QUALITY CONTROL ASPECTS OF ACTIVE CAP MATERIALS & PLACEMENT AT EAST BRANCH GRAND CALUMET RIVER: EVALUATION OF SORPTION CHARACTERISTICS OF AQUAGATE+ORGANOCLAY™ COATED MATERIALS

John A. Collins[1] and John H. Hull[2], PE, BCEE
[1]AquaBlok, Ltd, U.S.A.

ABSTRACT

The East Branch of the Grand Calumet River (EBGCR) is a Great Lakes Area of Concern (AOC) remediated under the Great Lakes Legacy Act (GLA). The specification and design for the EBGCR project called for an active cap consisting of organoclay materials having certain minimum sorptive properties (partition coefficients – Kd values) for two target dissolved phase PAH contaminants. The objective of the additional laboratory-based work in this paper was to determine possible detrimental impacts that either the AquaGate manufacturing process (incorporating CETCO's organoclay powder material into a coated particle) or the act of placing the product in the river may have had on the organoclay sorption capability for either separate phase contamination (oil) and/or dissolved-phase contaminants (selected PAH compounds, including naphthalene; phenanthrene; pyrene, and benzo(a)pyrene). Data demonstrates that use of the project's approach for delivering active-treatment materials to the sediments provided a result that supports the modeling assumptions which were incorporated into the EBGCR remedial design. It can be concluded that such an approach enables full-scale application of active capping materials and construction methods which allows for verification of both the quantity and post-placement material properties relative to project material specifications, design standards, performance goals, and objectives.

Keywords: Active Capping In-Situ Treatment, Quality Control/Quality Assurance, Contaminated Sediment, Organoclay, Treatment Materials

INTRODUCTION

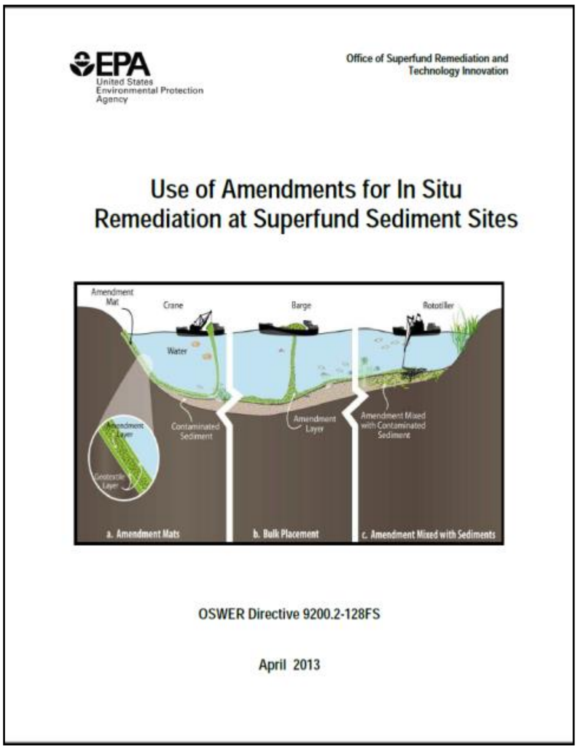
East Branch of the Grand Calumet River (EBGCR) is a Great Lakes Area of Concern (AOC) remediated under the Great Lakes Legacy Act (GLA). The specification and design for the EBGCR was developed by SulTRAC (a TetraTech joint venture) and called for an active cap consisting of organoclay materials having certain minimum sorptive properties (partition coefficients – Kd values) for two target dissolved phase PAH contaminants. Extensive site characterization, and modeling of reactive cap designs were created to evaluate the remedial objectives for sequestration/break-through. To construct the active cap, Great Lakes Sediment Remediation, LLC (GLSR), a joint venture of Natural Resource Technology (NRT), J.F. Brennan Company, Inc., and Environmental Restoration, LLC selected AquaGate+Organoclay (manufactured by AquaBlok®) as the active capping product and J.F. Brennan placed the materials with their proprietary broadcast spreader system. AquaBlok provided quality control data on the as-manufactured/shipped product and NRT performed monitoring and quality control during subaqueous installation of the cap materials in accordance with project specifications. After installation of the active layer, NRT collected additional samples of as-placed cap materials for AquaBlok. AquaBlok subsequently engaged SAO Environmental Consulting to oversee laboratory sorption testing to evaluate the relative sorption characteristics of both manufactured and as-placed product samples.

