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Part X: Remediation

Chapter 23

ORGANOCLAYS TRAP RECALCITRANT METALS AND ORGANIC COMPOUNDS IN SEDIMENTS SIMULTANEOUSLY

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ABSTRACT

The capability of organoclays as components of permeable sediment barriers has been researched extensively over the past several years.

Organoclays have been used in permeable walls to block the movement of a DNAPL plume from an abandoned wood treating site, and for sediment stabilization at an old MGP site (from a power and light company).

Laboratory column tests and batch tests with organoclays have revealed that a standard, non-polar organoclay fixates all heavy metals, including lead, zinc, nickel, chrome and cadmium, but also inorganic aqueous mercury. In terms of organic hydrocarbons, such diverse compounds as dioxin and nitro-benzenes, as well as PCP, PCB, PNHA and BTEX are trapped effectively.

Studies with polar organoclays, which can easily be blended with the non-polar types, fixate arsenate, selenite, chromate, perchlorate, etc.

This article presents data showing these capabilities, as well as case histories.

1.   INTRODUCTION

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

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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 type consists of powdered cement, bentonite, and organoclay, with the emphasis of the design being 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, at the microscopic level, the organoclay and the 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).

1.1 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 animal's 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).

1.2   Laboratory Testing Methods:

1.2.1   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, 2,002).

1.2.2   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.

1.2.3   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 poured into a container and spiked with 6 metals, in this case Cu, Cd, CrIII, Ni, Zn, and Pb, and the solution was 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 where 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.

2.   RESULTS OF LABORATORY TESTS

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

2.2   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.

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.
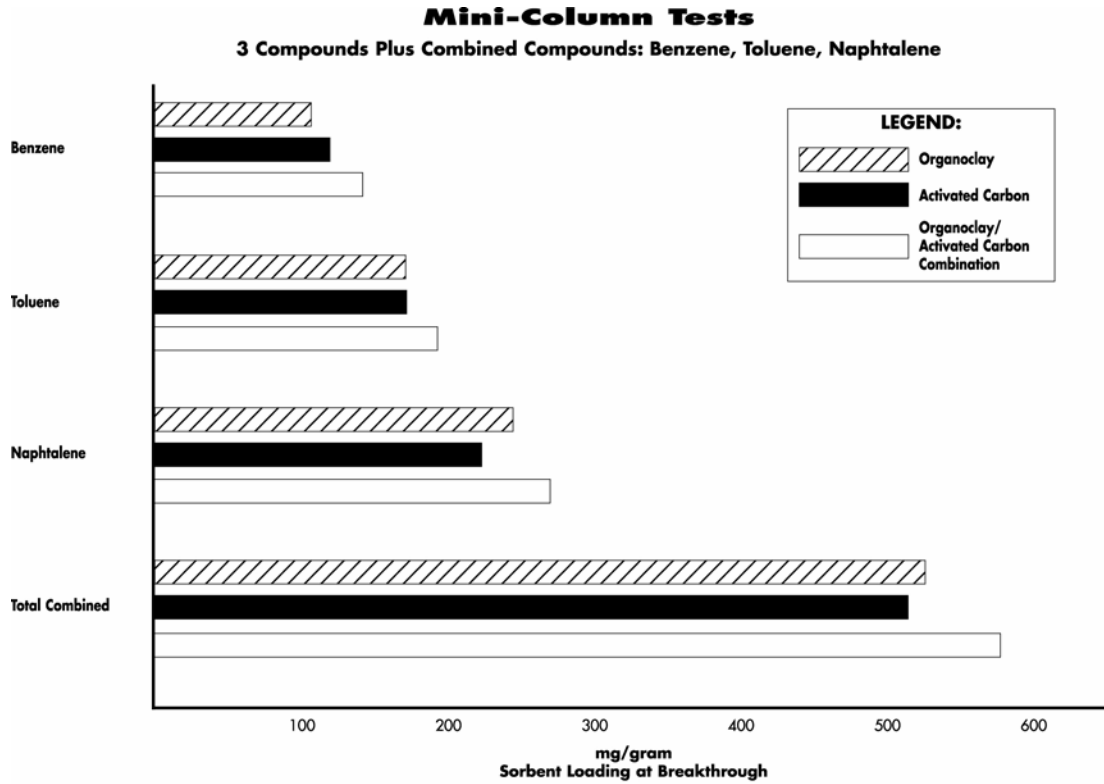
Mini-Column Tests
3 Compounds Plus Combined Compounds: Benzene, Toluene, Naphtalene

LEGEND:
- Organoclay
- Activated Carbon
- Organoclay/Activated Carbon Combination

mg/gram
Sorbent Loading at Breakthrough

Figure 1. Mini-column tests showing the efficiency of non-ionic organoclay for removing organics 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.

