

EVALUATING THE IMPACT OF ACTIVATED CARBON ON THE  
ENVIRONMENTAL AND ENGINEERING PROPERTIES OF CEMENT-  
STABILIZED CONTAMINATED DREDGED SEDIMENT

By

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## ABSTRACT OF THE THESIS

Evaluating the Impact of Activated Carbon on the Environmental and Engineering

Properties of Cement-Stabilized Contaminated Dredged Sediment

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The objective of this study was to evaluate the impact of activated carbon on the engineering properties of Portland cement-stabilized contaminated dredged sediment, while investigating its potential to immobilize contaminants for beneficial use applications. Historically contaminated sediment was sampled from five locations in the United States and Norway: three locations within New York/New Jersey Harbor in the United States and two locations within Stavanger Harbor in Norway. Triplicate laboratory samples were generated for each of the five sediment types at various mixing ratios for stabilization/solidification (S/S). New York/New Jersey Harbor sediments were mixed with 0, 1, and 3% (by wet weight of sediment) powdered activated carbon (PAC) and 8% Portland cement (PC). Stavanger Harbor sediments were mixed with 0, 1, and 3% (by wet weight of sediment) PAC and 0, 4, 8 and 12% PC. After 28 days of curing, the samples were tested for unconfined compressive strength (UCS). The leaching potential of metals, polycyclic aromatic hydrocarbons (PAHs), and tributyltin was evaluated via the Synthetic Precipitation Leaching Procedure (SPLP). The results of the study indicate that though it may marginally decrease the material's strength gain, activated carbon has the potential to

aid in the effectiveness of sediment S/S techniques for beneficial use by reducing contaminant mobility. Statistically significant ( $\alpha = 0.05$ ) reductions in strength between 13% and 53% were observed for soft, fine-grained sediments for mixtures of 8% PC with 1% and 3% doses of AC in this study. However, the addition of AC was instrumental in reducing the leaching concentrations of contaminants below standard criteria, in many cases to non-detectable values. It was particularly effective in reducing the leaching potential of PAHs and tributyltin in cases where PC alone was not effective.

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## Introduction

The solidification and stabilization (S/S) of dredged sediments has the potential to turn large volumes of contaminated sediments unsuitable for aquatic placement into beneficially usable materials. Since the 1950's, Portland cement has been the primary binding agent used in sediment S/S projects in the United States, effectively encapsulating soil and sediment fine fractions and reducing the mobility of contaminants (Wilk, 2004). As S/S and beneficial use applications have grown more common in practice, so has awareness of the unique challenges facing their success. Two such challenges include the reduced strength gain commonly associated with highly organic sediment and the need to immobilize emerging or persistent contaminants of concern.

Though several studies have been conducted to assess the impact of activated carbon on contaminant mobility in S/S applications, very few also evaluated the engineering properties (such as shear strength or permeability) of the stabilized material. Several pieces of literature address the reduction in shear strength associated with highly organic sediment, however the majority of these studies focus on humus and humic acid, rather than activated or other solid forms of carbon (Tremblay, Duchesne, Locat, & Leroueil, 2002; Huat, Maail, & Mohamed, 2005). For sediment management and beneficial use decision-making, it is important that the potential benefits provided by activated carbon in reducing contaminant mobility be understood within the context of its increase or reduction of the material's strength gain. The objective of this study is to evaluate the impact of activated carbon on the engineering properties and leaching potential of Portland cement-stabilized contaminated dredged sediment, while investigating its potential to immobilize contaminants of concern for beneficial use applications. The main question to

be addressed is whether or not activated carbon has the ability to further reduce contaminant leaching from stabilized/solidified material without jeopardizing its unconfined compressive strength gain.

This thesis is divided into five chapters: Chapter 1 presents a comprehensive review of existing literature on sediment S/S and the use of activated carbon; Chapter 2 provides a description of the sediments and materials used in the study; Chapter 3 presents the overall experimental design and geotechnical methods for sample creation and testing, as well as the results for engineering performance parameters (unconfined compressive strength, moisture content, and organic content); Chapter 4 presents the experimental design and methods for chemical testing, as well as the results for environmental performance parameters (leaching and total concentrations); and Chapter 5 provides an overall discussion of the results, conclusions, and recommendations for future work.

## **Chapter 1: Review of Existing Literature**

### Overview of Stabilization/Solidification

The presence of contaminated sediment in and around places of human activity can pose significant risks to human and environmental health (Bates & Hills, 2015). Methods for dealing with contaminated sediment typically involve removal and confinement (e.g. dredging with subsequent placement in confined disposal facilities), treatment (ex-situ or in-situ), or containment (e.g. sand-capping) (IADC/CEDA, 2008). Though removal and treatment are most useful from the perspective of beneficial sediment and site re-use, they can be accompanied by several challenges. Some of the most notable challenges include high project costs, environmental concerns associated with contaminant disturbance, and limited disposal site capacities. Sediment stabilization and solidification (S/S) is a treatment technique that has seen increasing popularity in recent years, both in the United States and around the globe, and has the potential to address several of these challenges (Bates & Hills, 2015).