TREATMENT AMENDMENTS AND EFFECTIVENESS

Beginning in the early 2000s, a significant amount of laboratory activity and testing, as well as small-scale field studies began to establish the practice and acceptability of remediating, or managing, contaminated sediments in situ. The performance of sorptive treatment amendments such as organoclay, activated carbon (AC), apatite, biochar, coke, zeolites, and zero valent iron (USEPA 2013a) provided the impetus to further pursue these amendment approaches. Three of the amendments; organoclay, AC and zero valent Iron, provided results that were considered to be particularly promising due to more extensive understanding and the range of contaminants that could be addressed with these amendments for in situ sediment remediation. Of these, AC has been used more widely in laboratory experiments and field-scale applications to control dissolved hydrophobic organic compounds (HOCs). However, organoclay has been used extensively in oil field operations, permeable barriers and water treatment. Both adsorptive materials have been used successfully for decades.

REGULATORY ACCEPTANCE

In the U.S., the benefits of amendment materials has been recognized by both the U.S. EPA and at the State level as well. The U.S. EPA provided the below document in April of 2013 to document and discuss the used of amendments at Superfund sediment sites.



EPA
United States Environmental Protection Agency

Office of Superfund Remediation and Technology Innovation

Use of Amendments for In Situ Remediation at Superfund Sediment Sites

OSWER Directive 9200.2-128FS

April 2013

In part, the above document points out that; "The appropriate use of amendments has much potential to limit exposure to contaminants and, thus, to reduce risks."

The primary benefits of amendment use, as outlined in this and other regulatory documents include the following:

- Less obtrusive than dredging
- Focused on reducing risk/bioavailability
- Shorter recovery time
- Less costly and more expedient

PROJECT OVERVIEW

EBGCR is located at the southern base of Lake Michigan in a highly industrialized area. The region is home to some of the country's largest steel making operations and also supports coal, mineral and energy (refinery) operations for many firms. The EBGCR is connected to Lake Michigan via the Indiana Harbor Canal. The river has been identified as an Area of Concern (AOC) for many years and several segments of the west branch of the Calumet River has previously undergone significant remediation efforts. Below are two graphics that show the overall location and the specific reach of the river, which is the subject of this paper.

The EBGCR project is shown in the box below labeled "B". This reach is approximately 1.8 miles in length and runs from Indianapolis Avenue to Holman Avenue.

The project approach includes dredging of over 350,000 cubic yards of sediment, placement of the reactive cap and restoration of large sections of the river bank and adjacent marsh.

ACTIVE CAP DESIGN & MATERIALS

As noted previously, the design of the active cap was determined to provide isolation of residual contamination for a period of time, determined to be acceptable to project owner. The thickness and organoclay content was determined by modeling the "time to break-through" of residual contamination moving upward through the cap, driven by advection and diffusion. The specification was expressed in terms of layer thickness and organoclay content – on a pounds per cubic foot basis. However, the adsorptive properties of the organoclay were also called out in the specification. Key aspects of the specification are as follows:

- The organoclay shall have minimal swelling after placement and shall have a minimum predicted long-term permeability of 10-3 centimeters per second (cm/s)
- 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).
- The organoclay will have a minimum quaternary amine loading of 25%.
- The organoclay shall applied such that the loading is at a minimum 4.1 kg/m2/cm (25.5 lb/ft3) in Area A and 1.37 kg/m2/cm (8.5 lb/ft3) in Area B.
- Aggregate material used in the adsorptive layer shall meet the gradation shown in Table 2 (essentially an AASHTO #8).

The product selected was AquaGate+Organoclay as shown in the photo below:

There are a number of key assumptions and design aspects of the reactive cap that are important to the overall design. Below is a list of some of these considerations:

Uniform Distribution of Treatment Material within Layer is Most Critical.
Residence Time for Adsorption AND ***Capacity*** determines Thickness.
Isolated Seep Zones May require larger Quantity of Treatment Material to Protect Against breakthrough.
Reduction in Permeability can occur from long-term saturation of reactive material.
Rate of Sorption Is faster with Powder Materials as compared to Granular forms of reactive material.

