UCONN
SCHOOL OF ENGINEERING

PAC Placement Testing Report

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1. Introduction

Many underwater sites contain concentrations of metals, PCBs and PAH contaminants that could continue to cause injury to the biota in the sediments and overlaying water. Currently, the primary remedial options for underwater sites include dredging, isolation capping, and Monitored Natural Recovery (MNR). Although in-situ treatment is discussed in the United States Environmental Protection Agency (USEPA) Guidance for Contaminated Sediment Remediation (2005), implementation and acceptance remain limited. Dredging can have adverse short-term effects such as impacts to the benthic community and surface water. MNR is generally targeted to quiescent, depositional environments and is generally thought to be poorly suited to high-energy environments subject to significant vessel traffic. MNR is likely to be ineffective for highly contaminated sites. Conventional sand-based isolation capping may be limited by vessel draft requirements, and can be unstable in the face of tides, currents, ship and tug movements.

Cap erosion is well documented for noncohesive granular materials that constitute various caps and for material used to armor caps. The potential impacts of cap placement include an increase in turbidity due to suspended sediment in the water column and a destabilization of the underlying sediment, causing slope failure and resuspension of the contaminated sediment. Meeting long-term cap performance goals depends on the stability of the cap for its design life. The cap must withstand erosive forces from the overlying water body. Caps are typically designed to resist erosion during expected flow events and to resist erosional forces from propeller wash and tidal pumping. In general, currents greater than 1 ft/s increase the difficulty of sand cap placement and increase the potential for cap erosion. Placement of a cap and its longevity also require that the underlying sediment withstand potential excessive cap loading. Slopes with a low factor of safety for stability (e.g. less than 1.5) and low undrained shear strengths (less than 1 kPa) may require more complex cap design, greater thickness, and more advanced placement methods. Erosion resistance may sometimes be improved by incorporating more cohesive materials such as clay. There is a need, however, for more innovative approaches for rendering non-colhesive granual materials more erosion-resistant.

Groundwater movement through a conventional or amended cap typically controls contaminant transport. Groundwater upwelling of greater than 1 cm/day is dominated by advection, while diffusion dominates when groundwater upwelling is less than 1 cm/month. An advection-dominated groundwater rate of 1 cm/day would most likely require an amended cap to control contaminant transport through permeability reduction, contaminant sorption or degradation. and may have minimal capacity to control sources. Thus, amemdments to the caps are often considered in order to reduce these negative impacts. Active capping to control permeability or to retard the migration of contaminants through sorption is a technology that has been applied successfully in the field. A number of materials are available for amended active capping. Activated carbon (AC) strongly adsorbs organic compounds that are typically associated with sediment contamination and can be an effective cap amendment. However, placement of AC, and powdered activated carbon (PAC) in particular, for sediment capping is challenging due to the near neutral buoyancy of the material. One procedure for placing a thin layer of AC uses a Reactive Core Mat®, a permeable composite mat consisting of reactive material(s) encapsulated in a non-woven core matrix bound between two geotextiles. Other delivery system for AC include AquaGate+PAC, a powdered AC delivery system used with the AquaBlok® clay-based technology, and SediMite™ pellets that are comprised of 50% powdered activated carbon by weight, allowing for a high dose of activated carbon to be placed on contaminated sediment. There is a need, however, for more innovative approaches for improving the effectiveness of cap amendment placement.

An in-situ technology that uses protein polysaccharide biopolymer (PPB) amendments has been developed by Dr. Dahmani and SESI Consulting Engineers to render sand-based isolation capping of sediment more stable (Dahmani, et. al., 2018) and to enhance sand cap amendment placement. The product formulations are composed of polysaccharides and protein extracts that are designed based on the characteristics of the site. The dispersible PPB products abiotically react with the materials treated. In addition, the products act as biostimulants and accelerate the generation of biotic exudates from microorganisms. The impact of natural biopolymers on sediment cohesion has been actively studied. The studies have demonstrated that extracellular organic secretions from microorganisms and microphytobenthos can coat sediment clasts, act as a mucilage glue, and increase the cohesive nature of the sediment (Yallop et al., 1994; Le Hir et al., 2007). The organic exudates (proteins and carbohydrates) form biofilms on the surface of sand grains and enhance the cohesion of sediment by forming tiny aggregates that grow larger as the activity from microorganisms and microphytobenthos continues. Studies also determined that a positive correlation exists between soil concentrations of extracellular organic secretions and soil aggregate stability (Rillig 2005). In addition, the secretions increased critical erosion velocity of intertidal sediment (Widdows et al. 2006). The secretions contain polysaccharide structures that include a main backbone with attached polar groups. This results in a high water-holding capacity (Mikkelsen, 1994) and enhances biological activity (Zhang et al., 2005). The soils typically have a higher density of saturated pores and higher volumetric water content (Rillig, 2005), resulting in higher erosion thresholds throughout periods of desiccation (Perkins et al., 2004). The increased release and decomposition of dissolved organic matter within aggregates during the wetting cycle results in an increase in sediment stability and strength (Park et al., 2007).

