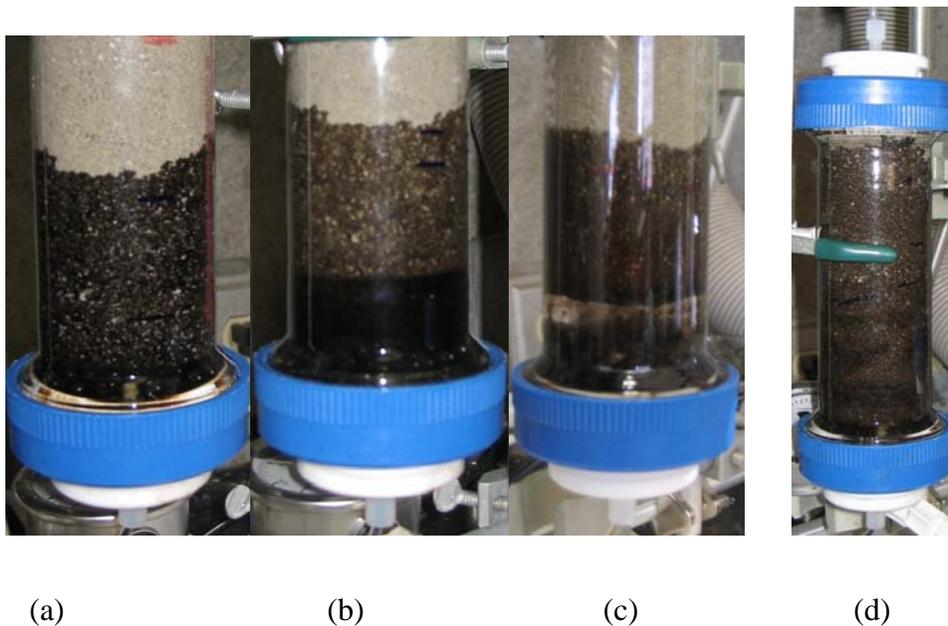
Figure 5. Intermittent pumping of FWDA-LNAPL through the 15 cm column with PM-200 organoclay (a) First 60 ml NAPL. (b) more NAPL after 2.5hr pause and organoclay swelling (c) bed lifting associated with injection of water into a fully swollen PM-200 organoclay (not the same experiment as Figure 4a and b) (d) Injection to breakthrough with 2:1 mixture of sand and PM-200

3.2.2 Slow continuous injection of NAPL

A) Pure organoclay experiments

Experiments under relatively high flows (0.28 cm/min darcy velocity) as described above showed uniform flow progression in the organoclay as shown in Figures 4 and 5. Injection of low flows (1 cm/day darcy velocity), however, gave rise to fingering of the NAPL into the water (Figures 6 a-d). This is presumably due to the increased importance of capillary rise of NAPL into the organoclay at low flow rates. Subsequent NAPL flow would then tend to follow channels already wetted by NAPL resulting in the development of prominent NAPL fingers. In most cases this appeared to be more of an issue with the more absorbent PM-200 organoclay.   This partially offsets the significant reduction in effective permeability of the PM-200 organoclay by encouraging vertical migration by means other than the mean pressure gradient but also offsets the significant potential advantage of the greater sorption capacity of the PM-200 organoclay. The injection of NAPL was continued to breakthrough in ET-1 columns. Some flow heterogeneity was

still noted at breakthrough (see Figure 7 a-d), thus not all of the capacity of the organoclay was effectively used before breakthrough.

(a)   (b)