MATERIAL STORAGE & PLACEMENT

AquaGate+Organoclay was packaged in Supersacks (bulk bags) of approximately one cubic yard in size. The material was stored on-site prior to placement. Below is a photo of the material stored on-site prior to placement.

Placement (installation) of the material was performed by J.F. Brennan utilizing its patented barge-based Broadcast Capping System (BCS^{TM}) equipment. Material was loaded onto barges via a hopper/conveyor system that had the ability to mix two material streams. The barges transported the bulk material out to the placement system. The placement system, shown in the photo below, provides a number of key advantages as described below:

- Spread materials in very thin lifts, while achieving even distribution
- Accurate placement on soft sediment with limited intermixing
- Limits resuspension
- Onboard tracking system records thickness, volume, and position of material placement

MANUFACTURING QUALITY CONTROL

All parties considered as-manufactured material quality control and reporting to be a critical aspect of the project, to insure that the delivered material would meet the intent of the design.

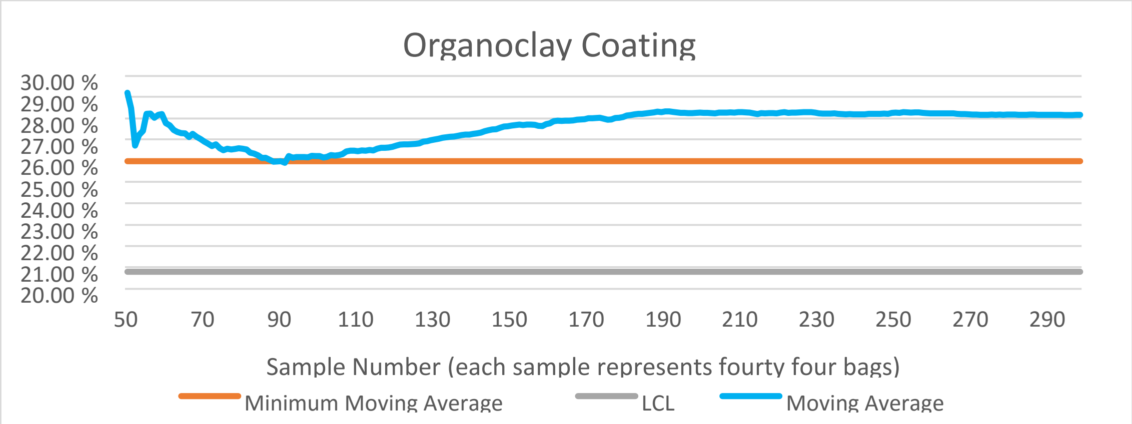


Fig. 1 Coating Percentage by Weight

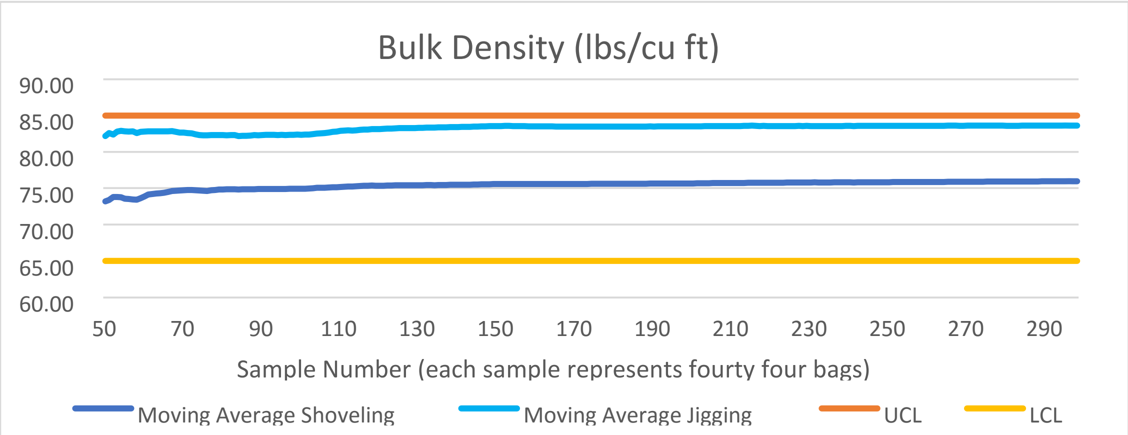


Fig. 2 Bulk Density

The two primary characteristics tracked were the coating content (percent by weight) and the bulk density of the manufactured product. The coating weight establishes the content of organoclay contained by the AquaGate+Organoclay composite particles. This percentage was utilized, along with bulk density, by the engineer during design of the active capping layer. The calculations and specification called for a quantity of organoclay based on pounds per cubic foot, which could be derived from the above two key material metrics.

Bulk density is important because it is a measurement that will determine layer thickness in a capping design. Since the material is to be placed through a water column to the sediment surface, it was determined that ASTM method for loosely placed material would be used (referred to as (Shoveling Method). However, in an effort to provide more information to the project team, the Jigging Method, which is an indication of a more compacted material bulk density, was also used and reported.

Detailed production quality control reports were also prepared and the information was made available to the project team under confidentiality agreements, since it was determined that proprietary manufacturing information was being made available. This approach created significant confidence that the as-manufactured product was meeting the specified material properties.

