REMOVAL OF ORGANIC POLLUTIONS BY ORGANOCLAY AND IT'S POTENTIAL APPLICATION AS A PERMEABLE REACTIVE BARRIER (PRB)

Introduction

The concept of permeable reactive barriers (PRB) had generated great interest in the field of groundwater remediation in the last few years. CETCO's proprietary media has become the choice of adsorption materials for this type of application due to its high adsorption capacity, high removal efficiency on a variety of organic species, and its characteristic excellent hydraulic conductivity even in the spent condition. Several pilot and field scale trials described below have illustrated the potential to use CETCO media as the passive reactive materials in construction of the permeable reactive barriers to treat contaminated water in-situ.

Case Study No. 1

The aquifer, located below a former refinery site, was contaminated by NAPL (non-aqueous phase liquid). The contaminated shallow aquifer became a threat to the nearby sea water bay when free oil product and soluble organics started showing on the surface of the bay. The potential solution to stop this pollution spreading through the bay and into the ocean is to install a passive reactive wall between the seawall and the bluff.

In order to prove that CETCO's proprietary media was the optimum choice of media materials for use in the passive reactive barrier, a field test was arranged and conducted during a 4-week period in 2003. Actual NAPL contaminated water from a site monitoring well was used for the first half of the test, and an additional 1000 ppm of concentrated site NAPL was injected into the site water stream for the second half of the test. The water was pumped at a nominal rate of 75 GPD into the two media walls consisting of 17 pounds of CETCO organoclay media and 8.5 lbs of granular activated carbon (GAC) media, respectively. The flow rate was approximately 60 times faster than the actual hydro-geologic flow rate.

In the first half of the test, CETCO reactive media demonstrated its effectiveness to remove oil and grease (O&G), BTEX (benzene, toluene, ethyl benzene, and xylene), PAH (polycyclic aromatic hydrocarbon) and other COCs (chemicals of concern). More than 99.8% of BTEX, 98.7% of PAH, and 92.3% of other COCs had been removed by the media. The detailed results listed in Table 1 show the analytical results from 16 days of injecting NAPL contaminated site water into the organoclay/GAC PRB.

			Analysis of Organoclay and GAC PRB Influent and Effluent on Day 16 of Test			
	unit	**Detection Limit**	**Organoclay Influent**	**Organoclay Effluent**	**GAC Effluent**	**% Removal**
Oil & Grease	ppm		4.17	ND	ND	
BTEX						
Benzene	mg/L	0.0004	0.504	0.00099	ND	
Toluene	mg/L	0.001	0.307	ND	ND	
Ethyl benzene	mg/L	0.001	0.765	ND	ND	
o-Xylene	mg/L	0.001	0.155	ND	ND	
m,p-Xylene	mg/L	0.002	1.17	ND	ND	
total	mg/L	0.0054	2.901	0.00099	ND	>99.8%
Polycyclic Aromatic Hydrocarbons (PAH)						
Acenaphthene						
Anthracene						
Chrysene						
Fluroanthene						
Fluorene	ug/L	0.0495	0.0554	0.05	ND	
Naphthalene	ug/L	0.0495	11.5	0.05	ND	
Phenanthrene	ug/L	0.0495	0.0524	0.05	ND	
Pyrene						
total	ug/L	0.1485	11.6078	0.15	ND	>98.7%
Other COCs						
1,2,4-trimethylbenzene	mg/L	0.001	0.08	ND	ND	
1,3,5-trimethylbenzene	mg/L	0.001				
n-Propylbenzene	mg/L	0.001	0.0362	ND	ND	
Isopropylbenzene	mg/L	0.001	0.061	ND	ND	
n-Butylbenzene	mg/L	0.001				
sec-Butylbenzene	mg/L	0.001				
4-Isopropyltoluene	mg/L	0.001				
Butanone (MEK)	mg/L	0.01	0.0438	0.0113	ND	
total	mg/L	0.017	0.221	0.0113	ND	>92.3%

Table 1. O&G, BTEX, PAH and other COCs removal by CETCO media with the use of actual site water

For the second half of the field test, an additional 1000 ppm of site NAPL was injected into the site contaminated water stream. Again, CETCO media was proved to be very effective on removing the contaminants. The detailed results are listed in Table 2. In summary, the inlet O&G level increased to 522 ppm, but the effluent stream concentration was still below the detection limit, thus the organoclay removal efficiency for O&G was greater than 99.2%. The NAPL spiked inlet level for PAH was increased significantly comparing to the test without any NAPL injection, but the removal efficiency was maintained at greater than 99%.

