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The Versatility Of Organoclay For Permeable Barriers

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Abstract: Permeable barriers at creosote and PNAH containing sediments require a barrier which is permeable and, at the same time, traps creosote and PNAH plumes. Such plumes can also include such organic hydrocarbons as PCP and other chlorinated phenolic compounds, PCB's and BTEX's. Lab tests and actual field applications have shown that organically modified clays are an excellent medium to trap such compounds in groundwater and in sediments at old MPG sites. The PNAH compounds include naphthalene, pyrene, fluorine, anthrazene and others. Organoclays are very well suited to trap these compounds efficiently. Since pesticides are also a serious problem for groundwater and sediments, a brief literature review is included. This article discusses various laboratory tests and actual field results, which have been obtained over the years, showing the suitability of organoclays as a component of permeable barriers.

Key words: organoclay; permeable barriers; sediment stabilization.

1. INTRODUCTION

Permeable barriers at creosote and PNAH containing sediments, require a barrier, which is permeable, and, at the same time, traps creosote and PNAH plumes. Such plumes can also include such organic hydrocarbons as PCP and other chlorinated phenolic compounds, PCB’s and BTEX’s. Lab tests and actual field applications have shown that organically modified clays are an excellent medium to trap such compounds in groundwater and in sediments at old MPG sites. The PNAH compounds include naphthalene, pyrene, fluorine, anthrazene and others. Organoclays are very well suited to trap these compounds efficiently. Since pesticides are also a serious problem for groundwater and sediments, a brief literature review is included. This article discusses various laboratory tests and actual field results, which have been obtained over the years, showing the suitability of organoclays as a component of permeable barriers.

2. WHAT IS AN ORGANOCLAY?

Organoclays have become an important part of the treatment train to remove creosote and PNAH from contaminated groundwater at old wood treating facilities and MGP sites. Organoclays consist of bentonite that is modified with quaternary amines. Bentonite is a volcanic rock whose main
Contaminated Soils - Remediation

constituent is the clay mineral montmorillonite. This gives the bentonite an ion exchange capacity of 70-90 meq/gram. By exchanging the nitrogen end of a quaternary amine onto the surface of the clay platelets, by cation exchange (Exchanging the sodium or calcium ion on the surface for the nitrogen which is positively charged), the bentonite now becomes organically modified and thus organophilic, which also means hydrophobic (Lagaly, 1984). The clay is arranged in a layered structure, platelets stacked on top of each other. When these platelets are placed into water, the amine chains are activated and stand up like dry hair causing pillaring of the platelets, and allowing the end of the amine chains to stand or dangle into the water, reacting with organics that pass by (Mortland et al, 1986). The chains will then dissolve or partition into large organic compounds such as sparingly soluble chlorinated hydrocarbons. Oil is the most prominent of these (Smith et al, 1990). These same compounds, on the other hand, will blind the pores of activated carbon.

3. CASE HISTORY FROM CLEANING A SUMP SLUDGE

A sump sludge contained a wastewater that required cleaning before it could be discharged. The water was passed through 300 lb of organoclay/anthracite and then discharged. The results are shown in Table 1.

Table 1. Sump Sludge Containing a Wastewater that Requires Cleaning Before Discharge