Stabilization and solidification refer to the processes of chemically manipulating the forms of harmful contaminants in sediment and changing the sediment's physical properties, respectively (Wilk, 2004). Though stabilization does not remove contaminants from the soil, it enhances the environmental quality of the sediment considerably by immobilizing and transforming the chemical species (Hakstege, 2007). Solidification occurs via hydration reactions involving Portland cement (PC) (or other pozzolanic reactions between lime and clay minerals) that form cementitious compounds within the sediment (Hossain, Lachemi, & Easa, 2007). Since the 1950's, PC has been the primary binding agent used in sediment S/S projects (Bates & Hills, 2015). It has been applied to a

wide range of wastes and is generally chosen for its ability to chemically bind and fix free liquids or hazardous contaminants, decrease permeability, and encapsulate waste particles (Wilk, 2004). In 2013, S/S was the second most frequently selected remediation technology in the U.S., selected in approximately 20-22% of Superfund remedy documents (Bates & Hills, 2015). S/S treatment of dredged sediment, in particular, has the potential to turn large categories of idle and contaminated waste into useable construction materials.

Improvements to the standard S/S method are desirable for several reasons; primarily, the acquisition of ample amounts of PC for large S/S projects can sustain high financial and environmental costs. The cement manufacturing industry emits approximately 5% of global CO<sub>2</sub> emissions, making it desirable to identify less energy intensive (and, accordingly, lower CO<sub>2</sub>-releasing) techniques for use as environmentally maintainable PC alternatives (Phetchuay, Horpibulsuk, Arulrajah, Suksiripattanapong, & Udomchai, 2016; Cho, Shim, & Park, 2015). Operational costs for S/S projects include those associated with the acquisition, transportation, and storage of large binder quantities. The identification of cheaper, locally available, or more effective S/S materials thus has the ability to reduce projects' operational costs. In addition, the growing availability of professional expertise and associated technologies help to reduce the costs associated with project management, labor, and machinery. However, these core financial challenges remain.

A number of alternative amendments have been studied in the past 20 years to fully or partially replace PC in S/S applications. These include industrial by-products such as fly ash, steel slag, and cement kiln dust, as well as natural and artificial pozzolanic materials such as volcanic ash, microsilica, calcined clay, and other localized natural resources.

Methods for displacing PC in projects without introducing similar cementitious compounds require focusing on the stabilization aspect of S/S techniques. In many cases, higher-than-necessary doses of PC are used to fully encapsulate the soil matrix so that contaminants become trapped within layers of cement and are successfully prevented from moving out (leaching) into the environmental system. In such applications, the strength, permeability, and other engineering performance criteria for the S/S material may be unnecessarily exceeded in order to ensure a maximum reduction in leaching potential. There exists a possibility, therefore, to reduce the quantity of PC or other binder required for S/S projects by introducing an additional or precursory stabilizing agent. One such agent, which has been used extensively in a variety of areas for contamination management (largely including water and wastewater treatment) is activated carbon (AC).

#### Carbon-based Amendments for Ground Improvement

AC has been used in a variety of applications to sequester or stabilize contaminants within sediments. Ground improvement work involving activated carbon has most extensively included active capping. Capping is a method which falls under the “containment” category for contaminated sediment management. Traditionally, it involves the use of natural geomaterials, such as sand or clay, to mitigate the impacts of physical, chemical, and biological processes on contaminants in the subsurface (Barth & Reible, 2008). Capping works by physically isolating and limiting the loss of contaminants through these transport pathways. Recently, the inclusion of other materials such as modified clays (organoclays) and activated carbon has enhanced the effectiveness of traditional sand caps through a method known as active capping. These materials are selected according to the

targeted contaminant(s) and aid in the degradation, sequestration, or immobilization of pollutants.

In S/S applications, carbon-based reagents can be used to stabilize metals and organic contaminants by mechanisms that slow or eliminate their release into the environment. In the case of contamination by metals, stabilization involves a reduction in solubility via the conversion of species into hydroxides or sulfides (Bates & Hills, 2015). Organic contaminants, on the other hand, are stabilized by reactions that alter the compounds themselves, or by encapsulation and adsorption processes that bind the contaminants and mitigate environmental impacts. Several carbon-based reagents have been studied and used in S/S projects, including organoclays, activated charcoal, and activated carbon.

Organoclays consist of naturally occurring clay materials with organophilic layers between the clay platelets, produced by the addition of organo-cations such as alkylammonium ions (Bates & Hills, 2015). The partitioning of organic compounds into organophilic layers results in the adsorption and, consequently, sequestration of organic contaminants. Similar to other physio-chemical processes, the specific capacity of organoclays for the partitioning and adsorption of organic compounds depends on both the organo-cation involved and the compound of concern.

Activated charcoal and carbons, on the other hand, are created through the pyrolysis of natural materials such as wood, peat, coal, and coconut shells or fibers in the absence of oxygen. The carbonized material is “activated” in an oxidizing environment at high temperatures (250° C) to produce an extremely porous material with a high surface area for adsorption (Bates & Hills, 2015). Activated charcoal and carbons can be used in the

form of powders (PAC) or granules (GAC). The much greater specific surface area of PAC compared to soil minerals and soil organic matter results in a preferential adsorption of organics that favors PAC amendments, even for clayey and organic soils (Crane, Cassidy, & Srivastava, 2014). Though AC is less commonly reported than organoclays for S/S treatment and has the potential to increase treatment costs, the use of AC may attract consideration once effectiveness is demonstrated on a specific project basis (Paria & Yuet, 2006).

#### Activated Carbon and Portland Cement Stabilization/Solidification

The compatibility of AC and PC for S/S applications has been researched to a minimal extent within the past decade. Crane et al. (2014) evaluated the performance of PAC and cementitious amendments (Type I PC, quicklime, and Class C fly ash) on the S/S of four types of sediment contaminated with organic compounds. The study was designed for in-situ stabilization applications of S/S procedures, targeting brownfield sites contaminated with manufactured gas plant waste. Doses of 1% PAC and 5% cements were used to stabilize and solidify soil contaminated with BTEX and PAHs. The mixtures' performances were evaluated using the Synthetic Precipitation Leaching Procedure (SPLP) and unconfined compressive (UC) strength testing via pocket penetrometer. Results indicated that both leaching potential and UC strength were significantly improved by a 20-week PAC preconditioning period compared to the simultaneous addition of PAC and cements (Crane et al., 2014).