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

Reagent: 90 percent silicates including cement 10 percent organoclay		Mix Ratio: 80 percent soil sludge 20 percent reagent (i.e. 2 percent organoclay)	
Test Number	**Contaminant**	**Contaminant Concentration**	
		Before Treatment	**After Treatment**
1	Vinyl Chloride	24 ppm	ND
	Methylene Chloride	38 ppm	7 ppb
	Acetone	2600 ppm	151 ppb
2	PCB (Alchor 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	0.1 ppm
	Toluene	110-320 ppm	1.2 ppm
	Xylene	20-55 ppm	0.2 ppm
	Naphthalene	22-43 ppm	0.02 ppm
	PCB	5-20 ppm	ND

The results are:

Input: 1 ppm Zn	Retained: less than 0.05 ppm;	Input: 2 ppm Cd	Retained 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
0.1.1	0.004 mg/l
0.2	

2.3   Column Tests, Heavy Metals Removal

Table 2 shows the results of a column test conducted with granular non-ionic organoclay, on a composite sample of 6 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 2a. Sorbent mass, porosity, flowrate and residence time information for each of the column experiments.

Metal	Sorbent	Mass (kg)	Mass (lbs)	Porosity	Flow Rate (mL/min)	Flow Rate (gal/hr)	Residence Time (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 2b. 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 (pore vol.)	Breakthrough (min)	Mass Sorbed (mg)	Mass Sorbed (lb)	Mass Sorbed/Mass of Sorbent (mg/kg)	Mass Sorbed/Mass of Sorbent (ln/lb)	Mass Sorbed/Mass of Sorbent (% by weight)
Pb	Organoclay	31.56	264	12,164	0.02682	4,321	0.004321	0.432%
Cd	Organoclay	13.9	162.9	4,319	0.0095	1841	0.0018	0.18%
Cu	Organoclay	48*	386*	3,580	0.00789	1,233	0.001233	0.12%
Zn	Organoclay	15.8	128	2,771	0.00611	950	0.000950	0.095%
Cr	Organoclay	6.2	67.77	820	0.00180	323	0.000323	0.032%
Ni	Organoclay	8.1	73.68	1,382	0.0029	572	0.000572	0.0572%

Below is a bar graph that shows the effectiveness of non-ionic organoclay to remove heavy metals from water. In graph A the water was spiked with various metals to determine which ones are removed preferentially. In graph B, ion exchange tests were conducted with each metal in a separate test.

Organoclay
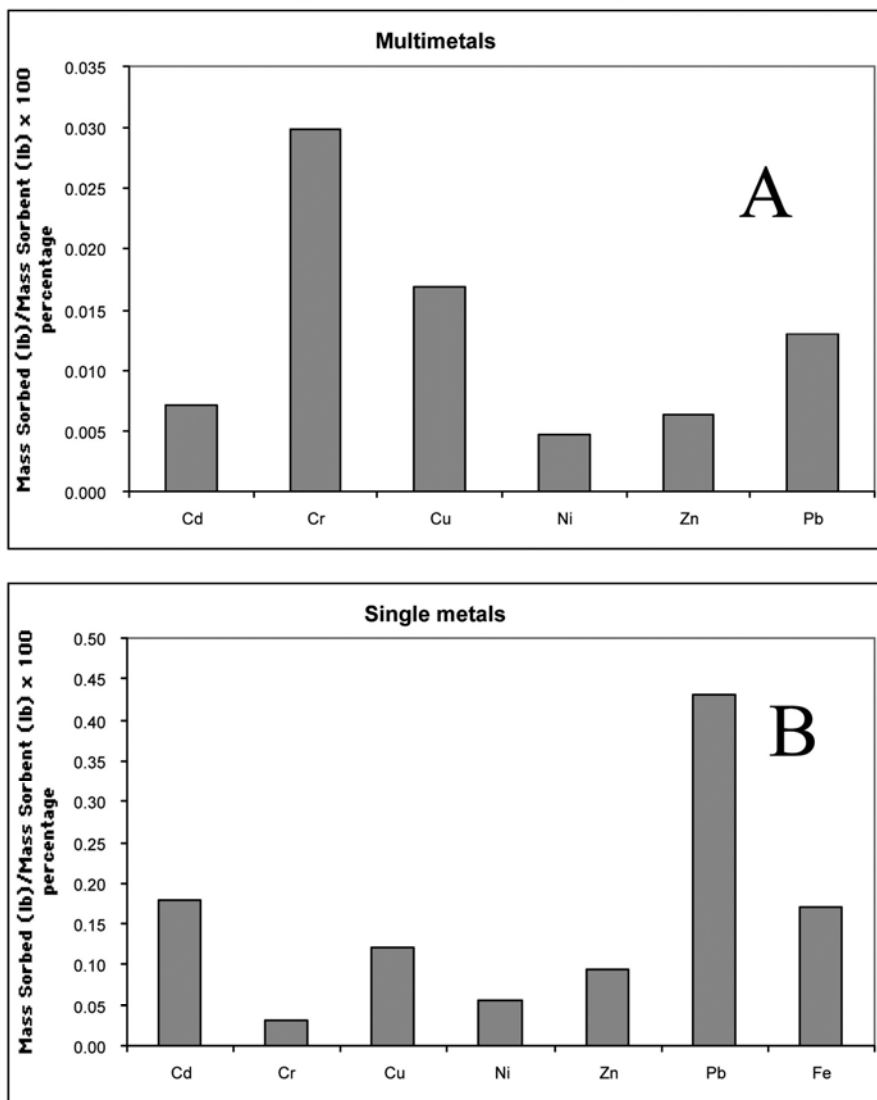
Bar charts quantifying the approximate sorption capacity of Organoclay for each of six metals. Graph A gives capacity data for each metal in the presence of the other metals; Graph B gives capacity data for each metal