			Analysis of Organoclay and GAC PRB Influent and Effluent after 6 days of 1000 ppm NAPL Injection			
	unit	**Detection Limit**	**Organoclay Influent**	**Organoclay Effluent**	**GAC Effluent**	
Oil & Grease	ppm	4.12	522	ND	ND	>99.2%
BTEX						
Benzene	mg/L	0.0004	0.211	0.00121	ND	
Toluene	mg/L	0.001	0.0586	ND	ND	
Ethylbenzene	mg/L	0.001	0.0726	ND	ND	
o-Xylene	mg/L	0.001	0.0227	ND	ND	
m,p-Xylene	mg/L	0.002	0.136	ND	ND	
total		0.0054	0.5009	0.00121	ND	>98.9%
Polycyclic Aromatic Hydrocarbons (PAH)						
Acenaphthene	ug/L	0.0495	12.5	15	ND	
Anthracene						
Chrysene	ug/L	0.0495	10.8	9.9	ND	
Fluroanthene	ug/L	0.0495	8.34	9.9	ND	
Fluorene	ug/L	0.0495	73.8	78.4	ND	
Naphthalene	ug/L	0.0495	319	230	0.091	
Phenanthrene	ug/L	0.0495	125	90.5	ND	
Pyrene	ug/L	0.0495	6.97	11.2	ND	
total	ug/L	0.3465	556.41	444.9	0.091	>99.9%
Other COCs						
1,2,4-trimethylbenzene	mg/L	0.001	0.142	0.00559	ND	
1,3,5-trimethylbenzene	mg/L	0.001	0.0387	0.00198	ND	
n-Propylbenzene	mg/L	0.001	0.011	ND	ND	
Isopropylbenzene	mg/L	0.001	0.0102	ND	ND	
n-Butylbenzene	mg/L	0.001	0.0138	ND	ND	
sec-Butylbenzene	mg/L	0.001				
4-Isopropyltoluene	mg/L	0.001				
Butanone (MEK)	mg/L	0.01				
total	mg/L	0.017	0.2157	0.00757	ND	>92.1%

Table 2. O&G, BTEX, PAH and Other COCs removal by CETCO media with actual site water used plus the additional NAPL injection @ 1000ppm.

The other significant observation was the media's hydraulic conductivity remained unchanged throughout the test. Based on the injection of the 1000 ppm NAPL, the results indicated that the organoclay permeable reactive barrier media life could last at least 25 years before the breakthrough occurred. It is estimated that greater than 0.6 lb of NAPL was removed by each pound of the organoclay media at the time media was spent.

Case Study No. 2

In another field test, CETCO media was evaluated for its ability to remove both PAH and NPD (naphthalene, phenanthrene, diibenzothiopene and their derivatives). The detailed results listed in Table 3 show that over 94% of the targeted organic species were removed by the organoclay. In this trial, the media had a wall thickness of about 4" with a flow rate giving the retention time of two minutes.

	Unit	Organoclay PRB Influent	Organoclay PRB Effluent	% Removal
PAH & NPD				
Naphthalene 2 ring	ug/L	1.9167	0.2	89.6%
C1-naphthalenes				
C2-naphthalenes				
C3-naphthalenes				
Acenaphthylene				
Acenaphthene				
Fluorene				
Phenanthrene				
Anthracene				
C1- anthracenes/phenant				
C2- anthracenes/phenant				
C3-anthracenes/phenant				
Fluoranthene				
Average 2,3 ring	ug/L	439.77	23.898	94.6%
Pyrene				
Benz(a)anthracene				
Chrysene				
Benzo(b)fluoranthene				
Benzo(j+k)fluoranthene				
Benzo(a)pyrene				
Indeno(1,2,3-c,d)pyrene				
Dibenz(a,h)anthracene				
Benzo(g,h,i)perylene				
Average 4,5,6 ring	ug/L	1.065	0.0675	93.7%
Total	ug/L	442.8	24.2	94.5%

Table 3. PAH and NPD removal by CETCO Organoclay media.

Case Study No. 3

In this field trial, CETCO media was evaluated for its effectiveness on the common contaminants of concern (BETX, PAH, NPD), and also on the partial water soluble organic molecules such as alkylated phenols. The detailed results are listed in Table 4. In this trial, the media had a wall thickness of about 4" with flow rate retention time of 2 minutes.

BTEX	Organoclay PRB Influent mg/l	Organoclay PRB Effluent mg/l	% Removed
Benzene	0.181	0.004	97.79
Toluene	0.065	<0.001	> 98.46
m-Xylene and p-Xylene	1.966	0.103	94.76
Ethyl benzene	0.059	0.002	96.61
o-Xylene	0.239	0.009	96.23

