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PART V: Remediation

Chapter 14

THE VALUE OF ORGANOCLAYS IN PERMEABLE BARRIERS

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Abstract: The function of permeable barriers is to first, allow the groundwater to flow freely through them, and second, to entrap or destroy chemical contaminants such as metals and organic hydrocarbons. Certain organically modified clays have the ability to act as anion and cation adsorbents, allowing them to remove heavy metals such as Pb and Zn.

A Polar Organoclay removes anions such as hexavalent chrome, arsenate, phosphates, sulfates and nitrates from water. It can also remove humic acids, perchlorate and other negatively charged organic compounds.

A neutral type of Organoclay removes creosote, PNAH's, PCB, dioxene, BTEX and other non-polar organic hydrocarbons of low solubility very effectively.

For good measure, powdered activated carbon can also be included in the barrier mix. Such a design allows for a barrier that retards the movement of organic compounds and metals into the surrounding environment, be that a river or a lake.

This article presents new data on the organoclays capacity for contaminant removal which were obtained in column studies in the laboratory of the University of Virginia.

Key words: Organoclay; sulfate; phosphate; nitrate; perchlorate; chromium

1. INTRODUCTION

Organoclays have been a main staple in the groundwater remediation industry and industrial wastewater cleanup for some 20 years. They are usually incorporated as part of an activated carbon treatment train, such as in “pump and treat systems”. Activated carbon becomes fouled quickly in the presence of oil, grease, natural organic matter, PNA’s, PCB, BTEX, chlorophenols and other large organic hydrocarbons of low solubility. The end user improves the economics of the system drastically by including organoclay, because this media removes seven times as much oil from water as does activated carbon, thus cutting operations costs in half. The “roll off” problem, which takes place in the pores of activated carbon when adsorbed benzene is kicked back off by toluene and xylene due to their lower solubility, is eliminated (Alther, 2004). In those applications, a blend of organoclay with anthracite is usually provided. The organoclay tends to swell somewhat due to the presence of oil (which also reduces channeling), and reduces the filling of interstitial pore spaces by oil, which also results in fouling. Anthracite’s bulk density is almost the same as that of organoclay; therefore separation of the two media after the first backwash is minimized.

When used as a sediment barrier, the organoclay is present as a granule of about 20 x 50 mesh size. The purpose of that size is so that the granules blend in with the sediments, which are usually sand or sandy silt. The organoclay functions as a cap to retard the upward movement of contaminants into the surface water. Groundwater discharges into rivers and lakes. The plume is then either intercepted in this manner, by capping the river sediments with organoclay, or a slurry wall intercepts it where organoclay is blended in with the back fill. Slurry walls are used either as a permeable barrier for new landfills or superfund-type sites, or they are placed as secondary barriers around old, existing walls, which are leaking. In that case, the vibrating-beam type slurry wall is used because it is only 10 inches wide, vs. the three feet of conventional types, and they are much easier and quicker to construct. The backfill of the vibrating-beam slurry wall consists of powdered cement, bentonite, and organoclay, with the emphasis of the design being on the creation of a permeable barrier (Alther et al, 2003). Landfill liners can be constructed with granular or powdered organoclay, depending on the existing soil type (Alther, et al, 1988).

Soil stabilization is conducted by admixing with the soil a blend of Portland cement, fly ash, powdered organoclay and powdered activated carbon. Such a system, which has to pass the TCLP test, fixates organic

hydrocarbons and heavy metals. There are two mechanisms by which organoclay and the contaminants are fixated:

In micro-encapsulation, the microscopic level, the organoclay and the entrapped organic contaminants are entrapped within the crystalline matrix of the solidified mass. This prevents degradation of the organoclay into ultra fine particles, which migrate and, potentially, release organic contaminants. Without the organoclay, the organic contaminants are not bound to the crystalline structure created by the cement and are easily released back into the environment.

In macro-encapsulation, at a larger scale, the organoclay with the sorbed organic contaminants is physically entrapped within the voids of the cementitious matrix inside the discontinuous pores. Only extreme freezing or thawing could break down this structure (Alther, et al, 1991).