Figure 2. The next page shows the effectiveness of polar organoclay to remove anions from water.

Table 3a. Column tests with arsenate, perchlorate and chromium (VI)
(same description as Table 2a).
TC75 = Polar Organoclay

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	(min)
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 3b. Column tests with arsenate, perchlorate and chromium (VI)
(same description as Table 2b).

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	1896	0.0017	0.18
TC-75 perchlorate	10	200	259	0.0006	655	0.0007	0.07
TC-75 chromium (VI)	25	500	2319	0.005	5858	0.0058	0.58

Table 4a. Sorbent mass, porosity, flow rate and residence time information for the removal of selenium IV column experiments.

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	(min)
TC-75 Selenite	2.1	4.7	0.26	50.5	0.81	20

Table 4b. 95% breakthrough for the sorbent given in pore volumes and minutes along with estimated mass of selenium IV sorbed per mass of sorbent in mg/kg, lb/lb and percent basis.

Sorbent	Breakthrough			Mass Sorbed		Mass Sorbed/Mass Sorbent		
	PV	BV	Min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
TC-75 Selenite	50.5	14.1	1,005	5,107	0.01	2,431	0.01	1.15

Table 5a. Sorbent mass, porosity, flow rate and residence time information for TC-75 sorbent column experiments.

Sorbent	Mass Sorbent		Porosity	Flow Rate		Residence
	(kg)	(lb)		(mL/min)	(gal/hr)	(min)
TC-75	2.3	5.1	0.34	59	0.94	20

Table 5b. 95% breakthrough for TC-75 sorbent materials given in pore volumes (PV), bed volumes (BV) and minutes along with estimated mass of CR(III) and Cr(VI) sorbed per mass of sorbent in mg/kg, lb/lb and percent basis.

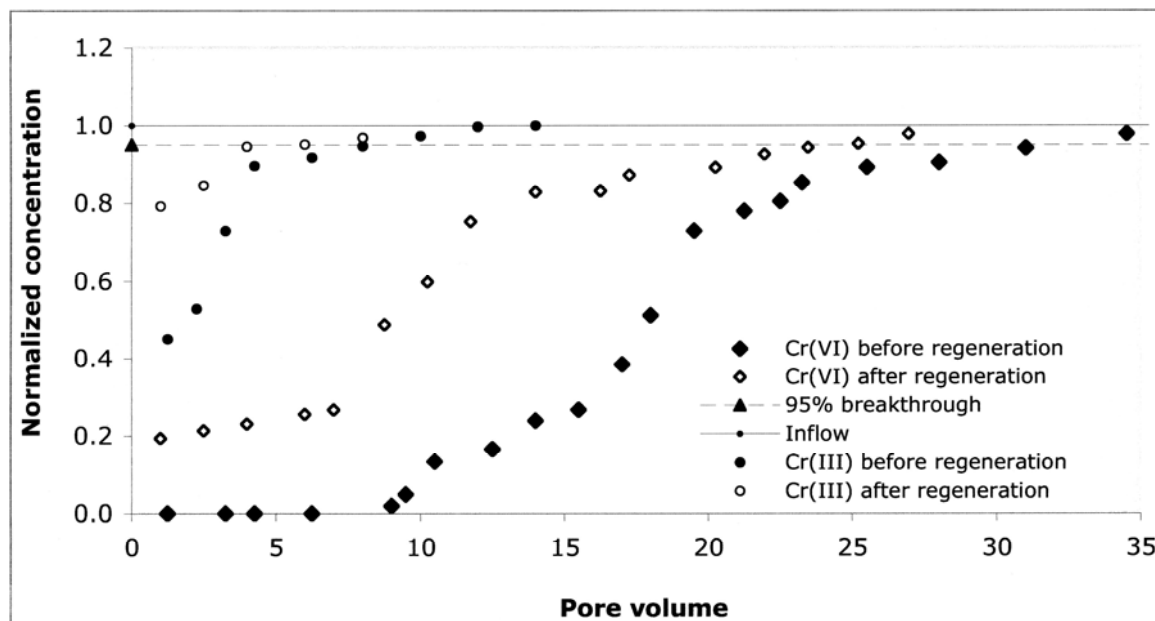| Sorbent	Breakthrough			Mass sorbed		Mass Sorbed/Mass Sorbent		
	PV	BV	min	(mg)	(lb)	(mg/kg)	(lb/lb)	(% by sorbent)
Cr(VI) before regeneration	31	10.5	620	9768	0.022	4247	0.004	0.425
Cr(VI) after regeneration	24	8.2	480	3657	0.0081	1590	0.0016	0.159
Cr(III) before regeneration	8	2.7	160	736	0.0016	320	0.0003	0.031
Cr(III) after regeneration	4	1.4	80	586	0.0013	255	0.0003	0.025

