



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



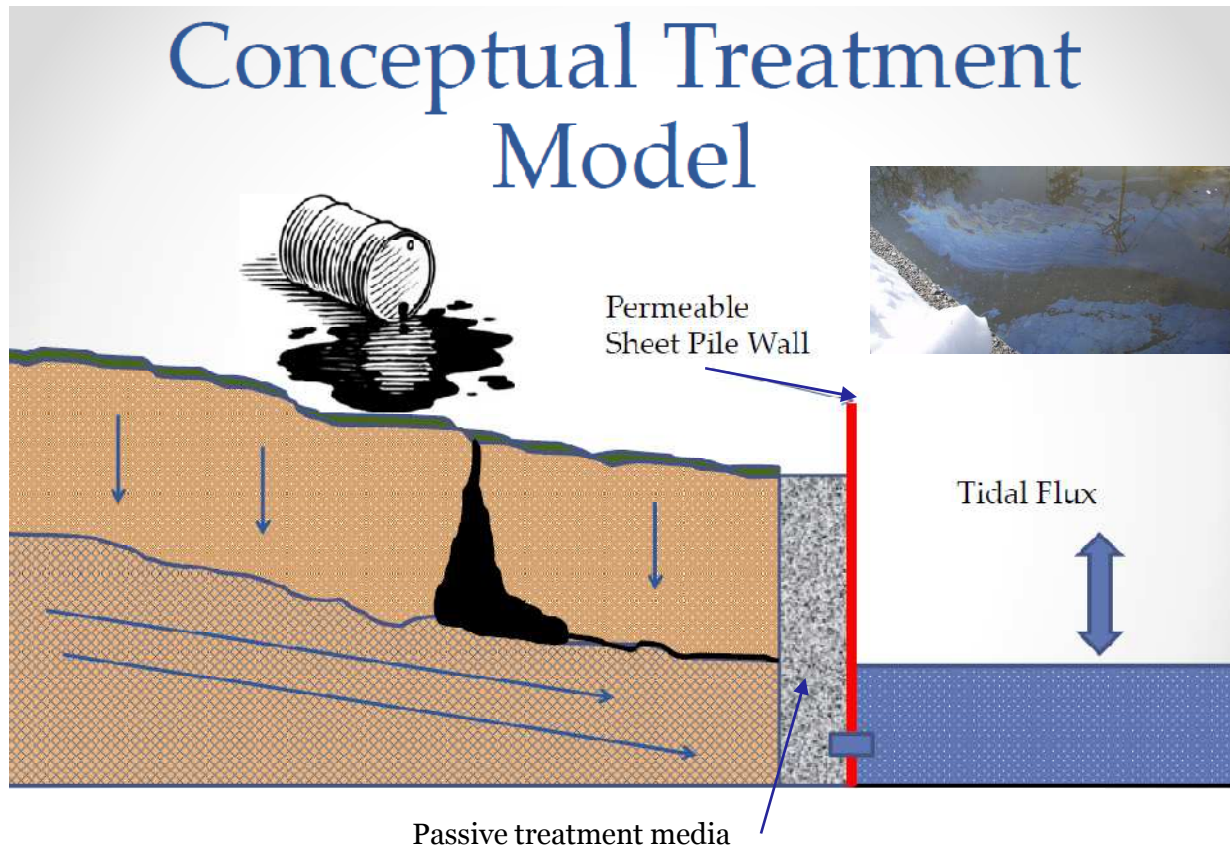
www.aquablok.com

Presentation Outline



- Problem Statement – Pathways
- Introduction to AquaBlok / AquaGate
- Overview of Various Applications
- Summary/Questions/Discussion