POST-PLACEMENT QUALITY CONTROL

As outlined in the Active Cap Design and Materials section above, the specified organoclay content in “Area A” (shown as the A-Cap in the table below) was 25.5 lb/CF and the organoclay content in “Area B” (shown as the B-Cap below) was 8.5 lb/CF.

B-Cap				
Bucket Number	ID #	Fines %	Ave. Fines	lb/cu ft
1	092514465	12.79%	14.38%	14.04
		15.87%		
		14.48%		
2	092614474	6.37%	5.36%	5.23
		4.91%		
		4.79%		
3	092914549	6.38%	8.82%	8.61
		7.34%		
		12.75%		
4	092914557	8.66%	8.89%	8.68
		7.67%		
		10.34%		
Average Fines			9.36%	
Target lb/cu ft			7.0 - 7.2	
Actual lb/cu ft			9.14	

A-Cap				
Bucket Number	ID #	Fines %	Ave. Fines	lb/cu ft
5	100214689	39.63%	31.08%	25.64
		27.49%		
		26.12%		
6	100814783	25.78%	31.15%	25.70
		36.48%		
		31.18%		
7	110614534	28.10%		23.19
8	111114665	28.03%		23.13
9	111814798	26.78%		22.09
Average Fines			29.03%	
Target lb/cu ft			21.45	
Actual lb/cu ft			23.95	

Fig. 3 Post-Placement Organoclay Content in Cap.

Materials for post-placement testing were recovered by Natural Resource Technology (NRT), Below is a photo of the AquaGate+Organoclay material in a sample bucket (recovered from the river bottom), as it was received at AquaBlok's facility prior to processing. It is apparent that the original form of the AquaGate material was retained almost completely intact following, transport, handling and placement of the material.

Fig. 4 Post-Placement Retrieved Cap QC Bucket

Figure 3 tabulates the results obtained on Sample Buckets 1 through 9.

Sample Buckets 1 - 6 were processed using the same method, using three replicate sub-samples from the bucket. However, sample buckets 7-9 utilized an expanded test method that essentially evaluated all of the material recovered in the sample buckets. All Sample Buckets registered results above the Target lbs. /cu ft. based on the "average fines" content within the buckets. The "fines" in the above tables consist of material recovered from the sample buckets which is less than 50 mesh in particle size. To recover this material it was necessary to remove the coating from all intact AquaGate particles. This material is assumed to represent the organoclay content within these samples. This assumption was confirmed by performing the following further testing on material recovered from these sample buckets.

AS-PLACED MATERIAL TESTING

The above post-placement evaluation essentially verified that organoclay 'fines' were successfully delivered to the sediment surface. However, the question that remained to be addressed was – were the specified material properties of the original raw organoclay material retained throughout the manufacturing and placement in the river.