Figure 3a. Breakthrough curves (in terms of pore volume) of Cr(III) and Cr(VI) through TC-75.
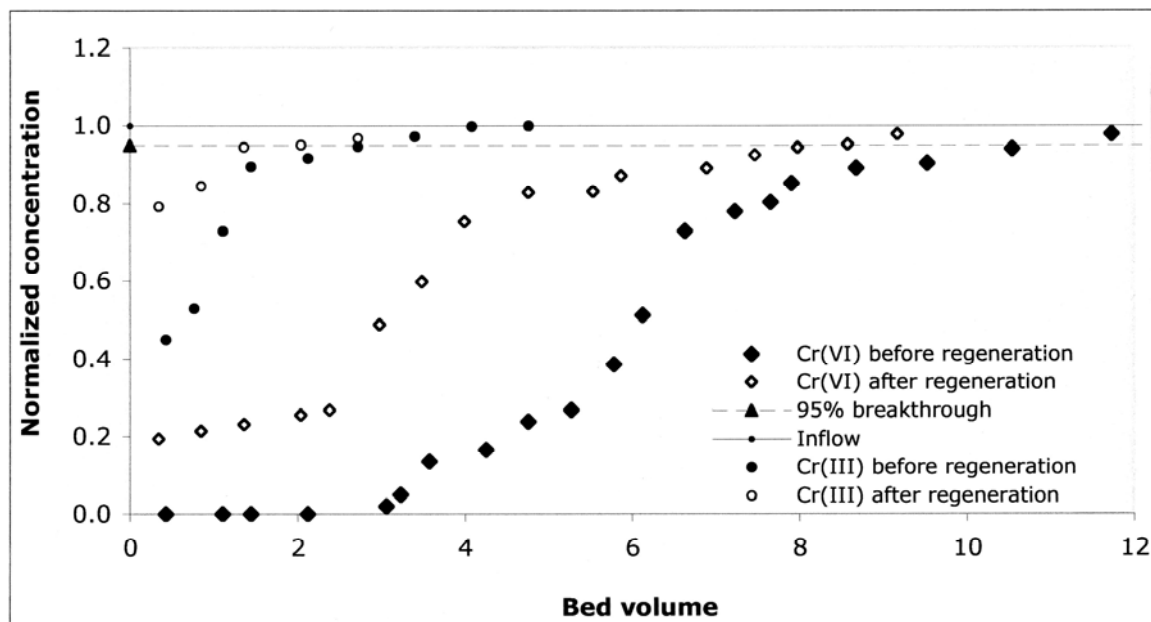
Figure 3b. Breakthrough curves (in terms of bed volume) of Cr(II) and Cr(VI) through TC-75.

3.   CASE HISTORIES: 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 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 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 debt between 12 to 25 feet. Sediments in the river where contaminated at the sediment/water interface, to a debt 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 both organoclay and activated carbon 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.

3.1   **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 feet 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 "bathtub" filled with water. Other authors have since conducted scientific studies, confirming the feasibility of this method (Lo et al, 1997).

3.2   **Landfill Liner Design**

Such liners, which include organoclay, where 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.

4.   **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.

The tests have also proven that a polar organoclay is capable of removing cations, anions and non-ionic organic compounds from water simultaneously. Organoclay is the only sorbent which has this capability.

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