Several studies have been conducted to assess the leaching of phenols, in particular, with AC adsorption and PC immobilization (Paria & Yuet, 2006). Hebatpuria et al. (1999) studied the effectiveness of regenerated activated carbon versus virgin activated carbon for



PC-based S/S of sediment contaminated with phenol. Results showed the successful retention of phenol when adsorbed to PAC and encapsulated in cement, with a one-step mixing process reflecting the rapid adsorption of phenol by PAC. The study reported reductions in leaching potential as high as 600% for mixtures including regenerated powdered activated carbon compared to those without reactivated carbon (Hebatpuria et al., 1999). The addition of 2% reactivated carbon drastically reduced the leaching of phenol from 87% (S/S without AC) to around 11% (S/S with AC) of the original amount, indicating a near-ineffectiveness of traditional S/S in comparison (Paria & Yuet, 2006). This can be explained by the poor performance of PC-based S/S for organic compounds that are volatile, water soluble, or have a pKa that is less than 12 (Su, Liu, Jin, Hou, & Nie, 2009). Su et al. (2009) studied the long-term leaching behavior of phenol-contaminated soil using doses of 30% to 50% PC and 0% to 10% PAC. Results indicated that low ratios of PAC (less than 3%) could significantly enhance the fixation of phenol, with further improved performance following a curing period of 28 days compared to 7 days.

The impact of AC on the S/S of metals-contaminated sediment has also been researched, though less extensively than organics-contaminated sediment. Guha, Hills, Carey, and MacLeod (2006) studied the S/S treatment of fresh water sediment contaminated with mercury (Hg). Binder additives included pulverized fuel ash (fly ash) and a blended combination of cements, including PC, at various doses. The study compared S/S performance with and without the subsequent addition of 1% virgin PAC. A German standard leaching procedure (DIN 38414-S4) was utilized following 28 days of curing to evaluate the S/S effectiveness on contaminant immobilization, and mercury analysis was performed on both the leachate and digested sediment. Results indicated that a reduction

in Hg leaching followed the addition of PAC, and that Hg leaching decreased as the solids content of the PC-solidified sediment increased. The study reported 100% adsorption of Hg by PAC (Guha et al., 2006). Zhang and Bishop (2002) also evaluated the performance of AC and PC S/S on Hg-containing wastes, using powder reactivated carbon (PRAC) as well as sulfur-treated PRAC. Toxicity Characteristic Leaching Procedure (TCLP) leaching tests were conducted to assess the S/S material's immobilization of Hg. The results indicated that doses from 0.5% to 20% PRAC had a range of increased Hg adsorption from 31.0% to 98.5% (Zhang & Bishop, 2002). Sulfur-treated PRAC at the same doses had a range of increased adsorption from 95.6% to over 99.0%. The results of both studies suggest that the stabilization of mercury in solid wastes is possible using activated and reactivated carbon, especially with virgin activated carbon and carbon soaked in  $C_2S$  (Guha et al., 2006; Zhang & Bishop, 2002).

One point of concern for this area of research involves the temporal sequencing of AC and PC for S/S mixing applications. While BTEX and naphthalene were reported to require approximately 20 weeks of preconditioning with AC to reach optimum effectiveness, phenols showed no significant difference between the immediate combination of AC with PC and a 2-hour delay (Crane et al., 2014; Paria & Yuet, 2006). The kinetics of adsorption for the particular contaminant of concern versus the rate of cement hydration are responsible for this discrepancy, and the sequencing of AC and PC will vary per application based on this comparison. The addition of PC to a sediment-AC mixture without allowing appropriate time for contaminant adsorption has the potential to reduce the method's effectiveness in two major ways: first, the precipitation of  $Ca(OH)_2$  onto the surface of AC could increase the pH of the system which, due to the pH sensitivity

of organic compound adsorption, could reduce the adsorption of contaminants such as phenol (Paria & Yuet, 2006). Second, the encapsulation or coating of activated carbon particles by pockets of cement could physically block the contaminant compounds from adsorbing to the surface of AC, reducing or negating its anticipated impact on the material's leaching potential (Crane et al., 2014).

Additional areas of concern include the variety of methods adopted to evaluate leaching potential and the corresponding measurement (or lack thereof) of the S/S material's strength. Both of these parameters are critical for the informed selection of S/S treatment for both ex-situ and in-situ applications. However, many studies have focused solely on the leaching behavior of treated material while ignoring its engineering properties. The strength of S/S material that includes AC is of particular importance due to the well-documented reduced strength gain of highly organic S/S sediments (Tremblay et al., 2002). Several pieces of literature address the reduction in shear strength associated with highly organic sediment, however the majority of these studies focus on humus and humic acid, rather than activated or other solid forms of carbon (Tremblay et al., 2002; Huat et al. 2005). Humic acids in organic soils have been found to slow the rate of cementitious reactions by lowering the pH of the material and inhibiting pozzolanic reactions between calcium hydroxide and pozzolanic minerals (Janz & Johansson, 2002). As a result, organic and peat soils of varying degrees of humification have been observed to have strength increases with increasing PC dosages and strength decreases with increasing peat organic content or humification (Huat et al., 2005). Other forms of organic matter in sediment, including certain nonhumic organic compounds and organic contaminants, have been found not to interfere as strongly with the hydration process as

organic acids, oils, and nonmiscible hydrocarbons (Tremblay et al., 2002). It is anticipated that, due to its chemical and physical characteristics, AC should not impact the strength gain of S/S sediment in the same manner as humic acids. However, the available literature currently lacks data to support or refute this hypothesis.

