Use and Application of Organophilic Clay Materials for Adsorption of Petroleum and to Address Pipeline and Storage Facility Related Water Issues

November 2016

* Unique stone-core design

www.aquablok.com
Presentation Outline

- Problem Statement – Pathways
- Introduction to AquaBllok / AquaGate
- Overview of Various Applications
- Summary/Questions/Discussion
Problem - Ground Water to Surface Water Interaction

Examples:

- Sheen
- Dissolved Phase PAH (i.e. BTEX)
- Metals
- PCBs
Problem – Preferential Pathways

PREFERENTIAL PATHWAYS; UNDERGROUND PIPES AND UTILITY LINES CAN BE CONDUITS FOR THE MIGRATION OF CONTAMINANTS
Written by Stephen R. Henshaw, P.G., President & CEO, EnviroForensics
As seen in the March 2013 issue of Cleaner & Launderer

Typical Pipeline Construction

Preferential Flow Pathways:
Conduits for Groundwater Contamination
by Lisa Weatherford
Tuesday, February 18th, 2014

"New research by the U.S. Geological Survey USGS) concerning the vulnerability of our nation’s underground drinking water supplies offers a better understanding of how contamination can occur and what we can do to stop it. Yesterday we reviewed three basic measures for drinking water analysis and today we will look at the importance of preferential flow pathways contribute to groundwater contamination."
Problem – Preferential Pathways

Spill Prevention, Control, and Countermeasure (SPCC)

SPCC rules are intended to prevent a discharge of oil into navigable waters or adjoining shorelines.

Pipe Penetrations as Containment Failure Point in Berm/Dike

Low-Permeability Materials for Flood Control & Spill Containment
AquaBlok Technology Platform

A Delivery Method for Uniform Placement of Small Quantities of High-Value Materials

- Uniform Distribution
- Flexible/Rapid Installation (Low Cost)
- Custom Blends for Targeted Designs
- Can Vary/Control Permeability
- Self-Compacting for Low Permeability
- Placement Through Standing Water
- Marine & Freshwater Blends
- Passive Adsorption/Treatment Media

powder coating + aggregate core = AquaBlok/AquaGate+ “composite particle”
Low-Permeability for Sealing and Chemical Isolation Barriers

Applied through standing water or in the dry

- Refinery/PAH Sites
- Metals/DDT
- PAH / PCBs
- MGP Sites
- Landfill Cap
Permeable Materials for In-Situ Treatment & Remediation Applications

AquaGate+PAC
+ORGANOCLAY
+Sorbster®

Refinery/PAH Sites

As
Hg
Pb
Se

<table>
<thead>
<tr>
<th></th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>53.76%</td>
<td>59.15%</td>
</tr>
<tr>
<td>Hg</td>
<td>100.00%</td>
<td>52.71%</td>
</tr>
<tr>
<td>Pb</td>
<td>9.94%</td>
<td>28.73%</td>
</tr>
<tr>
<td>Se</td>
<td>87.62%</td>
<td>51.94%</td>
</tr>
</tbody>
</table>

Concentration (µg/L)

Residence Time (hrs)
Range/Applications for Contaminated Water

Technologies Available – AquaGate+ Delivery

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Treatment Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs, Pesticides, BTEX, PCB’s (Free Product / Dissolved Phase)</td>
<td>Activated Carbon, Provect-IRM(^1), Organoclay, Rubber</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Provect-OX(^1), Oxygen Delivery, Nutrients</td>
</tr>
<tr>
<td>VOCs</td>
<td>Activated Carbon, Zero Valent Iron, Bimetallic</td>
</tr>
<tr>
<td>Metals, Ammonia (Arsenic, Chrome, Mercury, etc)</td>
<td>Sorbster(^2), Zero Valent Iron, Provect-IRM(^1), Zeolites, Ferric Sulfides, Organic Carbon,</td>
</tr>
</tbody>
</table>