Problem - Ground Water to Surface Water Interaction



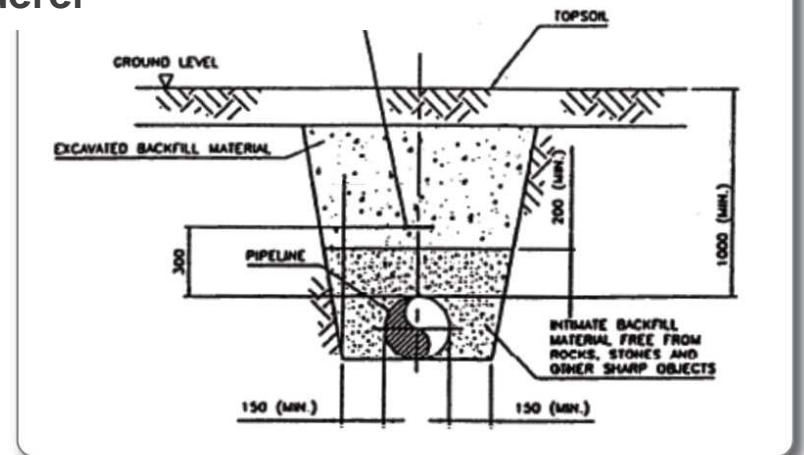
Examples:

- 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



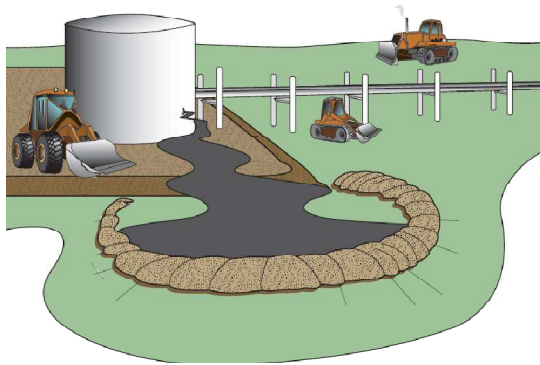
Preferential Flow Pathways: Conduits for Groundwater Contamination by Lisa Weatherford

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



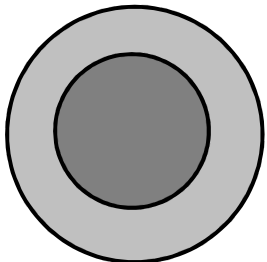
PAH / PCBs



MGP Sites



Landfill Cap

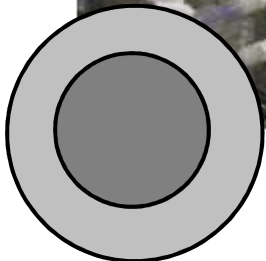
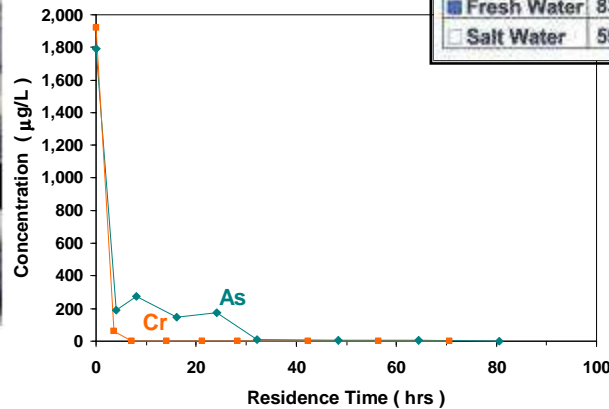
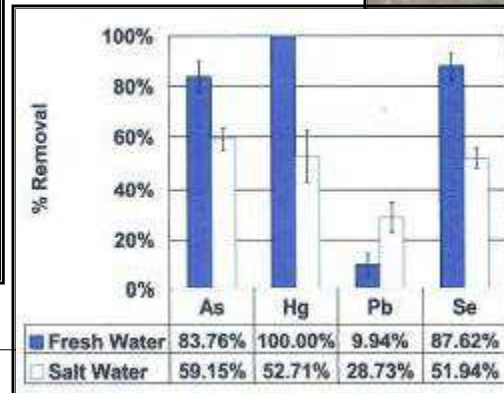


Aquagate₊

Permeable Materials for In-Situ Treatment & Remediation Applications



Refinery/PAH Sites



Range/Applications for Contaminated Water

Technologies Available – AquaGate+ Delivery

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

¹ Provectus Product

² MAR Systems Product



Adsorptive Material – Petroleum Based Contaminants

Aquagate, ORGANOCLAY™

REMEDICATION TECHNOLOGIES
Technical Data

CETCO®



Aggregate: Nominal AASHTO #8 (1/4-3/8”) or customized to meet project-specific need * Limestone or non-calcareous substitute, as deemed project-appropriate

Binder: Cellulosic polymer

Permeability: 1×10^{-2} to 1×10^{-5} cm/sec

Dry Bulk Density: 65 – 85 lbs/ft³

Moisture: 10 – 20% (maximum)

ORGANOCLAY® P ORGANIC ADSORPTION MEDIA (POWDER GRADE)

Product Description:

Organoclay® P is a proprietary powder adsorption media effective in removing oils, greases other non-aqueous phase liquids (NAPL) and other dissolved high molecular weight/low solubility organic contaminants.