(c)   (d)
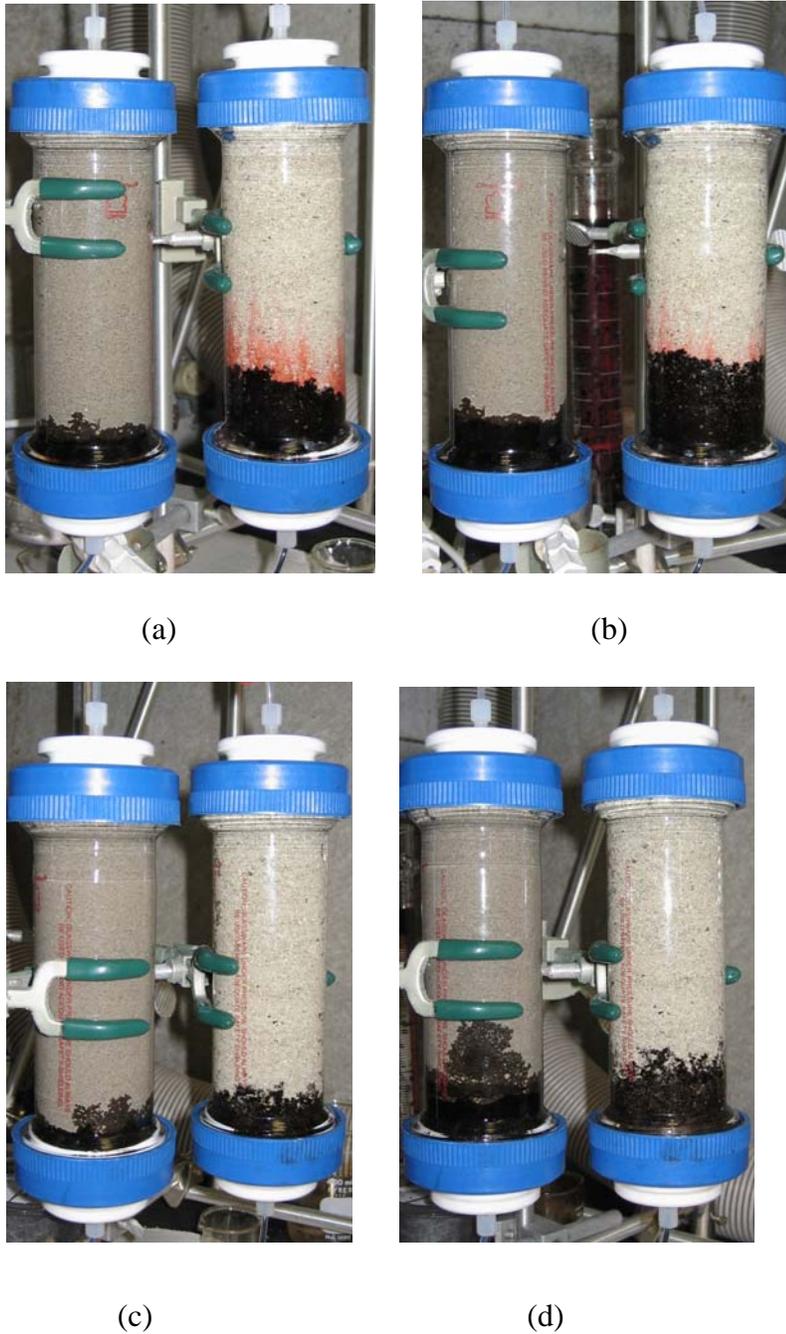
Figure 6. Migration of NAPL in column with PM-200 (left) and ET-1 (right) organoclay.(a) FWDA-LNAPL at 24 hours (b)FWDA-LNAPL at 48 hours (c) TFA-DNAPL at 24 hours (d) TFA-DNAPL at 48 hours
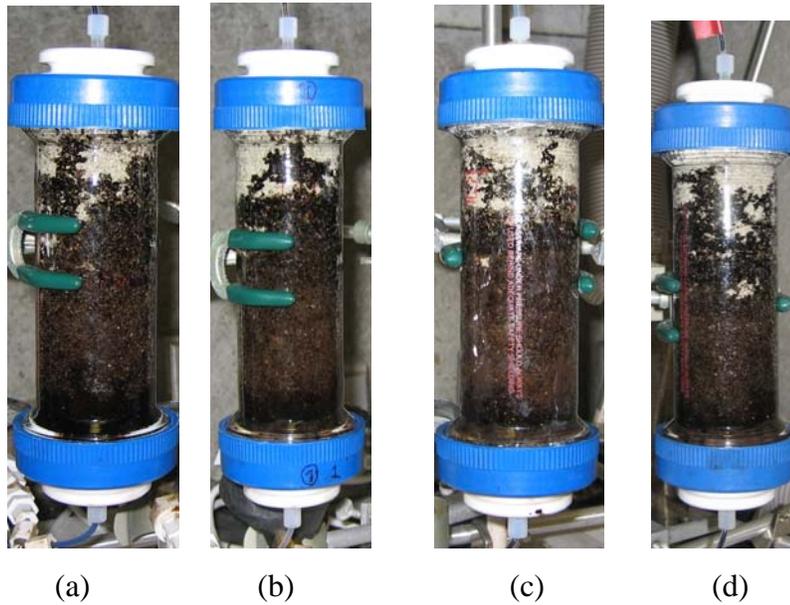
Figure 7. NAPL distributions in the column of ET-1 at breakthrough (a) FWDA-LNAPL
(b) FWDA-DNAPL (3) TFA-LNAPL (4) TFA-DNAPL

B) PM-200 and glass beads

As indicated previously, some columns were filled with a 2 cm layer of PM-200 and
glass beads filling the remainder. The thin organoclay layer led to relatively rapid
breakthrough and continued migration of NAPL through the wetted channel led to
significant flow maldistribution (Figure 8).