To ensure independence in this evaluation and testing, SAO Environmental Consulting was engaged to develop and supervise the testing program described herein, as well as provide an evaluation of the results.

Three different organoclay materials were evaluated from EBGCR Samples:

Sample #1 - Powder organoclay as-received from CETCO;

Sample #2 - Organoclay coating from as-manufactured AquaGate;

Sample #3 - Organoclay coating material recovered and removed from AquaGate placed in the river.

Two separate tests were performed, the first measured oil sorption (pure phase) – this test was designed and conducted by CETCO (the organoclay manufacturer); the second, measured sorption of dissolved-phase PAH compounds (determine K_d values) was designed and performed by Prof. Danny Reible's laboratory at Texas Tech University (TTU).

CETCO's Oil-Sorption Testing

As shown in Figure 5, data from three replicate tests of the above described samples resulted in percent sorption well above the target value of 50% of the organoclay, by weight. Other key results are as follows:

- Mean oil-sorption capacity for as-received powder material was ~70% (by dry wt.), whereas values for as-manufactured and as-placed coating materials were ~90% of this value (i.e. ~64 and ~62%, respectively).
- The difference between mean values for the two coating materials did not appear to be statistically significant. However, small yet significant differences were apparent when comparing mean values for coating materials with that for as-received powder material.
- If statistical interpretations of testing results are valid, the slightly lower sorption capacities displayed by both coating materials may be a temporary phenomenon, observed only during short-term laboratory testing. Coating materials likely (and uniquely) contain "micro-aggregates" of organoclay + polymer, which may initially limit oil sorption onto some organoclay particle surfaces. Over time after AquaGate placement, the polymer should degrade and expose previously occluded organoclay particles for additional oil sorption.
- Mean values for oil sorption presented herein for the EBGCR coating materials are at least 10% higher than values previously determined by CETCO for organoclay coating material from earlier AquaGate+Organoclay samples. This difference is likely an artifact of differences in methods used by CETCO and AquaBlok for sample preparation and processing.

Samples	Oil sorption capacity (%)
1-1	71.70
1-2	68.36
1-3	68.61
1-4	70.04
1	average 69.68
2-1	65.82
2-2	64.88
2-3	63.44
2-4	60.59
2	average 63.68
3-1	62.86
3-2	62.65
3-3	61.40
3-4	61.99
3	average 62.22

Fig. 5 CETCO Oil Sorption Results

Texas Tech Sorption Testing

As shown on Figure 6, data from partition coefficient testing resulted in linear expression that would be expected of the materials tested.

- Results from sorption testing suggest all samples meet or exceed specified partition coefficient (K_d) values for light weight PAHs, e.g. phenanthrene (at least 50,000 L/Kg) and mid to heavy weight PAHs, e.g. pyrene (at least 350,000 L/Kg). Project specifications do not clarify the nature of these minimum values, e.g. means from replicate sample testing. Regardless, although the mean K_d value