In order to demonstrate the impact of natural biopolymers on sand cohesion, Banagan et al. (2010) showed that biofilm produced by an aerobic Gram-negative bacterium that is commonly found in soil and freshwater, Flavobacterium johnsoniae, increased significantly the shear strength of saturated sand, thereby improving sand stability. Ayeldeen and Negm (2014) used direct shear measurements to demonstrate that xanthan gum treatment increased sand cohesion. In addition, they showed that sand cohesion was directly related to the biopolymer concentration used to treat the sand. Khatami and O'Kelly (2012) used triaxial compression testing to demonstrate that agar treatment can improve significantly the shear strength of sand. Finally, Guo (2014) used unconfined compression and direct shear tests to assess the effect of different biopolymers on sand and loess strength.

In a previous study, testing was conducted at the University of Connecticut (UCONN) to assess the cohesion-enhancing properties of PPB amendments by measuring direct shear strength (ASTM D3080) and Unconfined Compressive Strength (UCS) of treated sand (Dahmani, et. al., 2018). Testing was also conducted on sediment from a tidally influenced shallow creek system in southern New Jersey to assess PPB treatment effectiveness in reducing the turbidity and total suspended solids (TSS) of sediment/water mixtures. Finally, aquatic toxicity testing was conducted to assess toxicity of the PPB amendments. The tests (EPA-821-R-02-012) were performed using freshwater and saltwater species (Dahmani, et. al., 2018).

The PPB treatment increased significantly (greater than 10-fold) the cohesion and compressive strength of cured sand samples up to a dosage of 10 g/kg (1%). Enhanced cohesion generated by the PPB treatment is dependent on water saturation, curing time and temperature, among other parameters. PPB-treated sediment from the tidally influenced shallow creek system showed reductions of 76% in turbidity and 87% in total suspended solids (TSS) as compared to untreated sediment. This indicates that PPB treatment can reduce significantly the erodibility of sand-based caps, and minimize resuspension of sediment during cap placement. In addition, the aquatic toxicity results indicated that the PPB treatment passed the acute toxicity tests (> 90% survival).

The study presented here evaluates the use of PPBs to effectively place PAC-amended sand caps and minimize PAC suspension in the water column due to the near neutral buoyancy of the material.

2. Laboratory Testing Methodology

To evaluate the impact of PPB treatment on PAC dispersion in water during PAC-amended sand cap placement, turbidity, PAC concentration and visualization tests were conducted using different PPB formulations and dosages.

Materials Used

a) PPB Formulations

Two PPB formulations (SED-0 and SED-3), each containing a unique combination of protein extracts and polysaccharides were evaluated in the study. Pictures of the formulations are presented in Figure 1.

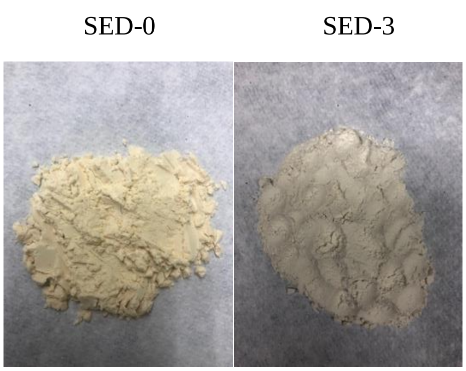

Fig. 1: PPB formulations

b) Sand and Activated Carbon

The sand used in the testing was Ottawa Flint Silica #13 (medium sand) from ITC, Inc. It is 99.8% silicon dioxide (Figure 2).

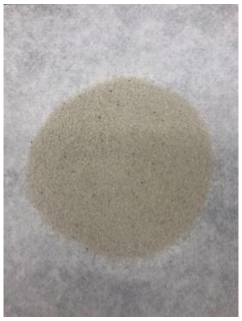

Fig. 2: Ottawa Flint Silica Sand

The powdered activated carbon (PAC) used in the study is the GC Powdered AG from General Carbon in New Jersey (Figure 3). It is a virgin carbon derived from selected grades of bituminous coal.