Figure 8. NAPL migration in the column with 2 cm PM-200 and 12 cm glass beads: TFA-DNAPL (left) and FWDA-LNAPL (right)

C) PM-200 and sand

Both FWDA-LNAPL(right) and TFA-DNAPL(left) were easily pumped through the PM-200 and sand mixture(1:10) until breakthrough of NAPLs with no significant increase in pressure required to maintain flow. In addition, flow heterogeneity was minimized suggesting that all of the organoclay was available for NAPL sorption. This suggests that an optimal organoclay design would be a mixture with sand, balancing reductions in effective permeability with effective utilization of organoclay.

Figure 9. NAPL migration in the column with PM-200 and sand mixture (1:10): FWDA-LNAPL(right), TFA-DNAPL (left)

4. Quantitative Results and Discussion

4.1 Sorption capacity of organoclays with respect to NAPLs

4.1.1 Batch test

A summary of the sorption capacities measured in batch studies with each of the NAPLs and organoclays and the respective degree of agreement material balances for both NAPL and water.

Table 4. Sorption capacity of organoclays (g/g) with respect to NAPLs in batch test

	ET-1			PM-200		
	Sorption Capacity g/g (std dev)	NAPL Balance %	Water Balance %	Sorption Capacity g/g (std dev)	NAPL Balance %	Water Balance %
FWDA-LNAPL	1.36 (0.08)	101(10)	106 (17)	4.60 (0.04)	97 (2)	120 (6)
FWDA-DNAPL	1.25 (0.12)	89 (8)	110 (14)	4.82 (0.06)	82 (1)	126 (4)
TFA-LNAPL	1.35 (0.03)	86 (3)	111 (1)	4.41 (0.03)	75 (3)	124 (3)
TFA-DNAPL	1.39(0.10)	82(4)	107(8)	4.50(0.11)	84(4)	115(5)

Sorption capacities of organoclays are not dependent on the NAPL density and NAPL characteristics although minor difference was observed for the sorption capacity of PM-200 with respect to NAPLs from FWDA site and from TFA site. Sorption capacities of PM-200 with respect to all four NAPLs were almost three times higher than ET-1; however, swelling and structure instability accompanied with the high sorption capacity. Material balances of NAPL was from 75% to 100% and material balance for water ranged from 100% to 125%, indicating some NAPL evaporation during drying or possibly incomplete evaporation of water during the water content measurement.

4.2.2 Column testing

A) Rapid intermittent injection tests

The sorption capacity of ET-1 and PM-200 in the flow-through experiment was less than observed in batch tests. Under the high NAPL injection rates, sorption capacities of the ET-1 and PM-200 organoclay with respect to FWDA-LNAPL were approximately 0.47 and 0.53 g/g, respectively. This is the result of both less than full NAPL saturation during initial injection and the time required for the organoclay to swell and achieve full sorption capacity. After allowing time for swelling of the organoclay and restarting NAPL injection which tended to increase the local NAPL sorption, the average sorption capacities approached but never equaled the batch absorption capacity. Organoclay that was not wetted by NAPL likely accounted for this difference. After a 5 day waiting period and then attempting to fully saturate the ET-1, the sorption capacity was approximately 0.88 g/g, which was 20-30% lower than that measured in batch tests. NAPL injection was not possible at reasonable pressure gradients with the PM-200 organoclay after a 5 day waiting time and a comparable capacity was not measured for that organoclay.

B) Slow continuous injection

Sorption capacity of ET-1 with respect to all four NAPLs, sorption capacity of ET-1 and sand mixture with respect to FWDA-LNAPL and sorption capacity of ET-1 after

saturation with site water with respect to FWDA-LNAPL in the slow flow-injection
experiment were calculated and are listed in Table 5. Sorption capacity of PM-200 and
sand & PM-200 mixture (10:1) with respect to FWDA-LNAPL and TFA-DNAPL are
listed in Table 6.

Table 5. Sorption capacity of ET-1 for NAPLs with slow continuous injection

	FWDA-L			FWDA-D	TFA-L	TFA-D
	ET1 Laboratory water	ET1 Site water	ET1&Sand(1:10) Laboratory water			
Saturated Sorption capacity (g/g)	1.00	1.10	0.17 (1.87 g/g OC)	0.97	0.87	1.14
Effective sorption capacity (g/g)	0.60	0.60	0.14 (1.54 g/g OC)	0.74	0.80	0.80

Note: Saturated sorption capacity represents the apparent capacity of the organoclay in the
saturated region at the entrance to the column while the effective sorption capacity is
estimated based upon the entire column at breakthrough and includes the effect of NAPL
fingering and flow maldistribution.