\(^1\) Provectus Product  
\(^2\) MAR Systems Product
Adsorptive Material – Petroleum Based Contaminants

Aggregates: Nominal AASHTO #8 (1/4-3/8") or custom-sized to meet project-specific need * Limestone or non-calcareous substitute, as deemed project-appropriate

Binder: Cellulosic polymer

Permeability: $1 \times 10^{-2}$ to $1 \times 10^{-5}$ cm/sec

Dry Bulk Density: 65 – 85 lbs/ft³

Moisture: 10 – 20% (maximum)
Mix of Historic Industrial Use Drives Target Contaminants & Remedy

- PAHs primary driver of remediation
- Remedy - Objectives

<table>
<thead>
<tr>
<th>Total PAH Bulk Sediment Concentration in bioturbation zone</th>
<th>27.0 mg/kg – dw (3.4 mg/kg-dw 1 %OC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cap Design Life</td>
<td>100 yrs</td>
</tr>
</tbody>
</table>
### Example Model Output Results

<table>
<thead>
<tr>
<th>Case</th>
<th>Media</th>
<th>Reactive layer</th>
<th>Sand thickness (cm)</th>
<th>Initial Porewater conc(C0)(ug/L)</th>
<th>Surface sediment (0 - 10 cm) Average bulk concentration (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Loading For model (kg/m²/cm)</td>
<td>% Oclay by wt</td>
<td>thickness (cm)</td>
<td>Log Koc</td>
</tr>
<tr>
<td><strong>Active Layer Mix of Organoclay and granular media</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oclay</td>
<td>2.28</td>
<td>14.20</td>
<td>14%</td>
<td>7.6</td>
<td>30.5</td>
</tr>
<tr>
<td>Oclay</td>
<td>1.52</td>
<td>9.47</td>
<td>9%</td>
<td>15.22</td>
<td>30.5</td>
</tr>
<tr>
<td>Oclay</td>
<td>5.32</td>
<td>33.14</td>
<td>45%</td>
<td>7.6</td>
<td>30.5</td>
</tr>
<tr>
<td>Oclay</td>
<td>2.28</td>
<td>14.20</td>
<td>14%</td>
<td>15.22</td>
<td>30.5</td>
</tr>
<tr>
<td><strong>Active Layer Mix of Organoclay and granular media</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oclay</td>
<td>3.8</td>
<td>23.67</td>
<td>27%</td>
<td>15.22</td>
<td>30.5</td>
</tr>
<tr>
<td>AC</td>
<td>1.95</td>
<td>na</td>
<td>na</td>
<td>1</td>
<td>30.5</td>
</tr>
</tbody>
</table>

### Area A:
- Extent of removal ranges from approx 1 foot to potentially 6 feet of sediment to reach a target elevation of 573 feet
- Porewater concentrations range from 1.6 ug/L to 958.2 ug/L with a mean of 195.8 ug/L and a 95 UCL of 427.5 ug/L
- Koc index ranges from 3.7 to 5.0 with a mean of 4.3

### Area B:
- Extent of removal ranges from none to 1 feet of sediment to reach a target elevation of 573 feet
- Porewater concentrations range from < 1 ug/L to 119.9 ug/L with a mean of 23.76 ug/L and a 95 UCL of 41 ug/L
- Koc index ranges from 3.8 to 5.6 with a mean of 4.6

### Reactive layer
- Sand thickness
- Initial Porewater conc(C0)(ug/L)

### Loading
- For model (kg/m²/cm)
- % Oclay by wt
Post-Placement Active Material Properties
Confirmation Testing & Analysis

Did the Reactive Material Placed Retain the Adsorptive Properties Assumed in the Design?