Fig. 3: Powdered Activated Carbon

c) Turbidity Meter

A Hach 2100N turbidity meter (Figure 4) was used to measure water turbidity in PPB/PAC-amended sand reactors.

Fig. 4: Turbidity Meter

Turbidity Testing

Turbidity measurements were obtained from 300-ml glass jar reactor tests containing a PPB-treated sand/PAC matrix mixed in tap water. The sand/PAC matrix consisted of 95 grams of sand and 5 grams of PAC (5% PAC by weight). The sand/PAC matrix was treated with PPB formulations at a 0.2% or 0.5% by weight concentration. A control test with no PPB treatment was also set up. For each reactor, dry sand was weighed and placed in the glass jars and 5 grams of PAC were added (5% by weight). The lid was placed on the jar and the sample was shaken to mix the PAC and sand uniformly. 20 mL of water was added to each sand/PAC mixture (approximately 20% moisture content) and stirred in. The PPB treatment (0.2 or 0.5% by weight) was subsequently mixed in to ensure uniform distribution of the treatments. Two PPB formulations, SED-0 and SED-3 were tested in these experiments. The glass jars were then filled to the top with tap water. Subsamples of each reactor were collected in duplicate 30-ml vials for turbidity measurement immediately following the treatments. The subsamples were inverted three times to allow for uniform PAC suspension in the water phase, and a timer was started for 60 minutes. Photographs were taken of the initial conditions of each jar, and additional photographs were taken after 5, 30, and 60 minutes. At each of these time increments, turbidity was measured in order to assess turbidity reductions during settling.

PAC Concentration Measurement

To quantify the amount of suspended PAC in each sample at the 5, 30, and 60-minute increments, a PAC concentration versus turbidity calibration curve was developed. PAC concentrations of 0% (control), 0.01%, 0.017%, 0.034%, 0.067%, 0.1%, 0.134%, 0.167% and 0.234% were plotted versus turbidity. The equation of the line generated from this data was used to determine the concentration of PAC in each sample collected in the experiments.

Water Column Visualization Tests

In order to visualize the impact of the PPB treament on PAC dispersion in the water column during cap placement, one optimum PPB-treated PAC-amended sand sample (based on turbidity and PAC content tests) and the untreated sand/PAC control samples were broadcasted in 1-L graduated cylinders filled with tap water. The samples were prepared in the same way as the turbidity tests. The PPB-treated PAC-amended sand sample and the control PAC-amended sand sample were gradually added to separate water-filled graduated cylinders and a video was recorded of the condition of the water columns during placement. The video was paused to capture visuals of the conditions of the water columns at different times throughout the process.

3. Results and Discussion

Duplicate samples were prepared for five different mixes of PPB-treated 5%PAC-amended sand and turbidity measurements were taken at 5, 30, and 60 minutes. The turbidity measurements were then correlated to PAC concentrations based on the PAC/turbidity calibration curve presented in Figure 5.

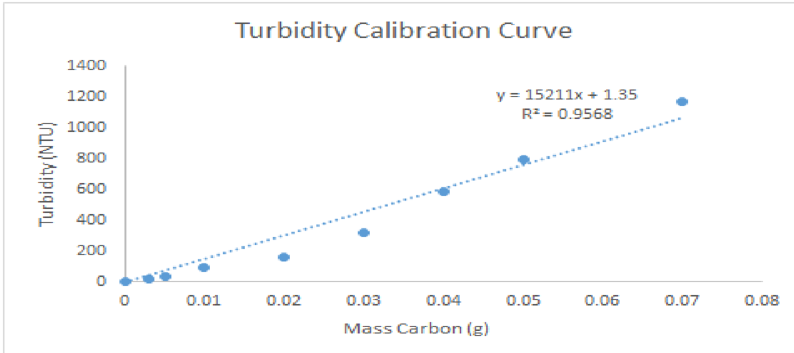

Figure 5. *Calibration curve correlating PAC content to turbidity*

Control Samples

The first duplicates tested were the control samples, consisting only of 5% PAC-amended sand. Table 1 presents the turbidity measurements and the corresponding suspended PAC content in 30 ml of water for each sample. The results indicate that the turbidity and suspended PAC content remained high in the control samples (> 290 NTU), even after 60 minutes. Figure 6 depicts turbidity variations with time for the control duplicates. Figure 7 depicts suspended PAC content with time for the control duplicates. As Figure 8 shows, the water in a control turbidity vial remained opaque after 60 minutes. Figures 9, 10 and 11 present pictures of the water column visualization tests showing the water column at the inititation of the 5% PAC-amended sand addition (Fig. 9), the water column after the addition of approximately 30 grams of 5%-amended sand (Fig. 10) and the water column after 100 grams of 5% PAC-amended sand were added (Fig. 11). The pictures indicate rapid dispersion of the PAC in the water column and gravity segregation of the sand and PAC at the bottom of the column.