Table 6. Sorption capacity of PM-200 and with sand mixture with slow continuous
injection

	PM-200		Sand & PM-200 (10:1)	
	FWDA-L	TFA-D	FWDA-L	TFA-D
Sorption capacity(g/g)	1.37	1.45	0.27 (2.97 g/gOC)	0.30 (3.30 g/gOC)
Effective sorption capacity(g/g)	N/A	N/A	0.24 (2.64 g/g OC)	0.30 (3.30 g/g oC)

The sorption capacity of ET-1 with respect to all four NAPLs in this slow-flow testing
was approaching but less than the sorption capacity measured in batch test. This is likely
due to the non-uniformities in flow that developed after 4 or 5 days and which resulted in
partial saturation of the upper portions of the organoclay with respect to NAPL.   The
effective sorption capacity of ET-1 with respect to FWDA-LNAPL was reduced about
40% due to partial saturation. Saturation of organoclay with site water did not change the
sorption capacity of NAPL significantly.

Sorption capacity of PM-200 was two times lower than that measured in the batch tests due to the greater flow nonuniformity noted in these tests. Sand and organoclay mixture (10:1) allowed sorption of NAPL at close to batch sorption experiments (i.e. NAPL sorbed per gram of organoclay).

4.3 NAPL mobilization and chemical retention

4.3.1 Dissolved Naphthalene and phenanthrene concentration

In the intermittent rapid injection experiments, no dissolved PAHs were detected in the effluent of the column until NAPL breakthrough. Neither NAPL nor dissolved phase were apparently mobilized by additional pumping of water after achieving near saturation of the column with NAPL. The organoclay appeared to effectively contain NAPL and dissolved contaminants until its capacity is exceeded. As indicated above, however, NAPL maldistribution led to less actual retention than the theoretical maximum of the organoclay column.

In the slow continuous injection experiments with ET-1, NAPLs were injected until breakthrough. Figure 10 shows the observed naphthalene in effluent water samples showing that the organoclay retained dissolved phase until just before NAPL breakthrough. Phenanthrene dissolved concentrations were also measured in the effluent and are also shown in Figure 10. In two of the four experiments, the observed behavior was identical to that observed with naphthalene. In one experiments (with FWDA-LNAPL and site water), a low level of phenanthrene (relative to post breakthrough levels) was observed continuously. The site water did not contain phenanthrene at these concentrations and there was no evidence of leaching of dissolved phase compared to other experiments. The relatively high effluent levels prior to breakthrough may have been due to inadequate cleaning of the columns in that some fittings and tubing were not replaced after breakthrough in preceding experiments. The much higher concentration of naphthalene in this experiment during and after breakthrough provides much clearer trends.

Two nonzero phenanthrene concentrations were also detected prior to breakthrough with TFA-LNAPL. Early detection of dissolved phase naphthalene was also noted with TFA-LNAPL but was well after the isolated detection of phenanthrene and included multiple