#1 Oil Sorption Capacity – Pre/Post Placement

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Samples</th>
<th>Oil sorption capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Orgaoclay (Control)</td>
<td>1-1</td>
<td>71.70</td>
</tr>
<tr>
<td></td>
<td>1-2</td>
<td>68.36</td>
</tr>
<tr>
<td></td>
<td>1-3</td>
<td>68.61</td>
</tr>
<tr>
<td></td>
<td>1-4</td>
<td>70.04</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>average 69.68</td>
</tr>
<tr>
<td>As Manufactured Organoclay</td>
<td>2-1</td>
<td>65.82</td>
</tr>
<tr>
<td></td>
<td>2-2</td>
<td>64.88</td>
</tr>
<tr>
<td></td>
<td>2-3</td>
<td>63.44</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>60.59</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>average 63.68</td>
</tr>
<tr>
<td>Sample Buckets - (As-Placed Material Recovered from River Bottom)</td>
<td>3-1</td>
<td>62.86</td>
</tr>
<tr>
<td></td>
<td>3-2</td>
<td>62.65</td>
</tr>
<tr>
<td></td>
<td>3-3</td>
<td>61.40</td>
</tr>
<tr>
<td></td>
<td>3-4</td>
<td>61.99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>average 62.22</td>
</tr>
</tbody>
</table>

Samples of material were sent to CETCO for testing utilizing Test Method: LP-Organoclay Powdered Sorption Oil Centrifuge-modified to 72 hours
Post-Placement Active Material Properties
Confirmation Testing & Analysis

Did the Reactive Material Placed Retain the Adsorptive Properties Assumed in the Design?

Texas Tech University Lab partition coefficients as a function of Kow.

Sample #1 – CETCO Powder OC as Received

Sample #2 – As Manufactured Coating, Prior to Placement

Sample #3 – Post Placement Sample Recovered From River

Octanol-water partition coefficients of PAHs and partition coefficients - standard deviation in estimate for the three tested organophilic clays. Values reported for CETCO PM-199 from TR-840[2]

<table>
<thead>
<tr>
<th></th>
<th>NAP</th>
<th>PHE</th>
<th>PYR</th>
<th>BaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Kow</td>
<td>3.41</td>
<td>4.57</td>
<td>5.18</td>
<td>6.54</td>
</tr>
<tr>
<td>Kow</td>
<td>2,570</td>
<td>37,154</td>
<td>151,356</td>
<td>3,467,369</td>
</tr>
<tr>
<td>Sample #1</td>
<td>3,223</td>
<td><strong>91,619</strong></td>
<td><strong>323,459</strong></td>
<td><strong>1,603,265</strong></td>
</tr>
<tr>
<td>Std Dev</td>
<td>178</td>
<td>8,709</td>
<td>45,948</td>
<td>404,779</td>
</tr>
<tr>
<td>Sample #2</td>
<td>3,161</td>
<td><strong>105,183</strong></td>
<td>406,830</td>
<td>1,747,376</td>
</tr>
<tr>
<td>Std Dev</td>
<td>432</td>
<td>9,499</td>
<td>57,680</td>
<td>532,597</td>
</tr>
<tr>
<td>Sample #3</td>
<td>2,609</td>
<td><strong>93,367</strong></td>
<td><strong>359,871</strong></td>
<td><strong>1,537,488</strong></td>
</tr>
<tr>
<td>Std Dev</td>
<td>86</td>
<td>4,516</td>
<td>30,370</td>
<td>684,176</td>
</tr>
<tr>
<td>CETCO PM-199</td>
<td>3280</td>
<td>68,000</td>
<td>454,000</td>
<td>3,510,000</td>
</tr>
</tbody>
</table>
| Std Dev        | 8,420| 104,900| 442,000
| +/- 95% confidence interval | 16,503| 205,604| 866,320

Specification: “The organoclay shall have a documented partition coefficient (Kd) of at least 50,000 L/Kg for light weight PAHs (eg. phenanthrene) and 350,000 L/Kg for mid to heavy weight PAHs (eg. pyrene).”
Permeable Reactive Barrier (PRB)

Conceptual Treatment Model

Contaminated Groundwater Flow  AquaGate+ Organoclay PRB  Tidal Estuary

Percent NAPL Sorbed

Hydrophobic dye partially dissolved indicating organic phase on water surface.