Characteristics:

- Hydrophobic; will not absorb water or swell when wetted
- Non-toxic to marine and benthic organisms
- High adsorption capacity of oils, greases and other NAPL
- Demonstrates noncompetitive sorption—can sorb multiple contaminants

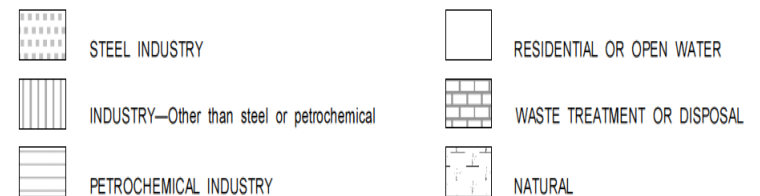
Properties:

Property	Value	Test Method
Particle Size	70% Min. passing 200 mesh sieve	CETCO Test Method
Bulk Density	50-54 lbs/ft ³	CETCO Test Method
Oil Adsorption Capacity	0.5 lb/lb Min.	CETCO Test Method
Quaternary Amine Content	25% Min.	CETCO Test Method

Mix of Historic Industrial Use Drives Target Contaminants & Remedy

- PAHs primary driver of remediation
- Remedy - Objectives

Total PAH Bulk Sediment Concentration in bioturbation zone	27.0 mg/kg – dw (3.4 mg/kg-dw 1 %OC)
Cap Design Life	100 yrs



Example Model Output Results

Case	Media	For model (kg/m2/cm)	Reactive layer Loading		thickness (cm)	Sand thickness (cm)	Log Koc	Initial Porewater conc(C0)(ug/L)	Surface sediment (0 -10 cm) Average bulk concentration (
			lb Oclay/cf	% Oclay by wt					Conc at 100 yrs	Conc at 200 yrs	Conc at 300 yrs	Conc at 400 yrs
Area A:												
Extent of removal ranges from approx 1 feet 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												
Active Layer Mix of Organoclay and granular media												
	Oclay	2.28	14.20	14%	7.6	30.5	4.3	427.5	24.75	281.05	439.28	482.73
	Oclay	1.52	9.47	9%	15.22	30.5	4.3	427.5	0.74	131.86	373.12	468.94
	Oclay	5.32	33.14	45%	7.6	30.5	4.3	427.5	0.02	15.03	103.24	230.87
	Oclay	2.28	14.20	14%	15.22	30.5	4.3	427.5	< 0.01	14.47	142.16	317.19
***	Oclay	3.8	23.67	27%	15.22	30.5	3.7	958.2	25.23	215.75	258.64	261.60
	AC	1.95	na	na	1	30.5	4.3	427.5	71.29	209.75	300.43	357.02
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												
Active Layer Mix of Organoclay and granular media												
	Oclay	0.76	4.73	4%	7.6	30.5	4.6	41	20.95	78.90	90.14	91.29
	Oclay	0.76	4.73	4%	15.22	30.5	4.6	41	0.11	23.04	67.93	86.38
	Oclay	1.52	9.47	9%	7.6	30.5	4.6	41	0.67	26.21	62.56	81.30
	Oclay	2.28	14.20	14%	7.6	30.5	4.6	41	0.02	5.63	28.73	54.64
	Oclay	2.28	14.20	14%	15.22	30.5	4.6	41	< 0.01	< 0.01	0.23	3.13
***	Oclay	3.8	23.67	27%	15.22	30.5	3.8	119.9	0.81	23.75	38.28	40.70
	AC	1.95	na	na	1	30.5	4.6	41	11.76	37.63	55.42	66.74