confirming samples. In the absence of confirmatory samples it is difficult to determine the significance, if any, of the phenanthrene detections.   Any breakthrough of isolated NAPL volumes would have been expected to cause exceedances in naphthalene as well as phenanthrene.
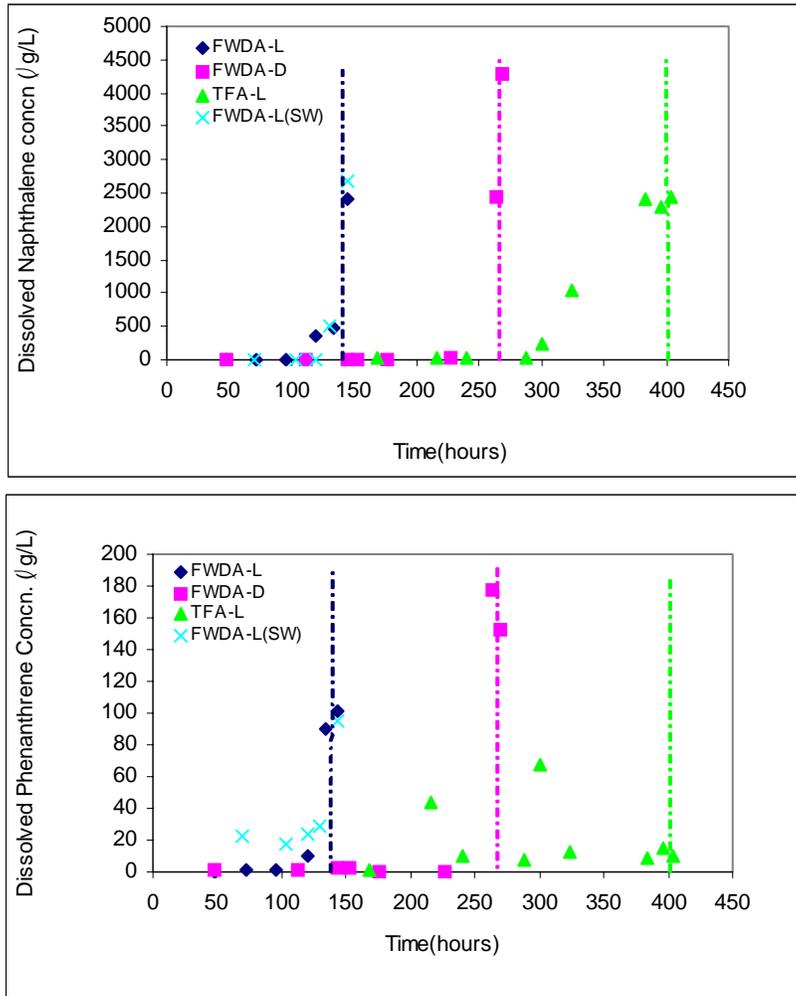
 Figure 10. Dissolved Naphthalene and phenanthrene concentration in the effluent with ET-1 organoclay. SW refers to experiments with site water and dashed lines refer to NAPL breakthrough

In the continuous slow-flow experiments, NAPL injection was halted upon breakthrough and water injection was initiated to evaluate leaching or mobilization of NAPL. 3-4 hours was required to remove NAPL that had already passed through the bed and had

filled the effluent dead volume at the top of the column. Continued water injection after removal of this NAPL led to no additional NAPL discharge or observation of NAPL migration in the column. For dissolved phase analysis, the effluent tubing that had been contaminated with NAPL was changed with clean tubing and water samples were taken for dissolved PAH concentration measurement during continued water injection. In all cases, however, dissolved phase from the NAPL saturated column remained at high levels before and after tubing replacement, as shown in Figure 11.   Although no NAPL was visually mobilized from the column after 3 or 4 hours, the dissolved naphthalene and phenanthrene was continually detected in the effluent even after one week and no decreasing trend was noted. The naphthalene and phenanthrene concentration are in the range of 3 to 8 mg/L and 40 to 80 µg/L, respectively. Although good control of both dissolved and free phase contamination was noted with fresh organoclay, once saturated with NAPL, the effluent water from the organoclay contained a continuous burden of contaminants.
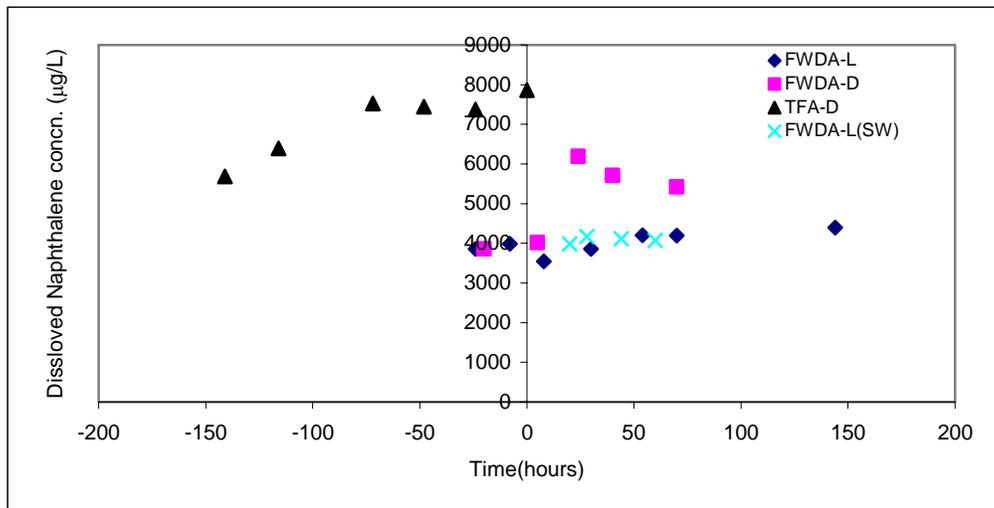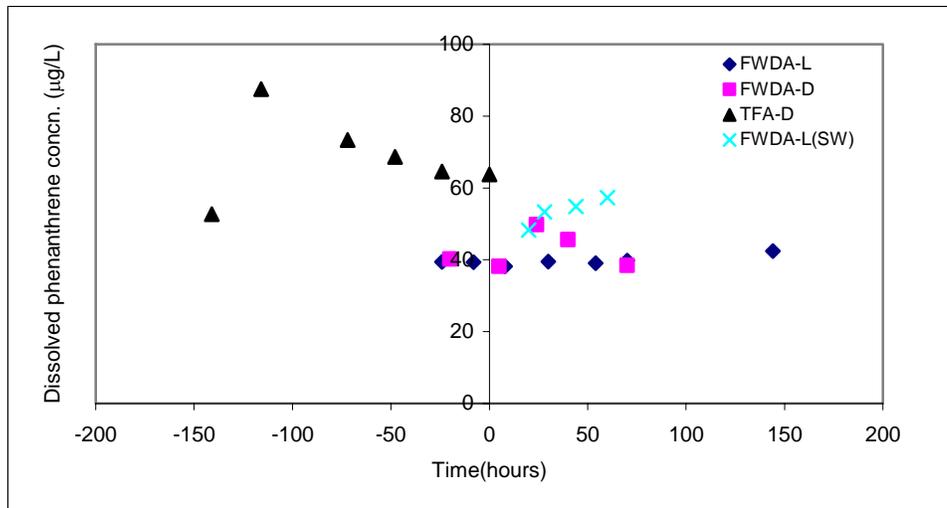
Figure 11. Dissolved naphthalene and phenanthrene concentrations in the effluent after NAPL breakthrough and water was pumped. Zero represents the time of effluent tubing replacement.