The various methods available to evaluate S/S material leaching make it difficult to compare applications of PC and AC across the literature, as each method has uniquely defined parameters that impact its reported results. Physical and chemical parameters that are known to influence leaching results include the particle size, shape, and surface area of the material exposed to leaching, the permeability of the material matrix, the heterogeneity of the material, the flow rate of the leaching fluid (if dynamic leachate testing), the physical properties and volume of the leaching fluid, the temperature at which tests are conducted, the duration of tests, the pH of the material and that of the leaching fluid, the presence of non-aqueous phase liquids (NAPL), chemical equilibrium and kinetic reaction rates, and the solubility, preferential partitioning, and complexation of chemical compounds (Washington State Department of Ecology, 2003).

Single extraction or “batch” tests such as the Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP) - US EPA Methods 1312 and 1311, respectively - are widely used to estimate leaching from stabilized material for compliance purposes. Several variations exist within the United States and around the world, including EN 12457/1-4 (Compliance Test for Granular Waste Materials and Sludges), ASTM D 3987 (Standard Test Method for Shake Extraction of Solid Waste with Water), and NEN 7341 (Availability Test), but the general procedure remains the same. The material is particle-size-reduced to a certain threshold, added to a solution of

specified pH at a specified liquid-to-solid ratio, and shaken for a short period of time, typically on the order of hours or days (Washington State Department of Ecology, 2003). These tests occur without the renewal of the leaching solution, and the liquid (leachate) from the test is chemically analyzed for the desired compounds following the completion of the shaking period (Figure 1).

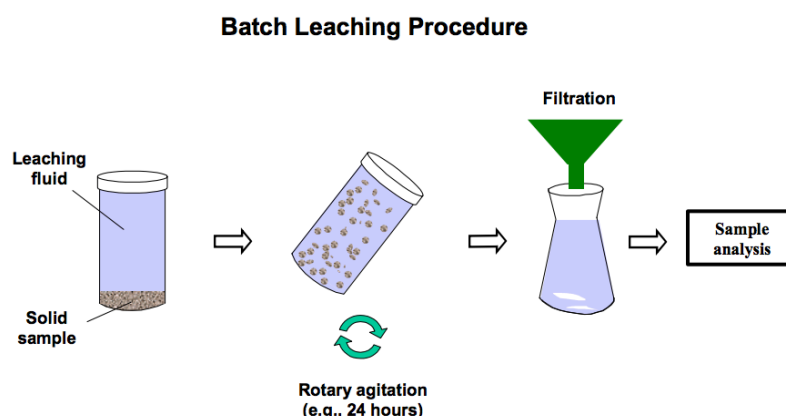


Figure 1. Simplified Batch Leaching Procedure Schematic  
(Washington State Department of Ecology, 2003)

Batch tests are simple and quick to perform but are known to overestimate the leaching of compounds due to the reduction in particle size; as the material is crushed and shaken, a greater particle surface area is exposed to the extraction fluid than if the material were left as a low-permeability monolith of S/S material (Sparrevik, Hernandez-Martinez, Eggen, & Eek, 2008). As a result, these tests are intended to classify wastes for disposal, rather than to predict leachate concentrations in the field.

Multiple extraction tests or “dynamic” leaching tests, on the other hand, involve the continuous or periodic renewal of the leaching solution over time. These tests include flow-through tests, flow-around tests, and serial batch tests (Washington State Department of

Ecology, 2003). Serial batch tests involve similar procedures to single extraction “batch” tests; however, the procedure is repeated at a sequence of specified liquid-to-solid ratios to provide data on the release of desired compounds over time. Examples of serial batch tests include ASTM D 4793 (Standard Test Method for Sequential Batch Extraction of Waste with Water) and the Sequential Batch Leachate Test (SBLT).

Examples of flow-through percolation or column leaching tests include ASTM D4874 (Standard Test Method for Leaching Solid Waste in a Column Apparatus), CEN/TS 14405 (Upflow Percolation Test), and NEN 7343 (Column Test). In general, the material is packed in a column and the leaching solution (of a specified pH) is percolated through the column at a constant flow rate (Figure 2). All of the liquid that passes through the column is collected, and the test is stopped for chemical analysis each time the collected leachate reaches a specified liquid-to-solid ratio (Sparrevik et al., 2008).

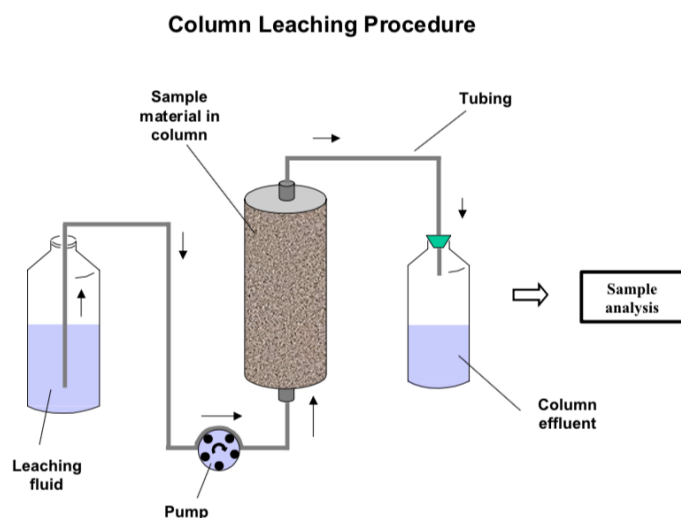


Figure 2. Simplified Column Leaching Procedure Schematic  
(Washington State Department of Ecology, 2003)

Flow-around or “diffusion” tests, such as NEN 7345 (Tank Leach Test) involve the placement of a solid block of S/S material into a solution of a specified pH. After a very long period of time, on the order of several months, the material is removed and the solution is analyzed for the desired compounds. As there is no agitation or flow of leaching solution involved in this method, the leaching results estimate diffusive transport only. In some cases, this may be the ideal assessment situation for low permeability S/S material, however it is known to underestimate the transport of contaminants overall (Sparrevik et al., 2008).