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Inlet</th>
<th>Outlet</th>
<th>Solubility mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>29%</td>
<td>65 mg/kg</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>12 mg/kg</td>
<td>1 mg/l</td>
<td></td>
</tr>
<tr>
<td>BOD</td>
<td>429 mg/kg</td>
<td>120 mg/kg</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>16,084 mg/l</td>
<td>202 mg/l</td>
<td></td>
</tr>
<tr>
<td>Anthrazene</td>
<td>2,000 mg/kg</td>
<td>&lt;10 mg/l</td>
<td>0.073</td>
</tr>
<tr>
<td>Benzo (A) Anthrazene</td>
<td>5,300</td>
<td>&lt;10</td>
<td>0.014</td>
</tr>
<tr>
<td>Fluorene</td>
<td>10,000</td>
<td>&lt;10</td>
<td>1.908</td>
</tr>
<tr>
<td>Indeno (1,2,3,C,D) Pyrene</td>
<td>200</td>
<td>&lt;25</td>
<td>0.62</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>29,000</td>
<td>&lt;10</td>
<td>34.4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>40,000</td>
<td>&lt;10</td>
<td>1.29</td>
</tr>
<tr>
<td>Pyrene</td>
<td>8,000</td>
<td>&lt;10</td>
<td>0.14</td>
</tr>
<tr>
<td>TPH</td>
<td>172,000</td>
<td>&lt;0.5 mg/l</td>
<td></td>
</tr>
</tbody>
</table>

No change-out of organoclay was required. The adsorber ran at 5 gpm.

3.1 Laboratory Test Results with 1,4 Dioxane

A batch test was conducted to determine the ability of a non-ionic organoclay to remove 1,4 dioxane from water. The testing method was:

Sorbent, 1,4 dioxane solution, and organic free, deionized (DI) water where combined in 10 ml glass tubes. The initial concentration of the contaminants was between 300-500 mg/l. The mass of sorbent used was between 0.5 and 1 grams. Tubes carrying the diluted contaminant, but no sorbent, where carried through the test and analyzed to determine losses due to reasons other than sorption to the sorbent. No significant losses where measured, and recovery in all tubes was determined to be greater than 95%. Tubes containing DI water and sorbent where carried through the test and analyzed to determine the possible presence of the contaminant on the sorbent. For each contaminant, negligible amounts where detected. The tubes where capped and shaken for one day at 23 degrees +/- C. After equilibration, the tubes where centrifuged at 2000 g and the supernatant was analyzed by gas chromatography with a flame ionized detector to quantify the concentration of the organic solute. The sorbed concentration of each solute was determined by difference assuming negligible losses of the solute. The results are:

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Water was spiked with 958 mg/l 1,4 dioxane aqueous equilibrium concentration. The mass sorbed by 2 grams organoclay was 27.09 mg/l, or 2.709% of the organoclays weight. These results confirm the ability of non-polar organoclays to remove chlorinated organic hydrocarbons from water.

### 3.2 Laboratory Test Result with Two Nitrobenzenes

Nitro aromatic compounds are used by industry in pesticides, explosives, solvents, and intermediates in chemical synthesis (Boyd et al., 2001). These contaminants appear in soils and sediments and can be toxic to humans and animals. The ability of a powdered, non-polar organoclay to remove substituted nitrobenzenes from water was tested in the lab with the same method as 1,4 dioxane. The compounds tested for are 1,3-Dinitrobenzene and 1,3,5-Trinitrobenzene. The same testing method was used as for 1,4 dioxane (see above). The results are shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium Aqueous Concentration (mg/l)</th>
<th>Mass Sorbed (mg/l)</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Dinitrobenzene</td>
<td>157.7</td>
<td>6.4</td>
<td>0.644</td>
</tr>
<tr>
<td>1,3,5-Trinitrobenzene</td>
<td>38.3</td>
<td>12</td>
<td>1.201</td>
</tr>
</tbody>
</table>

These results show that a regular organoclay can be used to fixate substituted nitrobenzene compounds, thus it is a viable component of permeable barriers.

### 3.3 Case History for Federal Creosote Superfund Site

The groundwater at this site showed the following data:

- COD influent: 68 ppm, primarily PCP and other phenols.
- 10-20 ppm benzene.
- COD effluent after organoclay tank: 19.5 ppm
- After lead Granular activated carbon tank: Non detect.

TSS readings were 35 ppm after the lead carbon unit. When organoclay was included, the effluent after organoclay was 3 ppm. TSS where primarily iron 3. Carbon removed all of the benzene.

- Flow rate: 170 gpm
- Organoclay used: 20,000 lb; activated carbon used: 40,000 lb.