Table 1. *Control tests Turbidity and Suspended PAC over a 1-hr period in duplicate trials*

Time (min)	Suspended PAC (g)	Turbidity (NTU)
5	**0.023**	**352**
5	**0.059**	**892**
30	**0.015**	**222**
30	**0.027**	**412**

60	**0.010**	**161**
60	**0.019**	**291**

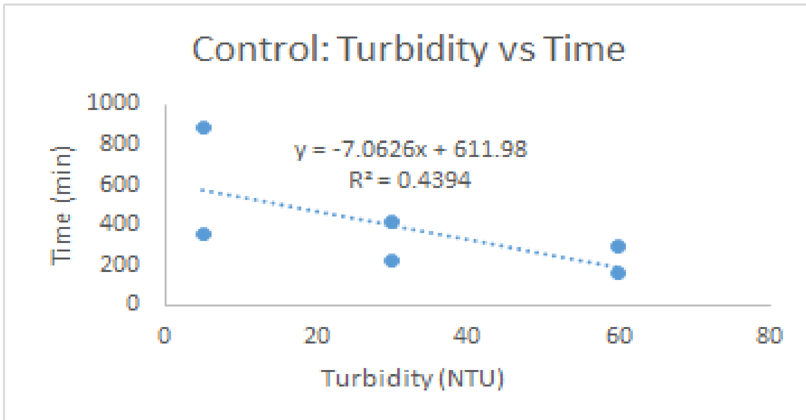

Figure 6. *Control samples turbidity vs. time in duplicate trials*

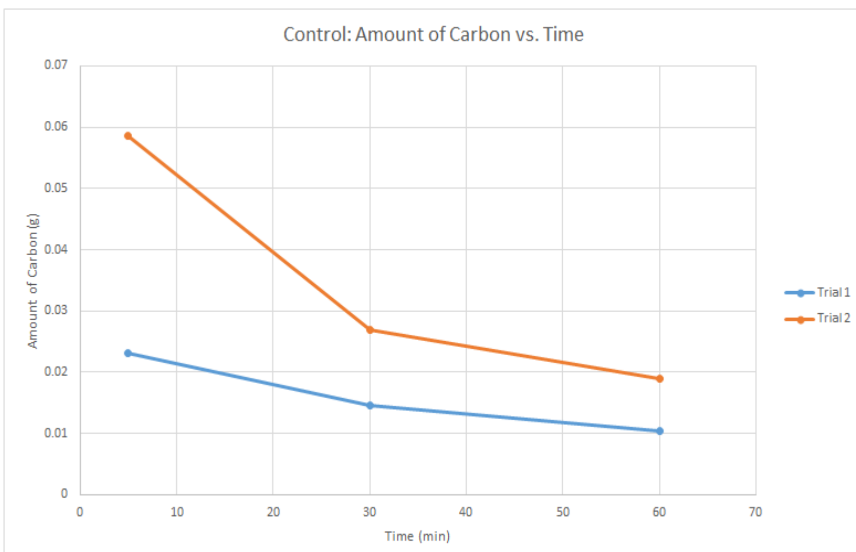

Figure 7. *Control samples Suspended PAC content vs. time*

Figure 8. *Control sample after 60 minutes*

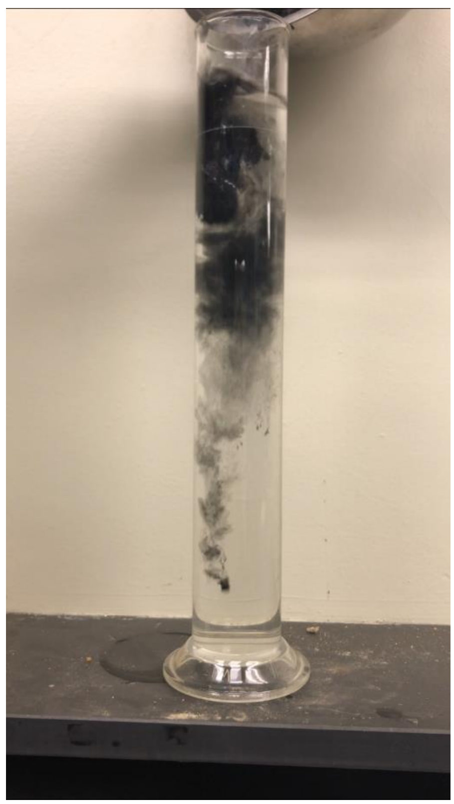

Figure 9. *Initiation of the addition of 5%PAC-amended Sand to Water Column*

Figure 10. *Water Column Condition after adding approximately 30 grams of 5%PAC-amended Sand*

Figure 11. *Water Column Condition after adding 100 grams of 5%PAC-amended Sand*

SED-3 Treatment Test Samples

The samples that yielded the best results in terms of minimizing PAC resuspension were the SED-3, 5% PAC-amended sand samples. Table 2 presents the turbidity measurements for the SED-3, 5% PAC-amended sand samples and the corresponding suspended PAC content in 30 ml of water for each sample. The turbidity and suspended PAC content were much lower (> 90% reduction) in these samples as compared to the Control samples (Tables 3 and 4). Suspended PAC