2. DESCRIPTION OF ORGANOCLAY

Organically modified clays consist of bentonite, which is modified with quaternary amines (Theng, 1974). The major constituent of bentonite, which is a chemically altered volcanic ash, is the clay mineral montmorillonite. It has a cation-exchange capacity of 70-95 meq/g. The quaternary amines, which are used for this purpose, are of the cationic ammonium chloride type, which have a positive charge on one end of the chain. This charge, derived from the nitrogen ion at the carboxylic head, ion exchanges with sodium, calcium and magnesium ions on the surface of the montmorillonite. In this fashion, the hydrophilic clay becomes hydrophobic or organophilic and the entire structure becomes a non-ionic surfactant with a solid base. Upon introduction of some moisture, the amine chain, which hitherto lies on the clay platelet surface like the hair of an animals fur lies on its body, extends now vertically into the water. As organic hydrocarbons of low solubility pass by the particle, they dissolve into the organic phase where they are more soluble. This process is called "partitioning" (Smith & Jaffe, 1994). When an immiscible organic solvent such as octanol is added to water, which includes contaminants of low solubility, such as PCB, a portion of this compound will move out of the water and into the octanol, where it is more soluble. The relative solubility determines the amount retained in each phase. The concentration ratio of this compound in the two phases is constant over a wide range. This is known as the "partition coefficient, k ", in this case the "Kow" octanol-water coefficient (Mortland et al, 1986).

This terminology can now be extended to contaminants partitioning from the water phase onto a solid phase, such as organic cations sorbed onto clay surfaces. The higher the solution concentration of a compound and the lower

its solubility, the larger the quantity removed by the organoclay through partition. For example, the removal efficiency of organoclay for phenolic compounds is inversely related to the water solubility and amount of chlorination of the compound. Therefore, Pentachlorophenol (PCP, 14 mg/kg solubility in water) is removed in much larger amounts than straight phenol (77,500 mg/kg solubility). By plotting the solubility vs. the n-octanol water partition coefficient onto a graph, the relative ease of removal of organic hydrocarbons by organoclays can be estimated.

Since there are always more amine chains available than can be stoichiometrically affixed to the montmorillonite, the remainder tends to adhere to the fixated surfactant chains by a "tail-tail interaction". That means that a non-ionic organoclay does have a small positive charge, which allows it to remove some anions, such as hexavalent chrome. Therefore, the organoclay has a slight anion removal capacity. It has become polar.

Since the bentonite, which makes up the bulk of the organoclay, is a natural cation-exchange resin, it retains some cation-exchange capacity, which helps in reducing the heavy metal content of the groundwater, which passes through the barrier (Alther, 2004).

3. LABORATORY TESTING METODS

3.1 The "Mini-Column" Technique

One gram of powdered organoclay is packed into a small vial or mini-column. A spiked solution of water is pumped through this column until the influent concentration of the contaminants equals that in the effluent. In this manner, the effectiveness of the organoclay for removing a certain organic hydrocarbon from water can be quickly determined. The advantage of this method is that the equilibrium concentration is the same as the influent concentration, and therefore under ready control (Alther, 2002).

3.2 The Jar Test

This test describes a single point isotherm, which is created by contacting a known weight of sorbent with the contaminated water. A known weight of sorbent, for example 1 gram, is slowly added into a 1000 ml jar filled with the contaminated water. The sorbent is then dispersed in the water by a shaking mechanism, a magnetic stirrer, or a paddle. After a predetermined time, usually 10 minutes, the solids are allowed to settle, followed by centrifugation. The amount of the remaining contaminant in the water is then

determined. This test provides a quick performance evaluation, without having to perform the 10-point ASTM Isotherm test.

3.3 Column Test

The capacity of granular (8x30 U.S. mesh size) organoclay to remove heavy metals was also tested by means of a column test. A 30-inch long and 3-inch diameter column was constructed from poly-vinyl-chloride (PVC) and filled with the organoclay. A large amount of water was pored into a container and spiked with six metals, in this case Cu, Cd, CrIII, Ni, Zn, and Pb, and the solution forced through the column with a peristaltic pump. The column was first backwashed for several hours to displace air in pores and remove any fines. Once in operation, samples of the water were periodically collected and analyzed by means of Acetylene-Air Flame/Atomic Adsorption (at the laboratory of the Dept. of Environmental Engineering, University of Virginia). Anions were also passed through columns in a separate set of tests.