Dynamic leaching tests are useful for their consideration of time, an important variable in the case of S/S material, which relies on a reduction in permeability to limit the potential leaching of contaminants. Some variations of the tests may require particle size reduction and column compaction, which introduces the same ambiguity of results (and risk of overestimation) as batch test procedures. Others allow for the testing of a solid monolith of S/S material, which is anticipated to more accurately reflect the material’s behavior in the field. However, these tests take a relatively long period of time to perform (on the order of days to months) and may pose challenges due to the high pressure required to drive the leaching solution through low-permeability material (Sparrevik et al., 2008).

With regard to laboratory studies, single batch extraction is the most efficient method for comparing the leaching potential of a variety of S/S treatments. Though the results may not be useful for the practical estimation of leaching in field applications, they are readily comparable to local standards for relative conclusions on the treatments’ effectiveness. The most appropriate method (with specified pH, liquid-to-solid ratio, and agitation parameters) can be selected to represent either a practical or conservative

placement scenario, depending on the individual study's objectives. Most importantly, these tests can be completed within a manageable amount of time for laboratory S/S studies, which often require the testing of dozens of samples at a time. SPLP is a US EPA batch test method designed to simulate the leaching potential of a material exposed to a minimally acidic rainfall (leaching solution pH = 4.2). It is a single extraction "batch" test for leaching that is optimal for experimental use due to the time-efficiency of tests (18-hour agitation period per sample), the availability of laboratory expertise due to its use in compliance regulations, and the availability of associated standards for a meaningful comparison of leachate concentrations.

Ultimately, there exists room for exploration of additional combinations of AC and PC for sediment S/S with respect to unique soil types and contaminants of concern. In particular, a great deal can be learned from studies investigating the relationships between environmental (leaching) parameters and engineering (strength) properties of S/S material resulting from a variety of AC and PC ratios. The experiment described in this thesis has been designed to better understand the potential usefulness of AC in ex-situ sediment S/S applications and to address many of the concerns identified by this literature review.



## **Chapter 2: Description of Materials**

Behavioral differences between various soil types in S/S and other geotechnical applications are well-documented and necessitate the classification of sediments prior to experimental analysis. Since sediment was collected from five unique locations (in two countries) for use in this study, the classification of sediments' grain size distributions, organic content, moisture content, and other index properties provides context for the comparison of experimental results. Also imperative to this experiment's success was the acquisition of highly contaminated sediments, or sediments containing high enough concentrations that contaminants could be reliably detected during post-treatment leachate tests. The original scope of the experiment involved sampling and performing tests on materials from only three locations within New York/New Jersey Harbor. However, preliminary chemical composition results indicated that the concentrations of contaminants present within these samples were not sufficient for the study. As a result, two additional sediment types with known contaminant concentrations from Galeivågen Harbor in Stavanger, Norway were provided by COWI A/S for use in the study.

This chapter describes the timeline and procedures for sediment sampling from the five sampled locations, presents preliminary chemical analysis results for each of the five sediments, provides data to classify the physical properties of the sediments, and includes a brief description of the materials used to amend the sediments via S/S.

### New York/New Jersey (NY/NJ) Harbor Sampling

On March 26 and 27, 2018, personnel from the Weeks Sediment Laboratory at Rutgers University and Monmouth University's Urban Coast Institute (UCI) acquired

sediment from three locations in New York/New Jersey (NY/NJ) Harbor using a Van Veen grab sampler and a HAPS sediment corer (Figure 3).



Figure 3. Van Veen (left) and HAPS (right) grab samples from NY/NJ Harbor

The samples were named after their locations of origin: Erie Basin, Port Elizabeth, and Brooklyn Navy Yard. One 1.5-gallon air-locked bucket of sediment was taken from each location. Figure 4 provides a map of the sampling locations within the harbor.