concentrations in the water phase decreased from 1.36 g/l in the Control sample to 0.12 g/l in the PPB-treated sample after 5 minutes and from 0.49 g/l in the Control sample to 0.04 g/l in the PPB-treated sample after 60 minutes. Figure 12 shows the variation of turbidity with time over the 60-min test. Figure 13 shows the variations of suspended PAC content with time. As Figure 14 shows, the water in a 0.5% SED-3, 5% PAC-amended sand sample vial was much less turbid than the Control after 60 minutes. Figures 15, 16 and 17 present pictures of the water column visualization tests showing the water column at the inititation of the 0.5% SED-3, 5% PAC-amended sand addition (Fig. 15), the water column after the addition of approximately 30 grams of 0.5% SED-3, 5%-amended sand (Fig. 16) and the water column after 100 grams of 0.5% SED-3, 5% PAC-amended sand were added (Fig. 17). The pictures indicate limited dispersion of the PAC in the water column and no segregation of the sand and PAC at the bottom of the column.

Table 2. *0.5% SED-3 Turbidity values and PAC content over 1-hr period in duplicate trials*

Time (min)	Amount of PAC (g)	Turbidity (NTU)
5	**0.0037**	**58.1**
5	**0.0032**	**49.6**
30	**0.0016**	**25**
30	**0.0015**	**24.9**
60	**0.0013**	**21.5**
60	**0.0013**	**21**