### Table 2. Ability of a Powdered, Non-Polar Organoclay to Remove Substituted Nitrobenzenes From Water

### Table 3. Non-Ionic Organoclays’ Removal Capacity of Phenolic Compounds as Determined by Batch Tests (Alther, 1997)

**This means that 100 grams of organoclay can remove 87 grams of PCP (Alther, 1997).**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>25ppm in Water</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>78.2% of organoclay weight</td>
<td>86 g/l</td>
</tr>
<tr>
<td>2,4,6 Trichlorophenol</td>
<td>98.3% of organoclay weight</td>
<td>800 mg/l</td>
</tr>
<tr>
<td>3 Chlorophenol</td>
<td>89.8% of organoclay weight</td>
<td>27.7 g/l</td>
</tr>
<tr>
<td>*Pentachlorophenol (PCP)</td>
<td>87% of organoclay weight</td>
<td>80 mg/l</td>
</tr>
</tbody>
</table>

*Table 4. Literature Review of the Ability of Organoclays to Remove Pesticides. A comprehensive analysis of pesticide removal by organoclays, from water, is found in Sanchez-Martin, et al, 2006. The following pesticides were studied:*

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical Formula</th>
<th>Water Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penconazole</td>
<td>1-[2-(2,4-dichlorophenyl)pentyl]-1,2,4-triazole</td>
<td>73</td>
</tr>
<tr>
<td>Linuron</td>
<td>3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea</td>
<td>81</td>
</tr>
<tr>
<td>Atrazine</td>
<td>2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine</td>
<td>30</td>
</tr>
<tr>
<td>Alachlor</td>
<td>2-chloro-2',6'-diethyl-N-methoxymethylacetanilide</td>
<td>240</td>
</tr>
<tr>
<td>Metalaxyl</td>
<td>methyl N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-DL-alanine</td>
<td>8400</td>
</tr>
<tr>
<td>Lindane</td>
<td></td>
<td>10 ppm</td>
</tr>
</tbody>
</table>

*(From Sanchez-Martin, et al, 2006)*
Comparing these solubilities with organic hydrocarbons of known affinity to organoclays, we surmise that the first 4 and Lindane will be easily removed. Excellent results where also reported by Hermosin and Cornejo (1992) for adsorption of 2,4-D pesticide (2,4-dichlorophenoxy acetic acid) by standard organoclays. Tests conducted in our laboratory revealed good removal capacity by non-ionic organoclay for alachlor, diazinin, metalochlor, trifuralin, and 2,4,5-T.

The authors of the pesticide article used a different organoclay, but the results when compared to the quaternary amine (octadecyltrimethylammonium bromide) used in this study will not be markedly different (di-methyl di-hydrogenated tallow ammonium chloride). Those authors concluded that soils containing organoclays provide barriers, which drastically decrease the mobility of these pesticides.

The lab results obtained from a mini-column test are shown in table 5 (Alther, 2004, 2002).

<table>
<thead>
<tr>
<th>Solubility</th>
<th>% By Organoclay Weight Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>39</td>
</tr>
<tr>
<td>Toluene</td>
<td>44</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>insoluble</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>24.3</td>
</tr>
<tr>
<td>PCB 1260</td>
<td>52 % by clay weight</td>
</tr>
</tbody>
</table>

Other case histories showed excellent removal capacity of organoclay for trichloroethene (sol. 1100 mg/l), and 1,1,1-dichloroethene (sol. 335 mg/l).