Post-Placement Active Material Properties Confirmation Testing & Analysis

#1 Oil Sorption Capacity – Pre/Post Placement

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



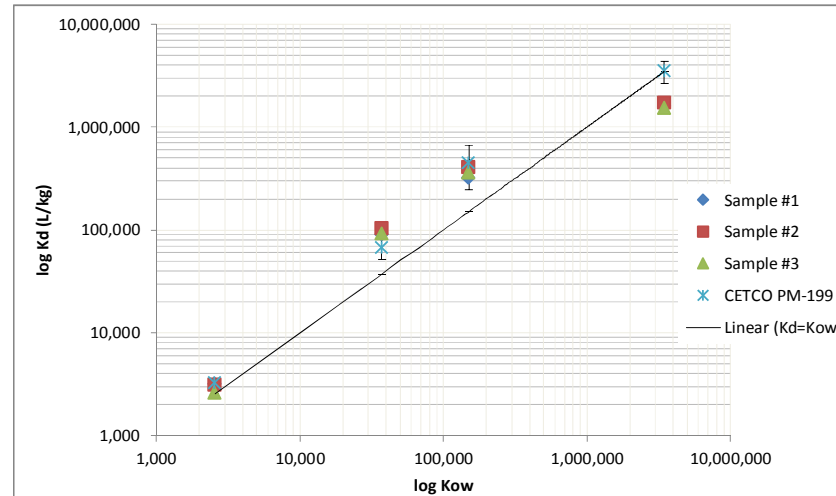
Sample Description	Samples	Oil sorption capacity (%)
Raw Organo clay (Control)	1-1	71.70
	1-2	68.36
	1-3	68.61
	1-4	70.04
	1	average 69.68
As Manufactured Organoclay	2-1	65.82
	2-2	64.88
	2-3	63.44
	2-4	60.59
	2	average 63.68
Sample Buckets - (As-Placed Material Recovered from River Bottom)	3-1	62.86
	3-2	62.65
	3-3	61.40
	3-4	61.99
	3	average 62.22

Oil Sorption Capacity (% dry wt.) for samples

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

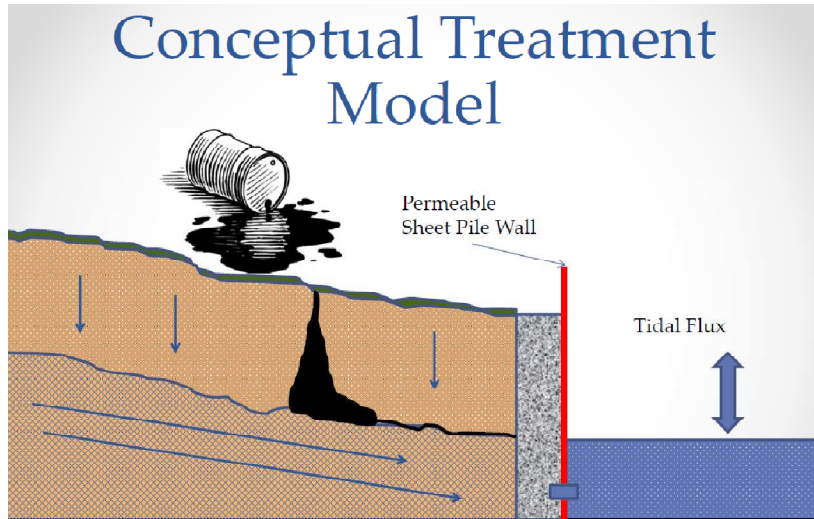
Sample #3 – Post Placement Sample Recovered From River

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

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]

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).”

