

NAPL SORPTION CAPACITY AND PERMEABILITY OF ORGANOCLAY/ SAND MIXTURE

This study was conducted by the University of Texas at Austin Department of Civil, Architectural and Environmental Engineering for the Oregon State Department of Environmental Quality. A series of experiments were conducted to assess the sorption capacity and permeability of organoclay when exposed to four different nonaqueous phase liquids (NAPLs) from the McCormick & Baxter Creosote Site. The capacity of the organoclay was independent of the type of NAPL. The capacity of CETCO PM-200 organoclay as measured by batch testing was ≥ 4.4 grams NAPL/gram organoclay. The capacity of CETCO PM-200 organoclay as measured by column testing was ~ 3 gram NAPL/ gram organoclay. The difference is likely attributed to partial saturation of the upper portion of organoclay in the column flow.

No significant swelling is expected with dilute aqueous emulsions of NAPL (e.g., $<1\%$ NAPL in water). Swelling of the organoclay and reduction of permeability did occur with concentrated NAPL. Swelling was reduced and permeability was less affected when sand was mixed with CETCO PM-200 organoclay in ratios of 3:1 to 10:1 (by weight), although sorption capacity was reduced.

The results indicate that optimal design of in-situ reactive caps and permeable reactive barriers need to take into account overall sorption capacity and effective permeability.

NAPL sorption Capacity and Permeability of Organoclay / Sand Mixtures

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Introduction

Strongly solids-associated contaminants such as metals, PCBs and PAHs can often be effectively managed with a combination of the conventional technologies of dredging or capping. Many of the most challenging sites awaiting effective remediation, however, are contaminated with separate phase contamination (nonaqueous phase liquids or NAPLs). Organoclays have a high capacity for sorption of nonaqueous phase liquids (NAPL) and have been employed in a variety of applications for the control of these contaminants. A developing application is the use of organoclay as a subaqueous cap to contain NAPL contaminants in sediments. At the McCormick and Baxter Creosote contaminated site in Portland OR, a 12" thick layer of organoclay was employed to contain NAPL migration front the site. Organoclay was also employed in CETCO reactive mats to control NAPL mobilized by gas seeps in particular areas at and near the river bank. The Oregon Department of Environmental Quality contracted with the University of Texas to evaluate the performance of the organoclay placement.

Initial studies with the bulk placement approach identified the potential for high NAPL sorption capacity of the placed organoclay but also identified problems with swelling and subsequent significant reductions in permeability of the organoclay (Reible, 2005). The permeability reductions suggested that full utilization of a pure bulk organoclay treatment bed might not occur due to flow diversion around the low permeability zones. Reible (2005) evaluated several possible approaches to overcoming this problem at future sites including placement of a bulk sand/organoclay mixture which would effectively disperse the organoclay for more efficient utilization.

These initial studies evaluated a limited range of organoclay and sand mixtures. In an effort to provide better guidance to subaqueous cap designers, the current study was undertaken. The objective of the current study was to determine the NAPL sorption capacity and permeability of a particular organoclay, CETCO PM-200, in a variety of sand/organoclay mixtures. Specific sand/organoclay mixtures evaluated included 3:1, 5:1 and 10:1. NAPL employed for the testing was collected from the McCormick and Baxter site. NAPL both less dense than water (LNAPL) and more dense than water (DNAPL) from both the tank farm area (TFA) and a former waste disposal area (FWDA) were used in the tests. Physical properties of the NAPLs are shown in Table 1

Table 1. Physical properties of NAPLs

NAPLs	FWDA (LNAPL)	FWDA (DNAPL)	TFA (LNAPL)	TFA (DNAPL)
Density (g/cm ³)	0.9867	1.0028	0.9721	1.0919
Viscosity (cp)	22.8	16.8	17.0	26.8
Water content (%)	11.9 (11.9-12)	32.8 (32.2-33.5)	45.7 (43.3-48.1)	5.3(4.3-6.3)

Methods

The sorption capacity of the CETCO PM-200 organoclay with respect to the different NAPLs was measured in both batch tests and column flow through tests. In batch tests, approximately 2g organoclay were first saturated with water. After removing the extra water, an excess volume of NAPL

was added to the water saturated organoclay and allowed to equilibrate. The free liquid phase including NAPL and water was removed by glass pipette, and the remaining organoclay and NAPL was dried at low temperature (~50 °C). Sorption capacity of NAPL was determined as the ratio of the weight of NAPL sorbed to the weight of organoclay.

In the column tests, NAPL was injected into a column (4.8*15cm) filled with an organoclay/sand mixture with a syringe pump. The organoclay was mixed with sand at different ratios (sand:organoclay of 3:1, 5:1 and 10:1). Two NAPLs from McCormick & Baxter Creosoting Company site, FWDA-LNAPL and TFA-LNAPL were pumped through the sand and PM-200 mixture at a superficial velocity of 1 cm/day. The effective sorption capacity was estimated by mass of NAPL injected at breakthrough. The conductivity of the NAPL saturated column was estimated from the pressure difference across the column required to maintain the superficial velocity of 1 cm/day. The conductivity was converted to an effective permeability with the viscosity and density of the injected NAPL.

Results

A) Batch test - Sorption Capacity

Extensive swelling and apparent loss of particle integrity was observed during batch sorption tests but these tests are designed to evaluate the maximum potential sorption capacity, not necessarily the sorption capacity. 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. A summary of the sorption capacities of PM-200 measured in batch studies with each of the NAPLs and the calculated material balance closure is listed in Table 2. Material balance differences from 100% indicate potential error in the measured sorption capacity due to failure to completely separate phases. The results indicate oh at the potential capacity of the PM-200 again clay, however, is well in excess of 4 g NAPL/gr organoday.