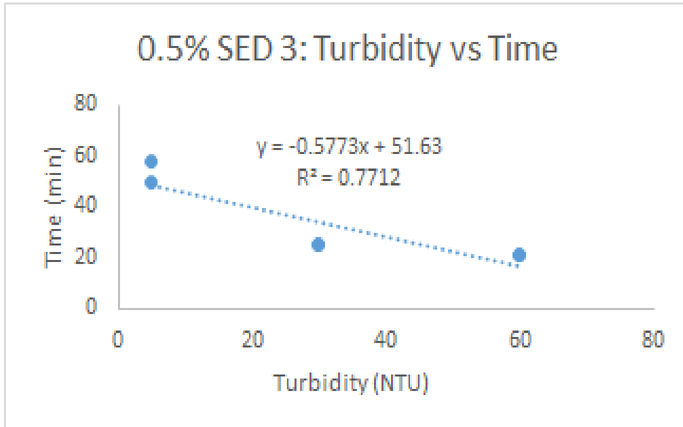

Figure 12. *0.5% SED-3 turbidity vs. time in duplicate trials*

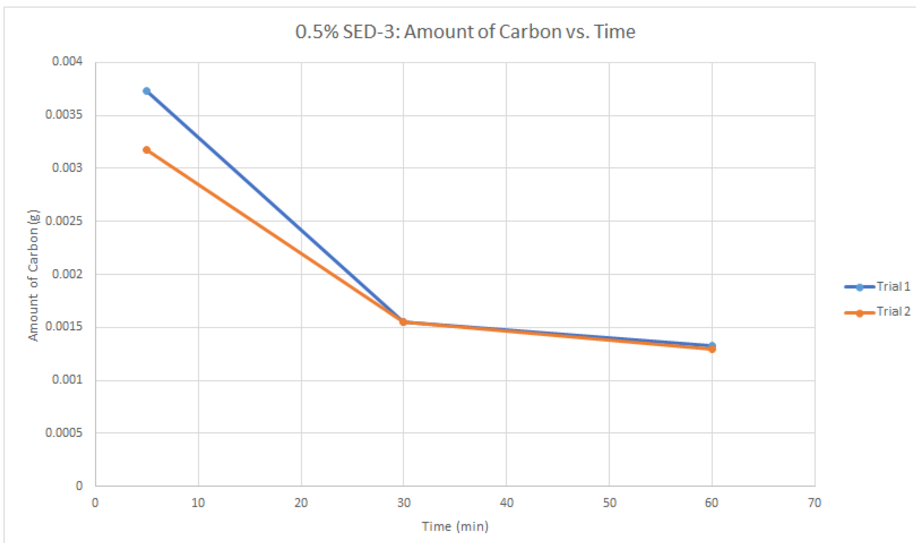

Figure 13. *0.5% SED-3 samples Suspended PAC content vs. time*

Time, Min	***Control***	***0.5% SED-3***	***% Decrease***
5	*622*	*53.9*	*91.3%*
30	*317*	*25.0*	*92.1%*
60	*226*	*21.3*	*90.6%*

Table 3. *0.5% SED-3 Treatment Turbidity Reduction*

Time, Min	***Control***	***PAC (g/l)***	***0.5% SED-3***	***PAC(g/l)***	***% Decrease***
5	*0.0408*	*1.36*	*0.0035*	*0.12*	*91.3%*
30	*0.0208*	*0.69*	*0.0016*	*0.05*	*92.1%*
60	*0.0148*	*0.49*	*0.0013*	*0.04*	*90.6%*

Table 4. *0.5% SED-3 Treatment Suspended PAC Reduction*

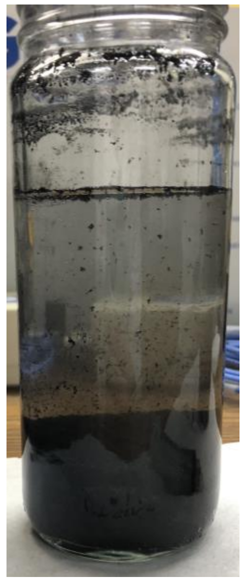

Figure 14. *0.5% SED-3, 5% PAC-amended sand sample in water after 60 minutes*

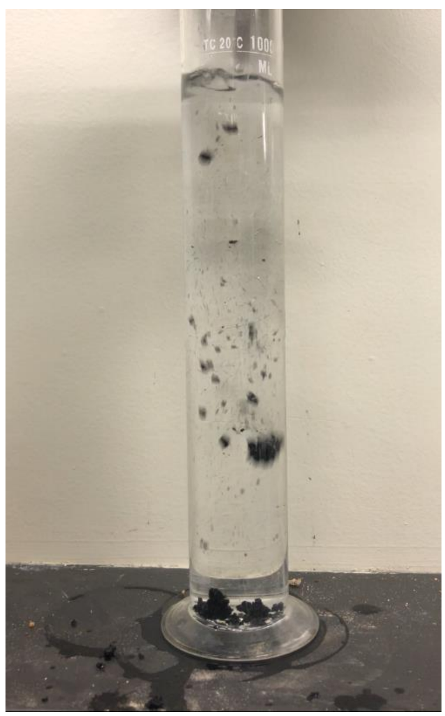

Figure 15. *Initiation of the addition of 0.5% SED-3, 5%PAC-amended Sand to Water Column*

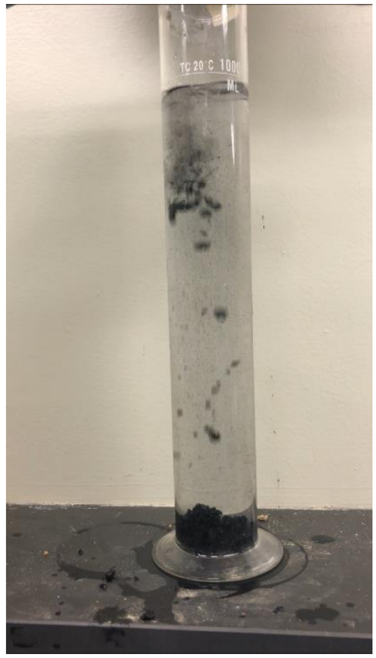

Figure 16. *Water Column Condition after adding approximately 30 grams of 0.5% SED-3, 5%PAC-amended sand*