After several days of water flow through the organoclay column saturated with FWDA-LNAPL, the column was allowed to drain and rewetted with water twice (once with laboratory water and once with site water). In both cases, no NAPL was observed in the effluent, and the dissolved naphthalene and phenanthrene concentration was not significantly changed after this draining-wetting cycle. The results indicated that NAPL migration was not influenced by the drainage and rewetting mechanism.   The volume of NAPL that saturates the organoclay to capacity is effectively sorbed to the organoclay even though the introduction of additional NAPL will pass through the organoclay layer.

4.4 Permeability

4.4.1 Permeability of organoclays with respect to water

Before injection of NAPLs to any column, organoclay or sand and organoclay mixture were first saturated with water. The permeability of ET-1 and PM-200 organoclays as defined by water injection was 20.0 and 11.3 darcy, respectively, equivalent to a medium sand. Permeability of sand and organoclay mixtures decreased by a factor of 2 to 5 depending on the ratio of the sand to organoclay (Table7). This is because the sand had finer particles than the organoclays and exhibited a lower intrinsic permeability.

Table 7. Permeability of organoclays and organoclay/sand mixtures to water

Media	ET-1	ET-1/SAND (1:10)	PM-200	PM-200/SAND (1:2)	PM/200/SAND (1:10)
Permeability (darcy)	20.0	4.9	11.3	6.4	2.5

4.4.1 Permeability of organoclays with respect to NAPLs

The injection of NAPL to the organoclays will reduce the effective permeability of the organoclays for two reasons. The partial saturation of the organoclays with NAPL decreases the relative permeability of the NAPL (i.e. the presence of residual water will limit the pore space available to the NAPL and resist its flow through the media). In addition, the media swells during the NAPL sorption process, filling some of the available pore space and further resisting flow of the NAPL. The time required for swelling to be complete (24-48 hours after coming in contact with NAPL) also meant that the permeability of organoclays with respect to NAPL was dependent upon time of exposure to NAPL and thus indirectly the injection flow rate. As a result, the injection of NAPL and allowance of time for NAPL sorption related swelling would give rise to dramatically decreased effective permeability. The more rapid and more significant swelling of the PM-200 product associated with its greater capacity for NAPL also gives rise to a more dramatic decrease in permeability. Note that applications of the organoclays to oilfield water cleanup shows little or no swelling of these organoclays when subjected to dilute aqueous emulsions of NAPL (e.g. <1% NAPL in water) (CETCO, personal communication). If the NAPL-water mixture contacting the organoclay at the McCormick and Baxter site was of this form, little or no swelling and changes in permeability would be expected.