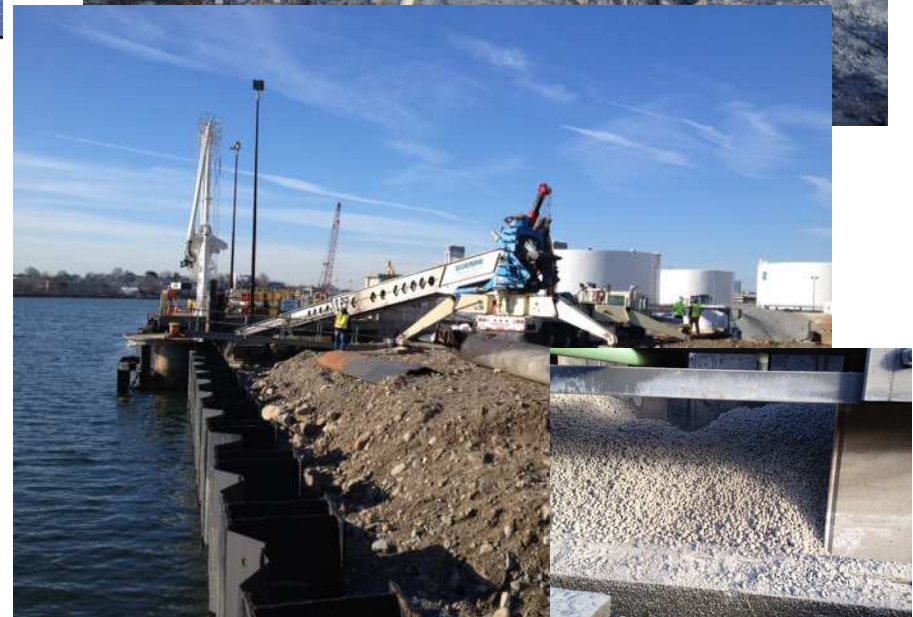
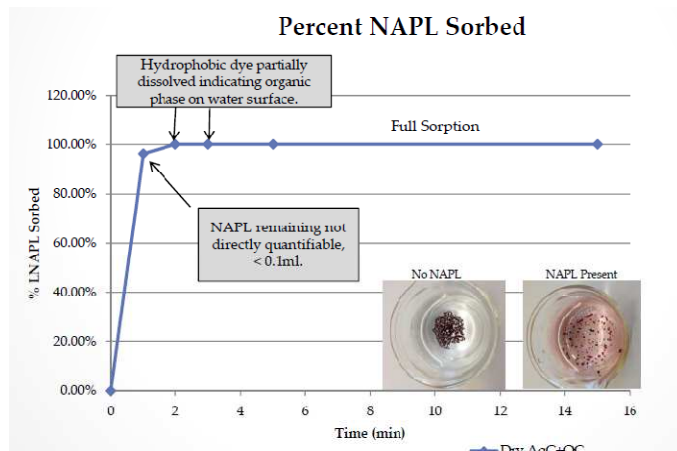
Permeable Reactive Barrier (PRB)