Figure 17. *Conditions after addition of 100 grams of 0.5% SED-3, 5%PAC-amended sand*

Testing Data Summary

The turbidity and suspended PAC content data from each duplicate data set was averaged in order to compare all treatments to the Control (Tables 3 and 4). Figure 18 presents turbidity vs. time results for each dosage and formulation. The suspended PAC content vs. time data is presented in Figure 19. The SED-3 treatment of 5% PAC-amended sand yielded the best reduction in turbidity and suspended PAC. SED-3 concentrations as low as 0.2% were sufficient to achieve >90% reductions in turbidity/suspended PAC. The data indicates that pre-treating PAC-amended sand with SED-3 before placement onto sediment can effectively minimize PAC dispersion in the water column and prevent gravity segregation of the PAC so that uniform placement of the PAC-amended sand can be achieved.

Time, Min	***0.5% SED-3***	***0.2% SED-3***	***0.5% SED-0***	***0.2% SED-0***	***control***
5	***53.9***	***44.9***	***50.6***	***110.5***	***622***
30	***25.0***	***21.0***	***36.3***	***47.9***	***317***
60	***21.3***	***17.3***	***28.3***	***37.7***	***226***

Table 3. *0.5% Turbidity measurement, NTU (duplicate averages)*

Time, Min	**.5% SED-3**	**.2% SED-3**	**.5% SED-0**	**.2% SED-0**	**control**
5	0.0035	0.0029	0.0032	0.0072	0.0408
30	0.0016	0.0013	0.0023	0.0031	0.0208
60	0.0013	0.0010	0.0018	0.0024	0.0148

Table 4. *Suspended PAC (g) vs. Time (duplicate averages)*

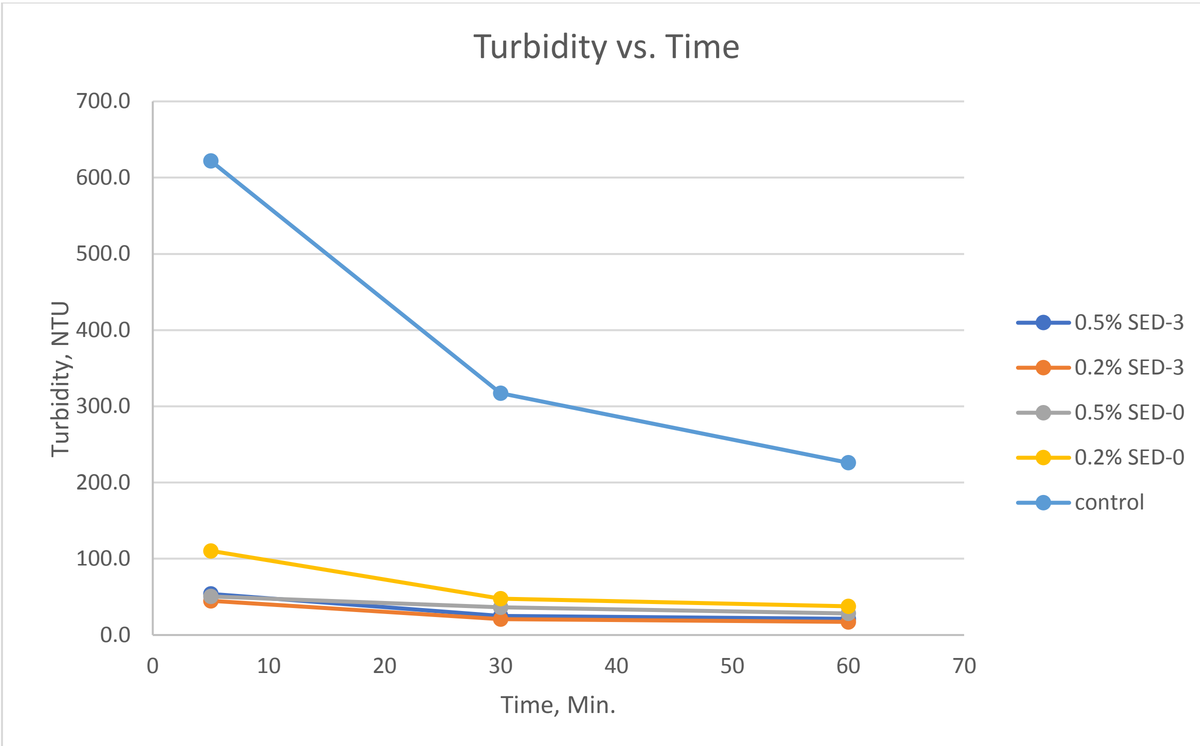

Figure 18. *Turbidity vs. Time for all formulations and dosages (duplicate averages)*