4. RESULTS OF LABORATORY TESTS

4.1 Mini-Column Tests

In this test, powdered organoclay (1 gram), powdered activated carbon (1 gram) and a combination of powdered organoclay (0.5 gram) followed by powdered activated carbon (0.5 gram, in the same vessel), were tested by passing distilled water spiked with benzene, toluene and naphthalene through the vessel (Alther, 2002). The results are shown in Figure 1.

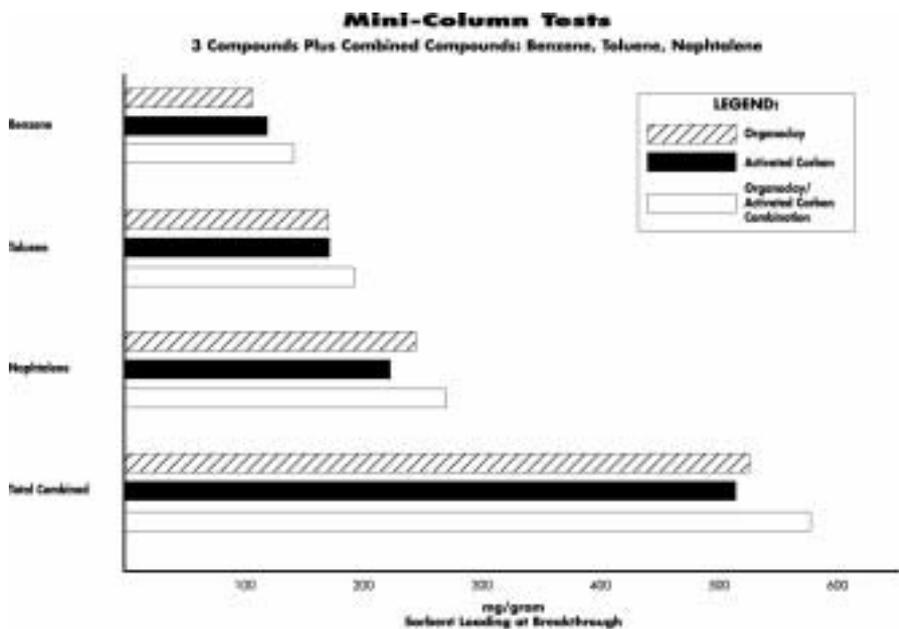


Figure 1. Mini-column tests showing the efficiency of organoclay for removing metals from water, followed by activated carbon, followed by the two sorbents in sequence in the same vial, in the removal of petroleum hydrocarbons from water.

Benzene breaks through first, followed by toluene and then naphthalene. This sequence is expected based on the solubility of these compounds.

Soil Stabilization. Table 1 below shows the results of tests conducted by mixing a sample of the solidification ingredients in a Hobart mixer with the contaminated soil.

An interesting observation is that the organoclay totally fixated highly soluble compounds such as vinyl and methylene chloride, acetone and chloro-ethylene compounds.

Table 1. Results of Laboratory Tests on Soil Stabilization. Jar tests for removal of heavy metals by organoclay.

Reagent: 90% silicates including cement 10% organoclay		Mix Ratio: 80% soil sludge 20% reagent (i.e. 2% organoclay)	
Test Number	Contaminant	Contaminant Concentration	
		Before Treatment	After Treatment
1	Vinyl Chloride	24 ppm	ND
	Methylene Chloride	38 ppm	7 ppb
	Acetone	2,600 ppm	151 ppb

Reagent: 90% silicates including cement 10% organoclay		Mix Ratio: 80% soil sludge 20% reagent (i.e. 2% organoclay)	
2	PCB (Achor 1260)	320 ppm	ND
3	Total Grease & Oil	15,000 ppm	5 ppm
4	Creosol	7.5 ppm	0.4 ppm
5	Dichloroethylene	26-110 ppm	0.8 ppm
	Trichloroethylene	17-95 ppm	ppm
	Toluene	110-320 ppm	1.2 ppm
	Xylene	20-55 ppm	0.2 ppm
	Napthalene	22-43 ppm	0.02 ppm
	PCB	5-20 ppm	ND

Two organoclays were evaluated for their removal capacity of Pb from water, using EPA 6010 method. The organoclay included 23% of quaternary amine. Testing it with water, which contained 5 ppm and 10 ppm of Pb, respectively, showed that the organoclay removed Pb to less than 0.05 ppm in either case.