Contaminated Groundwater Flow

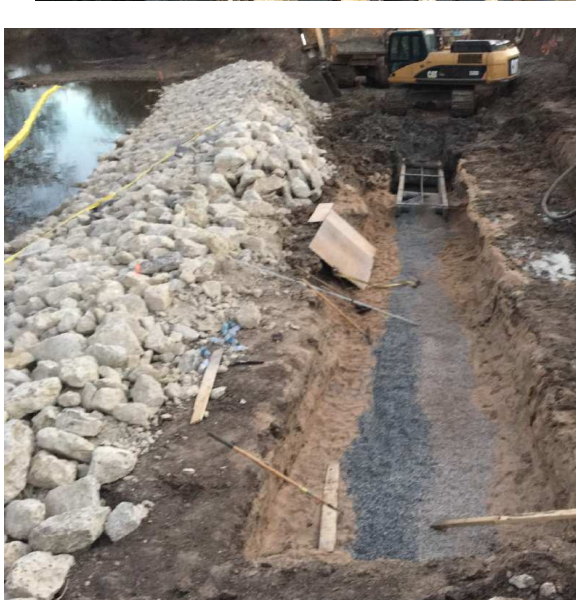
AquaGate+ Organoclay PRB

Tidal Estuary



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



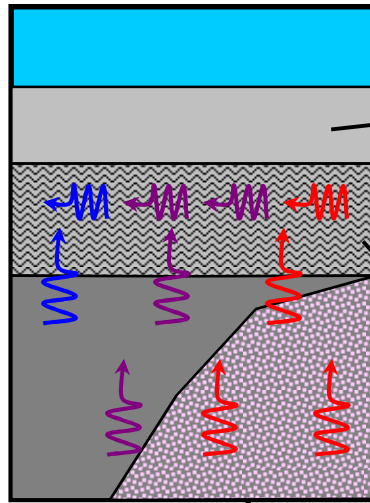
Example of Sheen



The Approach – Funnel & Gate

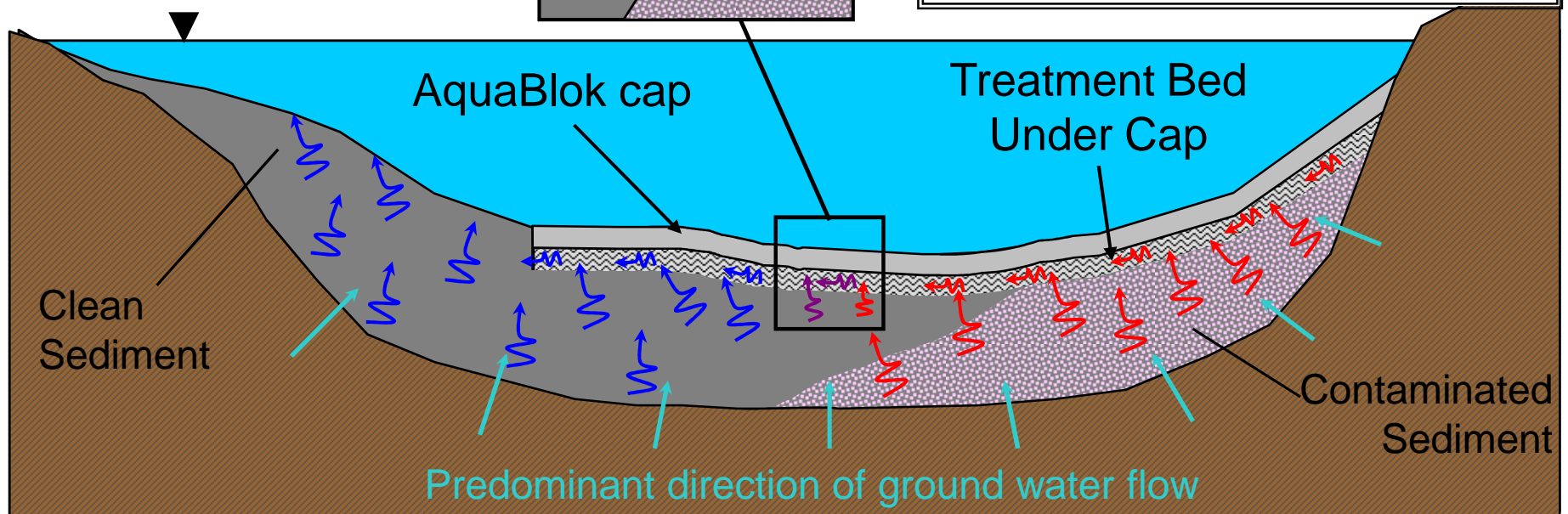
Key Objectives:

- No Localized Breakthrough
- Relatively Long Contact Time for Organoclay



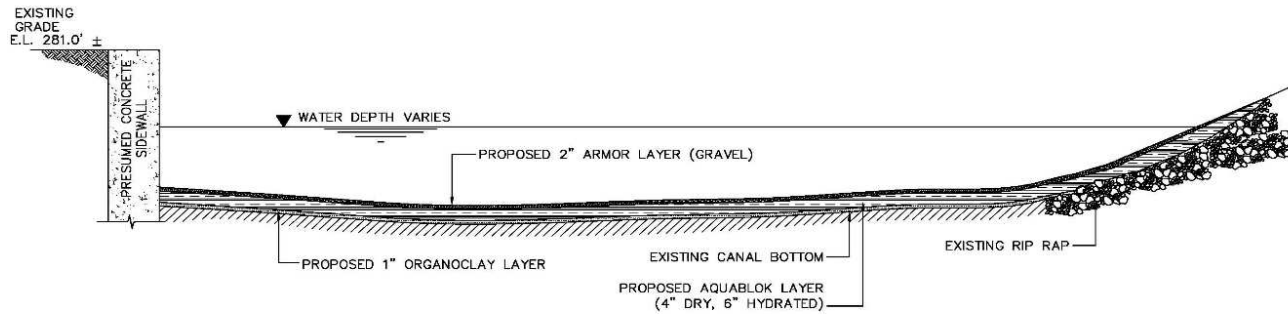
Funneling of Contaminant bearing sediment pore waters are directed beneath a low-permeability cap through a higher-permeability treatment layer that is below the cap

Higher-Permeability Treatment Zone (Gate – includes organoclay or other materials)



not to scale

Funnel & Gate Approach - Continued



PROPOSED SECTION A-A
SCALE 1/4"=1'-0"