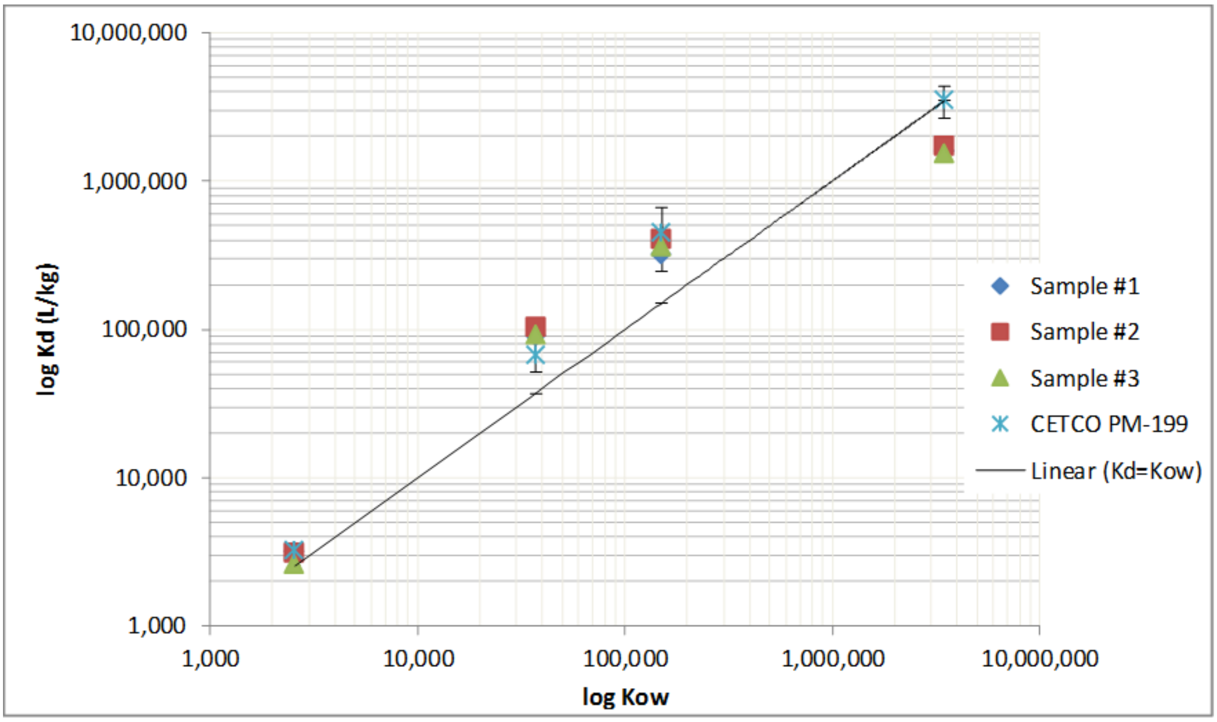


Fig. 6 Texas Tech Sorption Results.

measured herein for pyrene on the as-received organoclay sample (~323,000 L/Kg) was slightly below the above target, the difference between this mean value and mean values measured for the two coating samples – both of which exceed the target - was not considered statistically significant. Therefore, it was concluded all three samples effectively met the project specification.

- The test report concluded there were no substantial differences in mean K_d values between the three EBGCR organoclay materials for each dissolved-phase PAH compound. For this work, "substantial differences" would be considered differences in K_d values of greater than a factor of 2.
- There were not only no substantial differences in PAH-specific K_d values amongst the three EBGCR materials, these PAH-specific values were also essentially equivalent to PAH-specific values previously determined for CETCO's granular PM-199 product.
- Comparisons between current and past PM-199 testing data indicate organoclay particle size appears to have no real effect on organoclay sorption of dissolved-phase PAH compounds.

CONCLUSIONS

The results of this work provide important data for the future modeling, design and application of treatment or materials in an active cap sediment remedy. The following represents a list of key attributes that can be provided by improved quality control and quality assurance when using adsorptive or active materials within a cap design:

Ability to *confirm the quantity of high-value amendment material* (organoclay coating weight) being supplied and placed.

Confirmation of material properties such as bulk density (*determines layer thickness*) which is critical to demonstration that this key design parameter is met.

Verification of uniform distribution of active-treatment materials is achieved through the thickness of the capping layer.

Enables ability to perform post-placement confirmation of active-treatment material testing of *adsorption capacity* (partition coefficient) that satisfies the specification.

Modeling output can be confirmed through comparison of input/assumptions to post-placement physical and material property data.

Results can support modeling assumptions and be used to *reduce costs associated with excessive factors of safety* due to lack of certainty of achievement of a design / specification as well as the ability to provide post-placement verification.

Full-scale verification of quantity and post-placement material properties relative to project objectives

ACKNOWLEDGEMENTS

The Great Lakes Sediment Remediation, LLC (GLSR) team is a joint venture of NRT, J.F. Brennan Company, Inc., and Environmental Restoration, LLC. NRT acted as program manager for GLSR, and provided the key interface with the USEPA’s Great Lakes National Program Office (GLNPO).

SAO Environmental Consulting, AB is a Sweden based firm established by Joeseph Jersak, a Phd Soil Scientist who has been working in Sediment Remediation since 1998.

SulTRAC designed the remedy and served as the EPA’s representative during the project.