Polycyclic Aromatic Hydrocarbons (PAH)	Inlet µg/l	Outlet µg/l	% Removed
Acenaphthylene	8.89	1.87	78.97
Acenaphthene	10.57	1.45	86.28
Fluorene	21.54	3.02	85.98
Anthracene	<0.01	<0.01	N/a
Fluroanthene	0.4	<0.01	> 97.5
Pyrene	<0.01	<0.01	N/a
Benz(a)anthracene	0.19	0.09	52.63
Chrysene	<0.01	<0.01	N/a
Benzo(b)fluroanthene	<0.01	<0.01	N/a
Benzo(k)fluroanthene	<0.01	<0.01	N/a
Benzo(a)pyrene	0.64	<0.01	> 98.4
Benzo(g,h,l)perylene	<0.01	<0.01	N/a
Indeno(1,2,3cd)pyrene	<0.01	<0.01	N/a
Dibenz(a,h)anthracene	<0.01	<0.01	N/a

NPD	Inlet µg/l	Outlet µg/l	% Removed
Naphthalene	81.48	1	98.77
Phenanthrene	33.31	3.55	89.34
Dibenzothlophene	25.36	4	84.23
1-Methylnaphthalene	309.09	20.92	93.23
2-Methylnaphthalene	374.49	23.74	93.66
9-Methylphenanthrene	88.84	12.17	86.30
Other Methylphenanthrenes	126	15	88.10
4-Methyldibenzothiophene	25.43	4.91	80.69
Other Methyldibenzothiophenes			
2,6-Dimethylnaphthalene	265.8	24.74	90.69
Other C2 Naphthalenes	1016	116	88.58
9-Ethylphenanthrene	<0.01	<0.01	N/a
Other C2 Phenanthrenes	228	31	86.40
4-Ethyldibenzothiophene	<0.01	<0.01	N/a
Other C2 Dibenzothiophenes	54	7	87.04
2-Isopropylnaphthalene	20.92	3.83	81.69
Other C3 napthalenes	1663	269	83.82
1,2,6-Trimethylphenanthrene	<0.01	<0.01	N/a
Other C3 Phenanthrenes	154	23	85.06
4-Propyldibenzothiophenes	<0.01	<0.01	N/a
Other C3 Dibenzothiophenes	ND	ND	N/a

Alkylated Phenols	Inlet µg/l	Outlet µg/l	% Removed
Total C1-C3 alkyl phenols	750	120	84.00
Other C1-C3 alkyl phenols			N/a
2-methylphenol	28	1.7	93.93
3-methylphenol	10	0.8	92.00
4-methylphenol	13	<0.5	96.15
2, 5 dimethylphenol	17	<0.5	97.06
3,4 & 3,5 dimethyphenol	21	<0.5	97.62
2,4-dimethyphenol	25	1	96.00
4-ethylphenol	13	<0.5	> 96.1
2-n-propylphenol	1.1	<0.5	> 54.5
2,3,5-trimethylphenol	1.4	<0.5	> 64.2
4-n-propylphenol	5.4	<0.5	> 90.7
2,3,6-trimethylphenol	1.6	<0.5	> 68.7
Total C4-C5 alkyl phenols	1600	120	92.50
Other C4-C5 alkyl phenols			
4-tert-butylphenol	16	0.9	94.38
2-tert-butylphenol	4	<0.5	N/a
4-n-butylphenol	15	6.6	56.00
2-tert-butyl-4-methylphenol	5.4	<0.5	N/a
4-tert-butyl-2-methylphenol	7.4	<0.5	N/a
4-n-pentylphenol	7.5	<0.5	N/a
Total C6-C9 alkyl phenols	1900	440	76.84
Other C6-C9 alkyl phenols			
2,6-disopropylphenol	4.3	1.2	72.09
4-n-heptylphenol	7.9	1.3	83.54
4-n-octylphenol	8.5	1.4	83.53
2,6-di-tert-butylphenol	27	<0.5	> 98.0
2,4-di-sec-butylphenol	1.8	31	-1622.22
4-tert-octylphenol	61	8	86.89
2,6-di-tert-butylphenol	0.9	2.1	-133.33
4-n-nonylphenol	2.1	6.5	-209.52
2,6-di-tert-butyl-4-methylphenol	1.6	<0.5	> 69

Table 4. BETX, PAH, NPD and alkylated phenol removal by CETCO organoclay media.

It is noteworthy that the organoclay media was tested in all cases under the high flow rate conditions. Better performance could be expected from the media under actual slow ground water flow conditions.
The organoclay media could adsorb oil and grease as much as 60 percent of its own weight without compromising its hydraulic conductivity. However, the adsorption capacity would drop in the presence of organics with higher water solubility. The actual value could vary from 10 to 60 percent.

Conclusions

In conclusion, CETCO organoclay media has been evaluated in detail for over one hundred applications for its ability to remove oil & grease, PAH, NPD, and BTEX from contaminated water streams. Three case studies have been presented here and have shown the organoclay's ability to remove contaminants at both relatively low and high concentrations during in-situ field conditions. The required hydraulic characteristics and media's life needed were also demonstrated. The use of CETCO media for constructing permeable reactive barriers to treat contaminated water *in situ* is very promising.