Below and Right: View of AquaGate+Organoclay Being Applied & Close up View in Place



Case Study of Funnel & Gate Approach - Continued

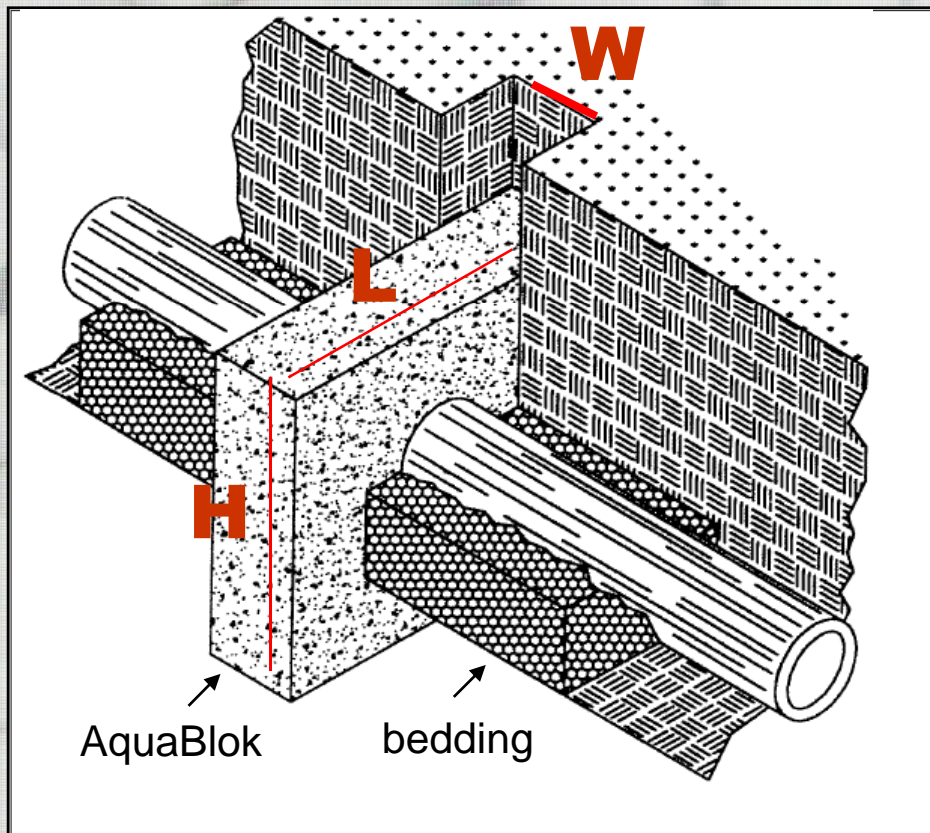
Completed Cap with
Armor Stone - Right



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

Application Examples

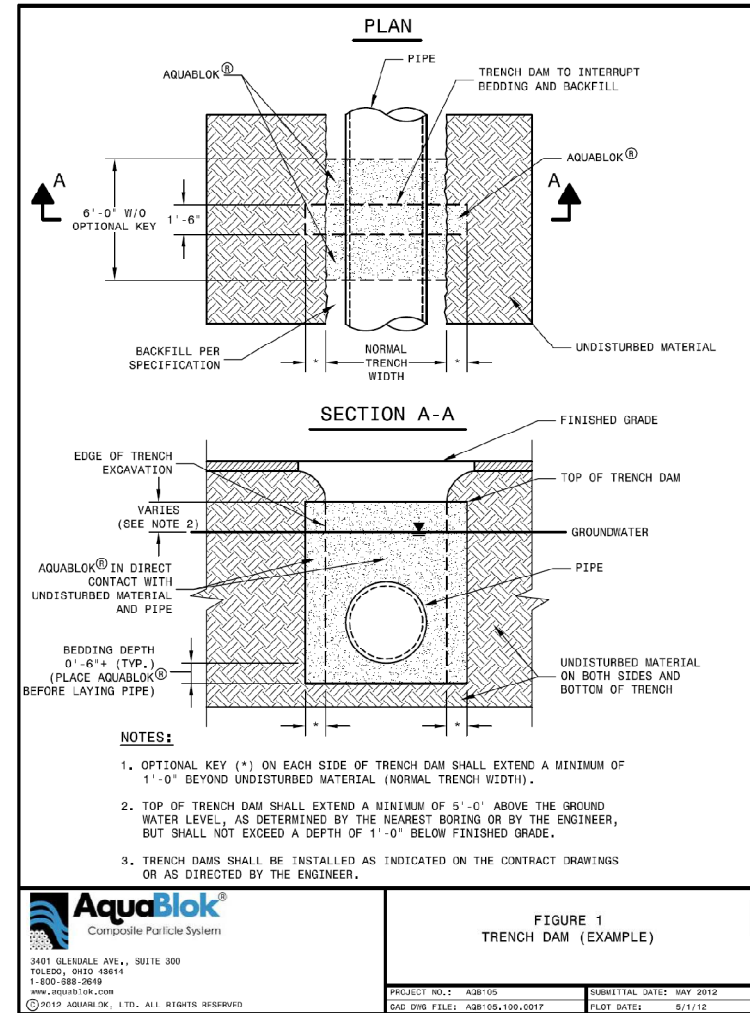
Pipeline & Utility-related Applications



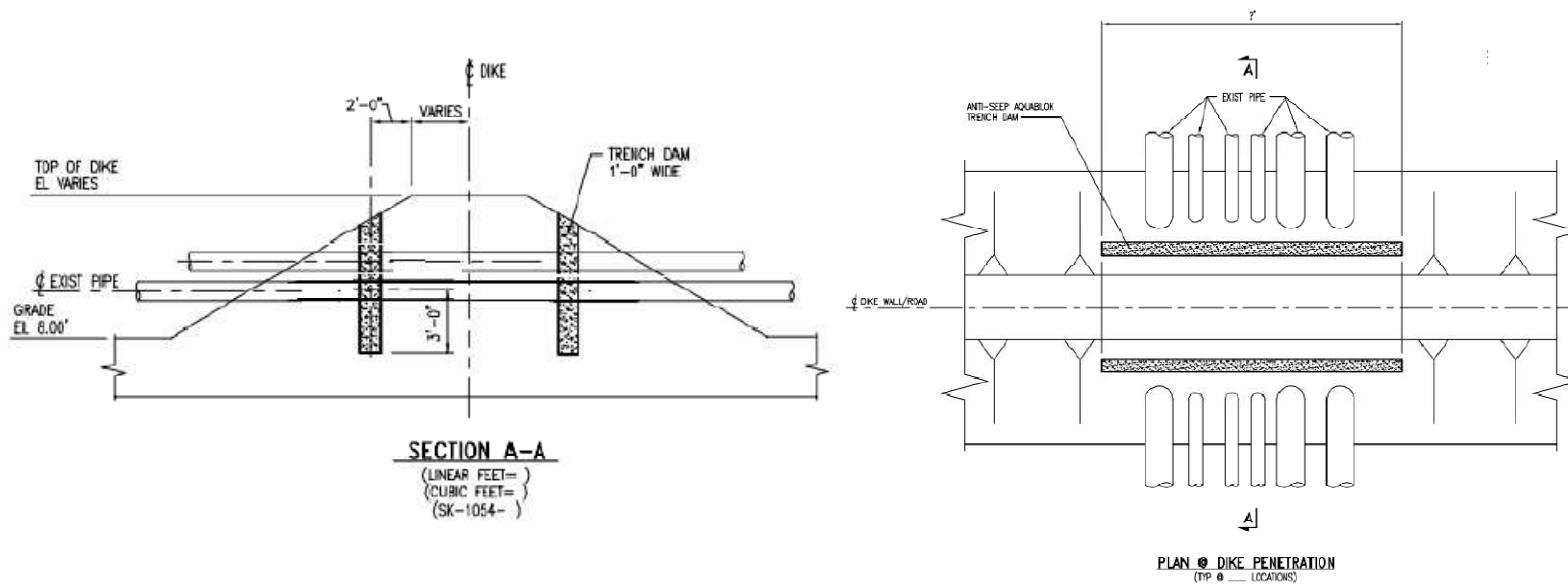
Trench Dams/Anti-Seep Collars

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 5×10^{-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:

- Cofferdam approach used to isolate pipe trench from surrounding soil
- Continuous measurement of AquaBlok performed to insure design thickness of cap

Summary – Q&A

AquaBlok[®]

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

Aquagate₊

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**