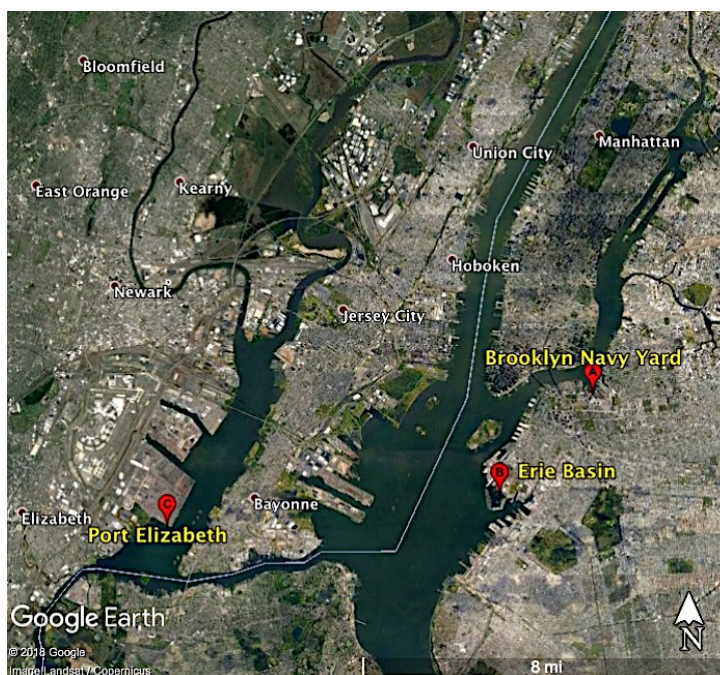


Figure 4. Sampling Locations in NY/NJ Harbor

The sediments were very wet, dark brown and black in color – visually similar to typical highly organic harbor-dredged silty clay sediments. Very little debris were found within the sediments, but some stones and plant material were removed by hand prior to homogenization in the laboratory. Once the sediment was thoroughly mixed, samples were submitted to Precision Testing Laboratories (PTL) in Toms River, New Jersey for a suite of tests to evaluate the total concentrations of environmental contaminants, including volatile organics, semivolatile organics, US EPA Target Analyte List (TAL) metals, pesticides, and polychlorinated biphenyls (PCBs) (Figure 5). The results of these tests were used during preliminary assessments to determine to what extent the sediments would be suitable for use in the study. Index property tests were then performed in the laboratory in order to classify the sediments.



Figure 5. NY/NJ Harbor samples prepared for chemical analysis

#### Stavanger Harbor Sampling

On June 22, 2018, the Weeks Sediment Laboratory in Piscataway, New Jersey received four 3-gallon buckets of dredged sediment from COWI A/S sites 19 and 29 in



Galeivågen Harbor, Stavanger, Norway (Figure 6). The sites will hereafter be referred to as Stavanger 19 and Stavanger 29.

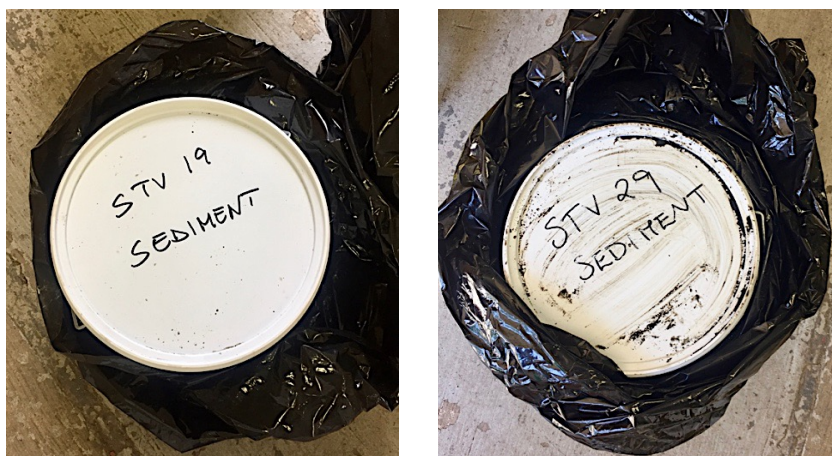


Figure 6. 3-gallon buckets of Stavanger Harbor material

As can be seen in Figure 7, Stavanger 19 corresponds to material sampled from the inner section of the harbor, whereas Stavanger 29 corresponds to the outer harbor region.

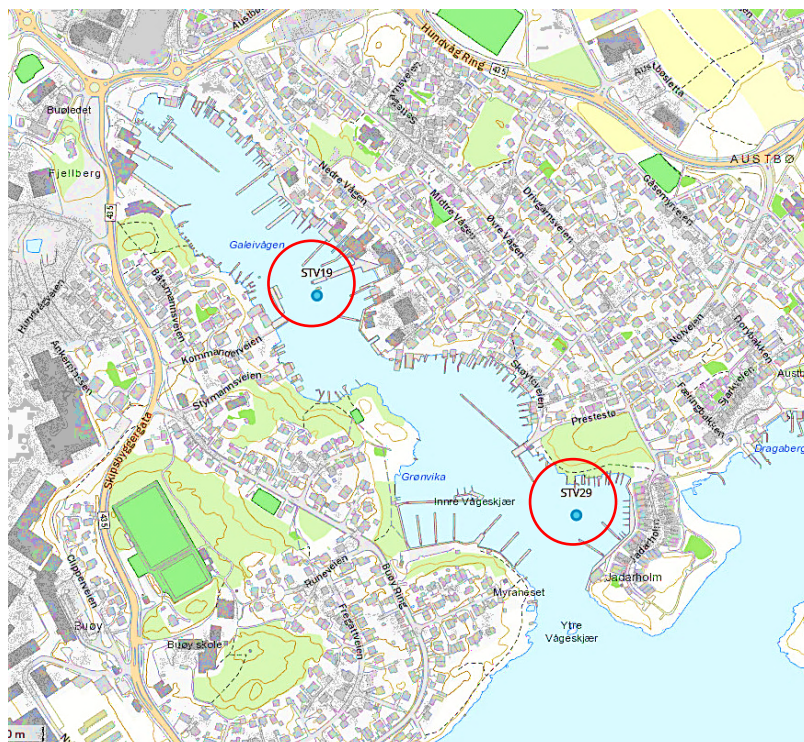


Figure 7. Sampling Locations in Stavanger Harbor

Rutgers personnel removed large debris such as rocks, glass, large shells, and plant material from the samples by hand. Material from each sampling site was then combined, homogenized, and stored in an air-locked 12-gallon bucket (Figure 8).



Figure 8. 12-gallon bucket containing Stavanger 19 material

COWI A/S provided data regarding the chemical composition of the materials, which was used during preliminary assessments to determine whether or not the sediments would be suitable for use in the study. Index property tests were performed by Rutgers personnel in order to classify the sediments.