NAPL remaining not directly quantifiable, < 1 ml.

No NAPL  NAPL Present

Dry Ash + OC
Site Location: **U.S. EPA Region 7**
Confidential Project, Kansas

**Project Status:**
Completed Fall 2015

**Products:**
- AquaGate+
- Organoclay
- AquaGate+IRM
- Treatment Train Approach
Funnel & Gate Approach to Address Ground Water Impacts from MGP Site

Site Location: U.S. EPA Region 2
Confidential Site – New York State

- **Setting/Purpose:** Canal/River (freshwater). MGP Site – PRB and low permeability barrier/cap over contaminated sediments. Site area was approximately 4,000 square feet.

- **Contaminant(s) of Concern:** Coal Tar associated with historic MGP site, including PAH (polynuclear aromatic hydrocarbons) and DNAPL (Dense Non-Aqueous Phase Liquids).

- **AquaBlok Cap Design/Site Area:** Multi-layer design comprised of a one inch basal layer AquaGate+ORGANOCLAY PRB covered with a hydrated layer (~6 inches in target thickness) of AquaBlok 3070FW. The cap was then armored with a two-inch layer of AASHTO #2 stone.

- **Method of AquaBlok Placement:** Shore-based excavator
The Approach – Funnel & Gate

Key Objectives:

- No Localized Breakthrough
- Relatively Long Contact Time for Organoclay

Funneling of Contaminant bearing sediment pore waters are directed beneath a low-permeability cap through a higher-permeability treatment layer that is below the cap.

Higher-Permeability Treatment Zone (Gate – includes organoclay or other materials)
Funnel & Gate Approach - Continued

Below and Right: View of AquaGate+Organoclay Being Applied & Close up View in Place
Case Study of Funnel & Gate Approach - Continued

Completed Cap with Armor Stone - Right

View of Completed Cap Following Spring – Water Levels Back to Normal Level - Left
Application Examples

Pipeline & Utility-related Applications

Trench Dams/Anti-Seep Collars
Design/Installation of Anti-Seep Collar
Elimination of Pipe Bedding as Preferential Pathway
Trench Dam
Construction Considerations -

1. **Width of Dam** – 6-inch thickness will provide hydraulic conductivity of approximately $5 \times 10^{-8}$ in hydrated state.
2. **Bedding Depth / Distance Under Pipes** – Typically recommended to be a minimum of 6-inch.
3. **Trench Width** – Where collars are keyed into surrounding soils, it is recommended that AquaBlok extend a minimum of 1-ft beyond undisturbed material.
Application Examples

Preferential Pathway - Flow Along Pipes

Setting / Purpose: Pipeline cap and Anti-Seep Collar. Objective was to cut off site contaminant pathways during excavation and installation of natural gas pipeline.

Key Benefits:
- Reduce potential impacts in Ecologically sensitive areas (River Crossings)
- Provide Seismic/Fatigue Dampening in Sensitive Areas

Installation Notes:
- Coffer Dam approach used to isolate pipe trench from surrounding soil
- Continuous measurement of AquaBlok performed to insure design thickness of cap
Summary – Q&A

AquaBloq as a Low-Permeability Material for Remediation & Geotechnical Applications:

Permeable Treatment Material for Remediation Applications:

Permeable Treatment Material for Sediment Remediation Applications

- Provides Uniform Delivery of Small Quantities of a High Value Treatment Material
- Use of Powder Treatment Materials = Faster Adsorption Rates
- Creates Thicker (uniform) Layers with Less Material Usage
- Ability to Mix Treatment Materials with other Granular Capping Materials and Provide Uniform Delivery in a Single Lift - Less Risk of Material Separation Wide Range of Treatment Materials

- Rapid Installation – Using Conventional Equipment
- Proven Full-Scale Production – On-Site Manufacturing