A) Rapid intermittent injection

Compared to the permeability with respect to water, the effective permeability of ET-1 decreased from 20 to 4.9 darcy (and 2.1 darcy in a replicate). At a Darcy velocity of 0.28 cm/min there is little opportunity for swelling of the organoclay to occur during the injection suggesting that the reduction in effective permeability is largely due to relative

permeability effects in the partially saturated organoclay.   After pausing injection for 2.5 hr, the permeability of the ET-1 decreased by an additional factor of approximately 2, presumably the effect of the beginning of organoclay swelling. The effective permeability of the higher capacity and more rapidly swelling PM-200 organoclay, however, decreased by two orders of magnitude to $1.7*10^{-2}$ darcy (see Table 8) during the same 2.5 hr pause. The ET-1 exhibited a comparable two order of magnitude reduction in permeability that was noted after allowing 5 days before reinitiating NAPL injection. The initial reduction in effective permeability of a sand /PM-200 mixture (2:1) was similar to that of pure ET-1 (Table 8). After allowing 5 days for swelling of the PM-200 organoclay, however, NAPL could not be pumped through the column even at a very slow flow rate (1.5 cm/day) indicating a reduction in permeability with time greater than that of the pure ET-1.

Table 8. Effective permeability of ET-1, PM-200, and sand/PM-200 mixture (2:1) to FWDA-LNAPL with rapid intermittent injection

Effective permeability(darcy)	ET-1	PM-200	sand/PM-200 mixture (2:1)
Initial	4.9	2.1	1.1
After 2.5 hrs of no flow	2.9	$1.7*10^{-2}$	0.7
After 5d of no flow	$2.2*10^{-2}$	N/A	N/A

B) Slow continuous injection

In low flow testing, the measured effective permeabilities of ET-1 were similar to that measured after waiting five days before restarting NAPL flow. That is, the injection was sufficiently slow that organoclay swelling was nearly complete by the time NAPL passage through the column was complete. The effective permeabilities of ET-1 with respect to FWDA-DNAPL, TFA-LNAPL, and TFA-D NAPL were not significantly different and displayed no clear trend with time (Figure 12). However, the effective permeability of ET-1 with respect to FWDA-LNAPL was significantly higher than the measurement with the other three NAPLs and increased with time. The increase in

permeability with time suggests that the FWDA- L NAPL degraded the resistance to flow of the ET-1 organoclay over time. It is unclear if this was the result of any physical degradation of the organoclay although it was apparently not associated with any significant change in sorption capacity.

Saturation of ET-1 with site water rather than laboratory water did not have significant effect on the effective permeability of ET-1 with respect to FWDA-LNAPL. As with laboratory water, however, the permeability increased over time when exposed to this NAPL.
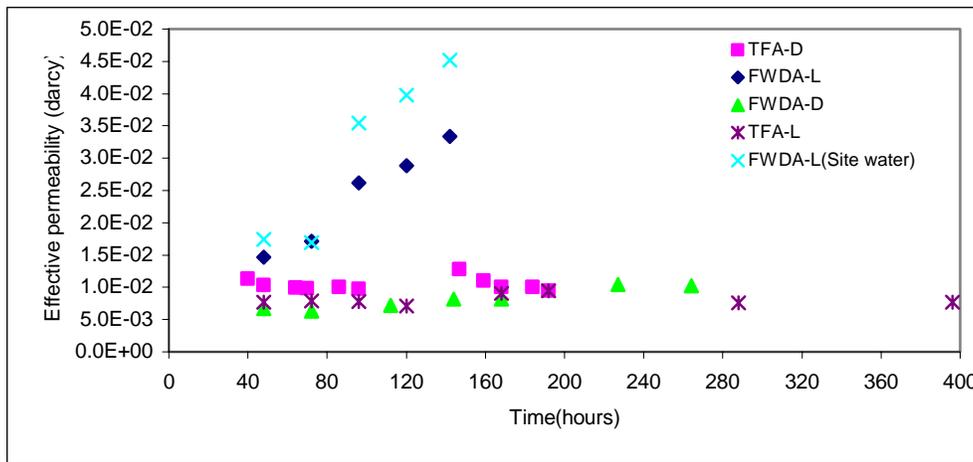
Figure 12. Effective permeability of ET-1 with respect to FWDA-LNAPL, FWDA-DNAPL, TFA-LNAPL and TFA-DNAPLs