#### Chemical Properties of the Material

Tables 1 and 3 provide summaries of the initial chemical compositions of each of the five sediments. Though the NY/NJ sediments (Erie Basin, Port Elizabeth, and Brooklyn Navy Yard) were tested for the full suite of environmental contaminants described above, all three sediments had non-detectable concentrations for volatile organics, PCBs, and pesticides. Therefore, the reported values for the NY/NJ sediments are limited to semivolatile organics and metals. The data provided by COWI A/S for the Stavanger

sediments (Stavanger 19 and Stavanger 29) also prioritized semivolatile organics and metals, with the addition of tributyltin (an emerging organometallic contaminant of concern). Table 1 presents a side-by-side comparison of the total semivolatile organic concentrations in the five sediments.

Table 1. Total Concentrations of Semivolatile Organics in Sediments

Chemical Compound	Total concentration (mg/kg)					NJ Non-Residential Direct Contact Soil Remediation Standard (mg/kg)
	Erie Basin	Port Elizabeth	Brooklyn Navy Yard	Stavanger 19	Stavanger 29	
<b>Semivolatile Organics</b>						
Acenaphthene	ND	ND	ND	0.140	0.066	37,000
Acenaphthylene	0.0462	0.056	0.0632	0.020	0.190	300,000
Anthracene	0.0404	0.0528	0.059	0.100	0.500	30,000
Benzo(a)anthracene	0.123	0.134	0.165	0.570	3.20	17
Benzo(a)pyrene	0.128	0.149	0.167	0.770	3.70	2
Benzo(b)fluoranthene	0.123	0.146	0.142	0.920	3.90	17
Benzo(g,h,i)perylene	0.111	0.142	0.146	0.480	2.40	30,000
Benzo(k)fluoranthene	0.122	0.132	0.160	0.560	2.10	170
Chrysene	0.161	0.170	0.209	0.730	3.80	1,700
Dibenz(a,h)anthracene	0.0501	ND	ND	0.200	1.00	2
Fluoranthene	0.217	0.245	0.274	1.30	4.70	24,000
Fluorene	ND	ND	ND	0.052	0.200	24,000
Indeno(1,2,3-cd)pyrene	0.0944	0.103	0.118	0.510	2.30	17
Naphthalene	ND	ND	ND	0.038	0.230	17
Phenanthrene	0.0751	0.0860	0.0937	0.580	1.80	300,000
Pyrene	0.228	0.251	0.295	1.40	5.70	18,000

From Table 1, it is clear that the concentrations of semivolatile organics in the Stavanger Harbor sediments (particularly Stavanger 29) far exceeded those in the NY/NJ sediments, often by an order of magnitude or more. In addition, the values reported for the

NY/NJ sediments, which prompted the acquisition of the more highly contaminated Stavanger sediments, were generally at or near the laboratory's Practical Quantitation Limits (PQL); for semivolatiles in Erie Basin, Port Elizabeth, and Brooklyn Navy Yard sediment, the laboratory's reported PQLs were 0.0963 mg/kg, 0.104 mg/kg, and 0.105 mg/kg, respectively. The concentration of benzo(a)pyrene in the Stavanger 29 sediment was the only concentration found to exceed the N.J.A.C. Non-Residential Direct Contact Soil Remediation Standards (reported as 3.70 mg/kg with a standard of 2.00 mg/kg); all other sediments and compounds were reported below the standard thresholds.

Table 2 presents a side-by-side comparison of the total metal and organometallic concentrations in the five sediments. Though the Stavanger sediments were only tested for select metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc), their concentration values still exceeded those of the NY/NJ sediments, sometimes by an order of magnitude or more. The only concentrations found to exceed the N.J.A.C. Non-Residential Direct Contact Soil Remediation Standards were arsenic and lead in the Stavanger 29 sediment (reported as 29.0 mg/kg and 1,980 mg/kg, with standards of 17.0 mg/kg and 800 mg/kg, respectively); all other sediments and compounds were reported below the standard threshold or lacked standards for comparison.

Table 2. Total Concentrations of Metals and Organometallics in Sediments

Chemical Compound	Total concentration (mg/kg)					NJ Non-Residential Direct Contact Soil Remediation Standard (mg/kg)
	Erie Basin	Port Elizabeth	Brooklyn Navy Yard	Stavanger 19	Stavanger 29	
<b>Metals</b>						
Aluminum	20,700	19,300	20,300			
Antimony	ND	ND	ND			450
Arsenic	13.5	17.0	14.5	16.0	29.0	19
Barium	73.1	122	81.3			59,000
Beryllium	0.922	0.914	0.990			140
Cadmium	0.245	0.690	0.326	1.80	2.50	78
Calcium	8,280	7,630	8,310			
Chromium	70.9	94.4	71.4	53.0	84.0	
Cobalt	11.5	11.5	12.5			590
Copper	81.8	118	113	1,050	517	45,000
Iron	39,800	37,700	38,600			
Lead	103	118	199	235	1,980	800
Magnesium	9,620	9,540	9,980			
Manganese	779	766	768			5,900
Mercury	0.796	1.92	0.814	2.5	5.0	65
Nickel	29.8	32.7	33.9	40	77	23,000
Potassium	5,030	4,890	5,090			
Selenium	2.62	3.53	2.12			5,700
Silver	1.51	1.59	1.74			5,700
Sodium	18,200	16,800	17,900			
Thallium	ND	ND	ND			
Tin	10.4	20.2	13.3			
Vanadium	46.7	45.5	45.5			1,100
Zinc	193	221	253	787	2,990	110,000
<b>Organometallics</b>						
Tributyltin				10	0.340	