Another organoclay that contained 28% quaternary amine, was tested for its capability to remove Zn and Cd from water (EPA 6010 method), using 2 grams of clay, 100 ml water, pH 3-5; mixed in jar for 20 minutes.

The results are:

Input: 1 ppm Zn	Ret. less than 0.05 ppm;	Input: 2 ppm Cd	Ret. 0.11 ppm
5	0.71	5	1.5
10	7.2	10	7.1
1 ppm Cu:	0.03	2 ppm Ni	0.2
5	0.09	5	1.8 ppm
10 ppm	4.4 ppm		

These data show that 2 gram (sample size) of the organoclay can remove about 1.5 ppm of the metal.

Mercury was removed from water with an organoclay containing 29% of quaternary amine, using EPA 7470 testing method:

Inflow: 1 mg/l mercury;	outflow: 0.04 mg/l
0.5 mg/l	0.026 mg/l
0.1 mg/l	0.004 mg/l
0.2 mg/l	

4.2 Column Tests, Heavy Metals Removal

Tables 2-11 show the results of a column test conducted with granular organoclay, on a composite sample of six different metals. The U.S. mesh

size of these granules is +8x-30 mesh, with a porosity of 36% (0.36). Calculations show that some 17% of the surface area of the bentonite is still available for ion exchange after conversion to an organoclay. Therefore the ion exchange capacity of the granular organoclay is about 0.16 meq/100 grams.

Table 2. Sorbent mass, porosity, flowrate and residence time information for each column experiment.

Metal	Sorbent	Mass	Porosity	Flow Rate		Residence Time	
		(kg)	(lbs)	(mL/min)	(gal/hr)	(min)	
Pb	Organoclay	2.8	6.2	0.32	135	216	8.40
Cd	Organoclay	2.3	5.17	0.42	125.5	199	11.2
Cu	Organoclay	2.9	6.4	0.27	114	182	8.05
Zn	Organoclay	2.9	6.4	0.31	133	213	8.10
Cr	Organoclay	2.54	5.6	0.37	164.4	263	8
Ni	Organoclay	2.41	5.3	0.38	147.3	236	9.09

Table 3. 95% Breakthrough of each metal for the sorbent material given in pore volumes and minutes with estimated mass of metal sorbed per mass of sorbent in mg/kg, lb/lb and percent basis.

Metal	Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass or Sorbent		
		(pore vol.)	(min)	(mg)	(lb)	(mg/kg)	(lb/lb)	% by weight
Pb	Organo-clay	31.56	264	12,164	0.02682	4,321	0.004321	0.432%
Cd	Organo-clay	13.9	162.9	4,319	0.0095	1,841	0.0018	0.18%
Cu	Organo-clay	48*	386*	3,580	0.00789	1,233	0.001233	0.12%
Zn	Organo-clay	15.8	128	2,771	0.00611	950	0.000950	0.095%
Cr	Organo-clay	6.2	67.77	820	0.00180	323	0.000323	0.032%
Ni	Organo-clay	8.1	73.68	1,382	0.0029	572	0.000572	0.0572%

Table 4. Column tests with sulfate (same description as Table 2). TC-75=Polar Organoclay

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	
TC-75	2.3	4.9	0.30	60	0.96	20

Table 5. Column tests with sulfate (same description as Table 3).

Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass Sorbent		
	PV	Min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
First 95%	47	940	27,745	0.062	12,644	0.0126	1.26%

Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass Sorbent		
breakthrough							
Second 95% breakthrough	12	240	2,697	0.006	1,226	0.0012	0.12%
Total	59	1,180	30,442	0.068	13,870	0.0138	1.38

Table 6. Column tests with phosphate (same description as Table 2).

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	
TC-75	2.2	4.9	0.30	60	0.96	20

Table 7. Column tests with phosphate (same description as Table 3).

Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass Sorbent		
	PV	Min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
First 95% breakthrough	60	1,200	9,648	0.021	4,385	0.0043	0.43%
Second 95% breakthrough	17	340	2,033	0.004	924	0.0009	0.09%
Total	77	1,540	11,681	0.025	5,309	0.0052	0.52%

Table 8. Column tests with nitrate (same description as Table 2). EC-199=Non-polar Organoclay.

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	
TC-75	2.3	5.0	0.30	156	2.5	6.4
EC-199	2.2	5.0	0.31	160	2.5	6.3

Table 9. Column tests with nitrate (same description as Table 3).

Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass Sorbent		
	PV	Min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
TC-75	142	928	52,485	0.117	23,850	0.023	2.385
EC-199	85	580	27,624	0.062	12,556	0.012	1.255

Table 10. Column tests with arsenate, perchlorate and chromium (VI) (same description as Table 2).

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	
TC-75 arsenate	0.396	0.88	0.33	8.3	0.133	20
TC-75 perchlorate	0.389	0.87	0.32	8.3	0.133	20
TC-75 chromium (VI)	0.391	0.87	0.33	8.3	0.133	20

Table 11. Column tests with arsenate, perchlorate and chromium (VI) (same description as Table 3).

Sorbent	Breakthrough		Mass Sorbed		Mass Sorbed/Mass Sorbent		
	PV	Min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
TC-75 arsenate	27	540	715	0.0017	1,896	0.0017	0.18%
TC-75 perchlorate	10	200	259	0.0006	655	0.0007	0.07%
TC-75 chromium (VI)	25	500	2,319	0.005	5,858	0.0058	0.58

5. CASE HISTORIES

5.1 Soil Stabilization

A rolling mill sludge, which contained 10% oil and grease, was stabilized with a mixture of cement, silica additives and organoclay. This resulted in a mixture of 80% sludge, 17.7% cement blend, and 2.3% organoclay. Treated with these compounds, the sludge had unconfined compression strength of greater than 50 psi (after 28 days of curing per TCLP), and the TCLP yielded less than 5-ppm oil and grease. Powdered organoclay has the capability of removing 80% or more of oil and grease, from water.

A large Midwestern utility company, which owned property that included a former manufactured gas plant (MGP) site next to a river, had a soil on its site stabilized. This soil was contaminated with coal tar, which includes heavy oils (Bunker C) and pitch. This mixture included benzene, toluene, naphthalene, phentathrine, pyrene and phenolic compounds. The coal tar contaminated the soil below the groundwater table to a depth between 12 to 25 feet. Sediments in the river were contaminated at the sediment/water interface, to a depth of 3 feet

The mixture that was blended with the soil and sediments consisted of fly ash, Portland cement, powdered organoclay and powdered activated carbon. 22 truckloads of organoclay and activated carbon, each, were used.

The mixing mechanism consisted of an *in-situ* drilling system whereby the mixture was injected into the soil, and soil/mixture columns were constructed. The mixing of the additives was performed with a pug mill (asphalt type) mixer. At the bottom of each column sodium silicate was added to ensure maximum strength. The columns showed consistently more than 50 psi unconfined compression strength and passed the TCLP test.

5.2 Barrier Construction Next to a Refinery

A refinery next to the terminal of the Port of Portland in Oregon was responsible for an oil-contaminated Superfund site, from which oils oozed into the estuarine and coastal waters. A 15-foot wide wall was constructed; the contaminated soil was excavated and disposed of in a Subtitle D disposal site. A backfill, blended with 1% of powdered organoclay, was installed to function as a permeable sorption barrier. Laboratory tests had established that such a system would prevent oil from passing through the barrier, without creating a "bath tub" filled with water. Other authors have since conducted scientific studies, corroborating the feasibility of this method (Lo et al, 1997).

5.3 Landfill Liner Design

Such liners, which include organoclay, were first discussed by Alther et al (1989), and later by Smith et al, 2000. The short of it is, that a permeable barrier is created which allows clean water to pass, but retards and prevents inorganic and organic contaminants from ever leaving the site (Young Yoo et al, 2004). If such a barrier ever starts leaking, a thin slurry wall using the vibrating beam technology can be constructed around the landfill at economical costs.

6. CONCLUSIONS

This brief description of methods to establish permeable barriers around contaminated sites establishes the feasibility of the concept. This technology is a system, which has been long in coming, but should now be accepted as "state of the art" technology.

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