The effective permeability of PM-200 organoclay also decreased dramatically in the continuous low flow experiments, decreasing an additional two orders of magnitude over the intermittent water injection experiments, presumably due to the greater time provided for swelling of the organoclay under low flow conditions. The permeability reduction in the PM-200 organoclay was reduced to the point that the design pressure of the column experiments (60 psi) was reached and the experiment had to be stopped.   At shutdown, the NAPL was wetting only approximately 2 cm of organoclay. Both FWDA-LNAPL and TFA-DNAPL was successfully pumped through the column with the mixture of PM-200 and sand at a ratio of 1:10. The effective permeability of this mixture was 4.7×10^{-2}

and $2.2*10^{-2}$ darcy for FWDA-L and TFA-DNAPL, respectively, which increased two
orders compared to the pure PM-200.   The permeability of the sand/PM-200 mixture was
higher than pure ET-1. Due to the greater capacity of the PM-200 for sorption of the
NAPL (compared to ET-1), it is expected that the least cost organoclay layer is one which
contains PM-200 mixed with sand. Such a layer would need to be equal or slightly
thicker than a pure ET-1 layer in order to achieve similar NAPL capacities, would exhibit
permeabilities similar to the pure ET-1 after exposure to NAPL, but would contain far
less of the relatively expensive organoclay. Offsetting this advantage is the difficulty of
mixing sand and organoclay and placing such a mixture uniformly.

5 Strength

The strength of water saturated ET-1, NAPL saturated ET-1, water saturated PM-200,
and NAPL saturated PM-200 are summarized in Table 9. This table presents the total
applied stress at specimen failure for each organoclay and treatment.

Table 9. Total stress of water saturated and NAPL saturated organoclays

Media	ET-1(water)	ET-1 (NAPL)	PM-200 (water)	PM-200 (NAPL)
Total stress at failure (lb/sq inch)	214.1 (205.1,223.2)	110.6 (117.3,103.9)	223.3 (228.4, 218.3)	37.2

NAPL saturated organoclays had significantly lower bearing total stress or load bearing
capacity compared to water saturated organoclays. NAPL saturated ET-1 has only half of
the loading bearing capacity compared to the water saturated NAPL, but these two
specimens behaved similarly during load test. There was no distinguishable failure plane
and only a slow bulge was observed in the specimen in response to the loading. The
NAPL saturated PM-200, however, failed at lower pressures and with a distinguishable
failure plane.   Although the stress applied at failure is only 15% of the stress sustained
by the water saturated PM-200, it still represents the pressure associated with a column of

sand more than 50 ft tall (at 100 lb/ft^2). Thus ET-1 and PM-200 are expected to support the weight of an overlying sand cap without failure if saturated with water or NAPL.

Summary

Two organoclays were found to be effective sorbent for NAPLs. PM-200 organoclay was found to exhibit greater sorption of NAPL but with greater swelling and permeability reduction as a result. The sorption capacity of both organoclays during flow-through experiments was found to be less than in batch experiments due to the time requirement for achievement of full sorption capacity and flow non-uniformities. Mixtures of sand and organoclay would more closely approach batch absorption capacities due to the more effective utilization of the organoclay. Initial movement into the organoclay column would create a partially NAPL saturated region that would slowly fill during swelling with continuous injection. No PAHs were detected in the column effluent until visual breakthrough of NAPL. Subsequent to NAPL breakthrough with no fresh organoclay to remove dissolved phase contamination, the effluent water contained high concentrations of dissolved PAHs, similar to that expected in equilibrium with the NAPL. NAPL, however, was not mobilized from the column by continued injection of water even after complete saturation of the organoclay.

Both of the test organoclays exhibited significantly reduced permeability as a result of swelling during sorption of NAPL. PM-200 has a higher sorption capacity and much lower effective permeability with respect to the NAPL phase. The effective permeability of the NAPL-contacted organoclay was similar to that expected for silt (PM-200) or silty sand (ET-1) and would tend to encourage lateral movement of NAPL ensuring more effective use of the sorption capacity of organoclay surrounding an active seep area. Note that the impact of the permeability change would not be significant if the surrounding media were composed of silty or finer sediments. Introducing organoclay in a mixture with sand increased the effective permeability and maintained or increased the sorption capacity per unit mass of organoclay. For ET-1 and sand mixtures, the increase in effective permeability was approximately inversely proportional to the reduction in sorption capacity. But for sand and PM-200 mixture, a similar reduction in sorption

capacity corresponded to dramatic increases in the effective permeability by two orders of magnitude. Because a mixture with sand increases the sorptive capacity of the organoclay (up to that expected during batch tests), and reduces the permeability reduction associated with organoclay swelling, an optimal organoclay design would be a mixture with sand, balancing reductions in effective permeability with effective utilization of organoclay.

After sorption of NAPL, both organoclays exhibited decreased strength compared to fresh organoclays. The PM-200 organoclay was much weaker than ET-1 after sorption of NAPL but neither would be expected to fail under normal sediment cap loading.

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