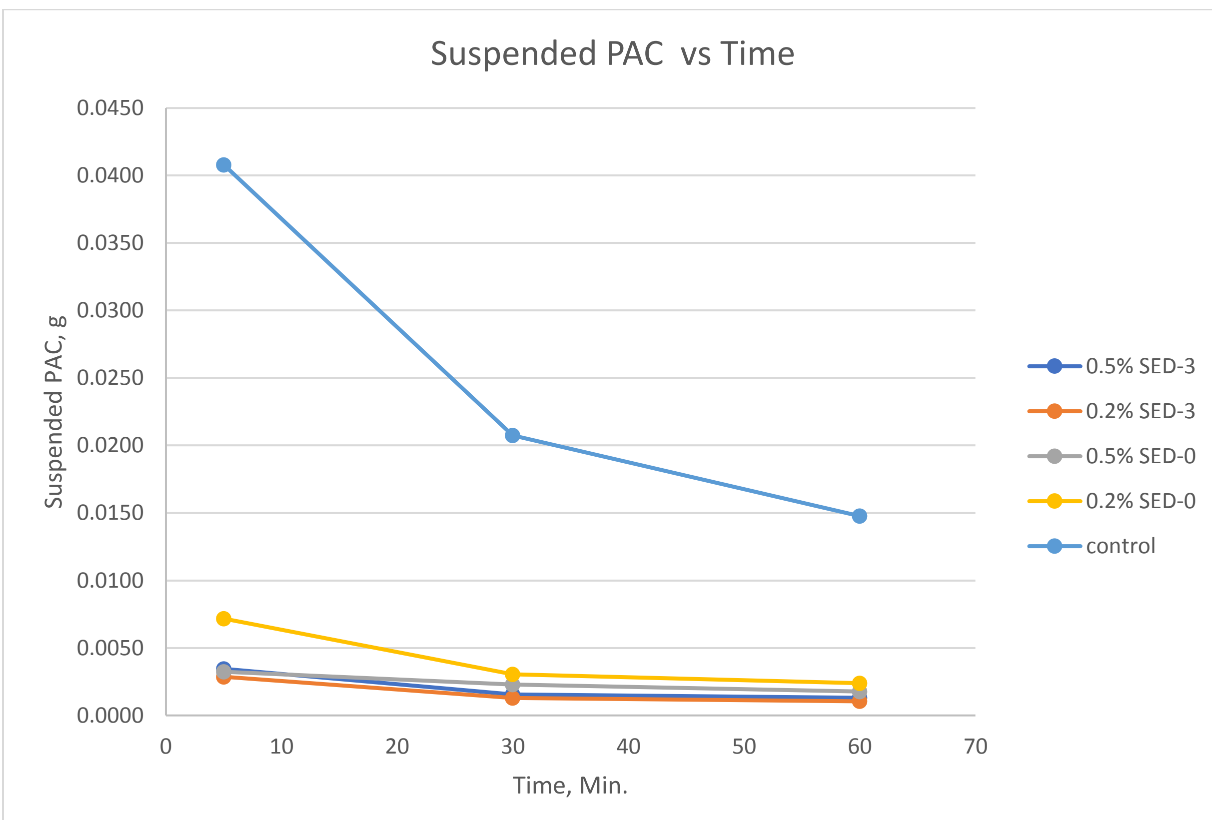

Figure 19. *Suspended PAC vs. Time for all formulations and dosages (duplicate averages)*

4. Conclusions

- The SED-0 and SED-3 treatments of 5% PAC-amended sand were effective in reducing turbidity and suspended PAC (> 90% reduction).
- The SED-3 treatment of 5% PAC-amended sand yielded the best reduction in turbidity and suspended PAC. SED-3 concentrations as low as 0.2% were sufficient to achieve >90% reductions in turbidity/suspended PAC.
- The results indicate that pre-treating PAC-amended sand with SED-3 before placement onto sediment can effectively minimize PAC dispersion in the water column and prevent gravity segregation of the PAC so that uniform placement of the PAC-amended sand can be achieved.
- PPB formulation, dosage and treatment effectiveness may be optimized through laboratory testing based on sand and PAC used at a site.

5. References

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