<table>
<thead>
<tr>
<th>Figure 1A: Organoclay Naphthalene Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1B: Organoclay Isotherm with PCB-1260</td>
</tr>
<tr>
<td>Adsorption = Concentration $^{0.5373441 \times 10^{2.352119}}$</td>
</tr>
<tr>
<td>Figure 1C: Organoclay Adsorption of Xylene (ortho)</td>
</tr>
<tr>
<td>Adsorption = Concentration $^{0.708464989 \times 10^{1.178918}}$</td>
</tr>
</tbody>
</table>

**Figure 1.** Isotherms for Three Compounds conducted by the ASTM Isotherm Method.

### 4. SUMMARY REPORT OF BATCH EXPERIMENTS INVESTIGATING THE SORPTION OF TCE ONTO PT-1 ORGANOCLAY POWDER

This report presents data from batch experiments studying the sorptive capacity of PT-1 sorbent to TCE solutions. Batch sorption experiments were performed by combining sorbent, aqueous TCE solution, and organic-free deionized (DI) water in 15-mL glass tubes. Sorbent mass used in each isotherm experiment was 0.3 g. The aqueous TCE solution was prepared at a concentration of 442 mg/L TCE. The aqueous TCE solution was mixed with DI water prior to contacting the sorbent materials in the following ratios: 100% (v/v) TCE solution; 80% TCE solution/20% DI water; 60% TCE solution/40% DI water; 40% TCE solution/60% DI water; 20% TCE solution/80% DI water.

The tubes were capped and shaken for 1 day at 23 ± 1 °C to allow sufficient time to reach equilibrium. The difference between the initial and final (equilibrium) TCE mass in the aqueous phase was considered equal to the mass sorbed to the solid phase. Samples were analyzed using gas chromatography. The results of sorption experiments were fit to Langmuir, Freundlich or linear isotherm, as described by equations 1 to 3 respectively:
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\begin{align*}
C_s &= \frac{bC_eQ}{1+bC_e} \quad \text{equation 1} \\
C_s &= K_f \cdot C_e^n \quad \text{equation 2} \\
C_s &= K_d \cdot C_e \quad \text{equation 3}
\end{align*}

where \( C_s \) = equilibrium sorbed metal concentration (mg/g), \( b \) (1/mg) and \( Q \) (mg/g) are fitted isotherm; parameters, \( C_e \) (mg/L) is the equilibrium aqueous solute concentration and \( K_d \) = sorption distribution; coefficient (L/g), \( K_f \) = Freundlich coefficient.

Results in this report are presented below in Figure 2, Table 6 and 7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Sorption of TCE onto PT-1}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{lllll}
\hline
Initial Concentration (mg/L) & Equilibrium aqueous concentration (mg/L) & Equilibrium sorbed concentration (mg/g) & Percentage Sorbed (%) \\
\hline
PT-1_0 & 0.00 & 0.00 & 0.00 & 0.00 \\
PT-1_1 & 93.61 & 9.81 & 3.64 & 0.36 \\
PT-1_2 & 193.14 & 24.73 & 6.55 & 0.65 \\
PT-1_3 & 278.68 & 50.79 & 11.22 & 1.12 \\
\hline
\end{tabular}
\caption{Estimated Mass of TCE Sorbed per Mass of Sorbent in mg/g, and Percent Basis.}
\end{table}
Table 7. Estimated Values for the Sorption Distribution Coefficients for PT-1

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Linear</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_d$ (L/g)</td>
<td>$R^2$</td>
<td>$Q$ (mg/g)</td>
</tr>
<tr>
<td>PT-1</td>
<td>0.244</td>
<td>0.989</td>
<td>4473</td>
</tr>
</tbody>
</table>

The results obtained fit with high regression coefficients all the isotherm models tested. However, the linear tendency of the data agrees with previous research. Linear isotherms for non-polar compounds indicate that the sorption is caused by TCE partitioning between water and the organic matter phase formed by the long chain of quaternary ammonium cations.

5. CONCLUSIONS

These data show the ability of organoclays to remove or fixate a variety of recalcitrant compounds of low solubility from water and in soils. There is an industry in existence which manufactures and sells organoclays for such applications, with a successful track record of 20 years.

REFERENCES

Hermosin, M. C., and Corneo, J., 1992, Removing 2,4-D from water by Organoclays, Chemosphere, 224(10):1493-1503.