Table 2. Sorption capacity of PM-200 (g water free oil /g of organoclay) with respect to NAPLs in batch test

	Sorption Capacity g/g (std dev)	NAPL Balance %	Water Balance %
FWDA-LNAPL	4.60 (0.04)	97 (2)	120 (6)
FWDA-DNAPL	4.82 (0.06)	82 (1)	126 (4)
TFA-LNAPL	4.41 (0.03)	75 (3)	124 (3)
TFA-DNAPL	4.50(0.11)	84(4)	115(5)

B) Column test - Sorption Capacity

As shown in Table 3, the sorption capacity of PM-200 in the flow-through experiments was less than observed in batch tests due to flow non-uniformity and loss of organoclay utilization efficiency. However, swelling and loss of particle integrity were similarly reduced. At higher sand/organoclay mixtures organoclay utilization was higher due to better control over flow maldistribution. Sand/organoclay ratio of (10:1) allowed sorption of NAPL at close to batch sorption experiments (i.e. NAPL sorbed per gram of organoclay) (Table 2). Sorption capacity of the mixture with respect to FWDA-LNAPL was typically lower than the measurement with the TFA-DNAPL although batch tests

did not show significant difference. The higher moisture content of the FWDA-LNAPL may have affected organoclay utilization.

Table 3. Sorption capacity of PM200 and sand mixture at slow continuous injections

Sand to clay ratio	FWDA-LNAPL			TFA-DNAPL		
	10:1	5:1	3:1	10:1	5:1	3:1
Sorption capacity(g/g)	0.27 (2.97 g/gOC)	0.31 (1.86 g/g OC)	0.34 (1.35 g/g OC)	0.30 (3.30 g/gOC)	0.38 (2.28 g/gOC)	0.44 1.76(g/gOC)
Effective sorption capacity(g/g)	0.24 (2.64 g/gOC)	0.29 (1.74 g/g OC)	0.34 (1.35 g/g OC)	0.30 (3.30 g/g oC)	0.35 (2.1 g/gOC)	0.43 (1.72 g/gOC)

Effective permeability

The sorption of NAPL by the organoclay will reduce the effective permeability of the media 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 effective permeability of pure PM-200 with water injection was measured to be approximately 11 darcys and 2.5 darcys at 10:1 sand/organoclay ratio (1 darcy = 10^{-3} cm = 10^{-8} cm²). The permeability of a pure PM-200 layer after saturation with NAPL was not measured because the experimental apparatus was designed to measure higher than the observed permeability. The permeability of the NAPL saturated pure PM-200 was below the measurable limit of the system at approximately 5 (10^{-4}) darcys, the approximate permeability of a fine silt. The permeability of a mixture of sand and PM-200 was much higher than this permeability due to the greater dispersion of the organoclay. The effective permeabilities of the sand and organoclay mixtures (10:1, 5:1 and 3:1) after NAPL saturation are listed in Table 4.

The variability between measurements, based upon a limited set of experiments with the FWDA-LNAPL, is approximately 10^{-2} darcys. Due to the particle size and density difference of the diluent sand and organoclay, homogeneous packing is difficult and gives rise to the sample to sample variability. Thus the apparent slight decrease in effective permeability of the 5:1 versus 3:1 mixtures of sand and organoclay is not significant. If a large number of replicates were conducted it would be expected that the effective permeability of the 5:1 mixture would be between that of the 3:1 and 10:1 mixtures. The permeability changes in all 3 mixtures are relatively modest (factor of two to three from highest organoclay mixture to lowest). The permeability of all of these mixtures is in the range of a silty sand.

Table 4. Effective permeability of PM-200 and sand mixture at slow continuous injections

Sand to clay ratio	FWDA-LNAPL			TFA-DNAPL		
	10:1	5:1	3:1	10:1	5:1	3:1
Permeability (darcy)	5.88×10^{-2}	2.16×10^{-2}	3.12×10^{-2}	2.24×10^{-2}	0.57×10^{-2}	0.67×10^{-2}

The mixture of 10:1 exhibited highest permeability and highest organoclay utilization efficiency. Due to the comparatively small amount of organoclay in the 10:1 layer, however, the total NAPL sorption for a given layer thickness will be less than the other two mixtures. Utilization efficiency and total capacity must be balanced in any sand/organoclay mixture design. Permeability seems to be less of an issue for sand/organoclay mixtures of greater than 3:1 because of all such mixtures are relatively permeable.

Summary

Pure PM-200 organoclay has high sorption capacity but also shows significant swelling and subsequent permeability reduction after contact with NAPL. The sorption capacity of PM-200 during flow-through experiments was found to be less than in batch experiments due to flow maldistribution and the time-dependent nature of the swelling and permeability reduction. Mixtures with sand and PM-200 limited the impact of NAPL associated permeability changes and increased the effective capacity (g NAPL per g organoclay) and therefore provided a lower cost per unit NAPL absorbed. This suggests that an optimal organoclay design would be a mixture of PM-200 with sand, balancing overall layer thickness capacity with effective permeability of the layer and efficient utilization of organoclay.

Reference

Reible, D.D. (2005) Final Report Organoclay Laboratory Study - McCormick & Baxter, Oregon Department of Environmental Quality Project 005-05