Tributyltin (TBT) had a very high reported concentration for the Stavanger 19 sediment: 10 mg/kg. As New Jersey standards for this compound have not yet been developed, concentrations were compared to the Norwegian soil quality criterion of 1.0 mg/kg, putting the reported concentration an order of magnitude in excess of the standard (Danish Environmental Protection Agency, 2013). The NY/NJ sediments were not tested for TBT due to laboratory method limitations, however they were tested for total tin (Sn). Considering a 2.44 conversion factor from mg Sn to mg TBT, the reported concentrations for total tin in the NY/NJ sediments (10.4 mg/kg, 20.2 mg/kg, and 13.3 mg/kg for Erie Basin, Port Elizabeth, and Brooklyn Navy Yard, respectively) indicate that they could potentially contain comparable concentrations of TBT to the Stavanger 19 sediment (Danish Environmental Protection Agency, 2013). However, this would only be the case if TBT made up at least 39.4%, 20.3%, and 30.8% of the total tin compounds detected in the Erie Basin, Port Elizabeth, and Brooklyn Navy Yard sediments. As no literature values or subsequent tests were available to confirm such requirements, Stavanger 19 sediment was presumed to include the highest concentration of TBT for this study.

#### Physical Properties of the Material

Index property and grain size distribution tests were performed to classify the sediments and determine their physical properties. Three moisture content samples per site were tested to determine the average natural water content of the materials. The oven-dried moisture samples were subsequently tested for their loss on ignition to determine the natural organic matter content of the material. Additional tests were performed to measure the specific gravity of solids and bulk density of the materials. Table 3 presents the ASTM standards associated with each of the index property tests.

Table 3. Physical Property Tests

Description of Test	ASTM Standard
Moisture Content	D2216-10
Organic Content (Loss on Ignition)	D2974
Specific Gravity of Solids	D854
Bulk Density	D7263-09

Grain size distributions were determined via wet sieve and hydrometer analyses, with particle sizes classified according to the Unified Soil Classification System (USCS). Figure 9 presents the sediments' experimentally determined particle size distributions. Table 4 provides a summary of the dredged sediments' physical properties.

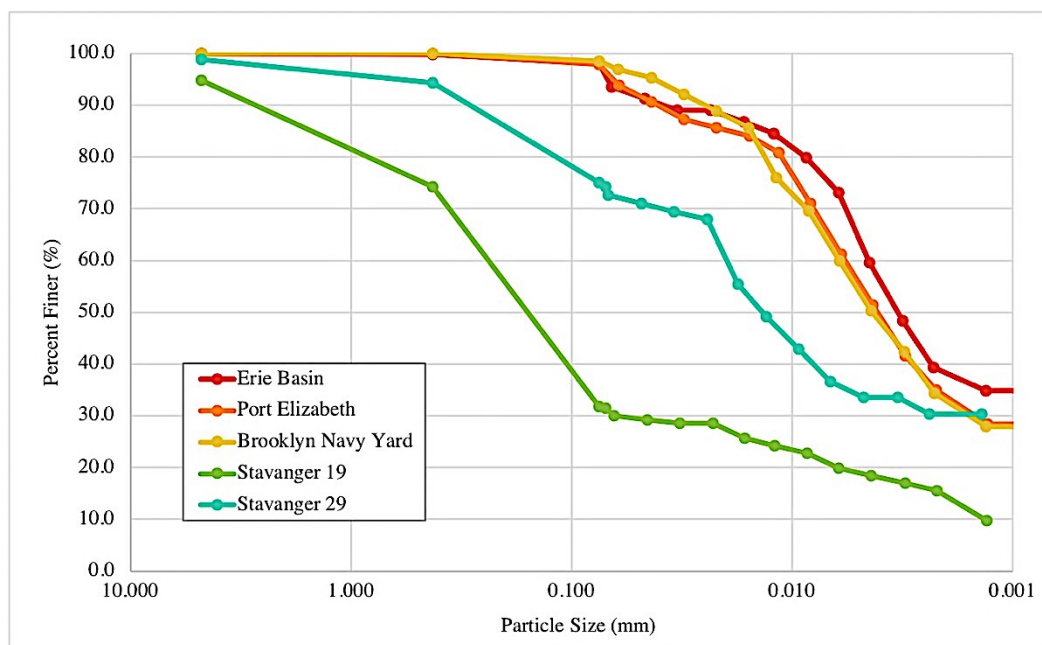


Figure 9. Sediment Particle Size Distributions

It can be seen in Figure 9, and in the data presented in Table 4, that the three NY/NJ sediments were very similar, consisting almost entirely of fine material (silty clays). All three had natural organic contents around 9.0%, and similar bulk densities and specific gravities of solids. The NY/NJ sediments differed most in their natural water content, with Brooklyn Navy Yard sediment containing the highest moisture percentage (237%) and Erie Basin sediment containing the lowest (187%).

Table 4. Physical Properties of the Dredged Material

Physical Property		Erie Basin	Port Elizabeth	Brooklyn Navy Yard	Stavanger 19	Stavanger 29
Specific gravity	$G_s$	2.67	2.68	2.62	2.69	2.46
Natural water content	$w_n$ (%)	187	213	237	160	326
Natural organic content	$OM$ (%)	9.5	8.9	9.2	8.0	20.3
Grain size distribution	Gravel (%)	0.0	0.0	0.0	5.2	1.2
	Sand (%)	2.0	2.2	1.5	62.9	23.7
	Silt and Clay (%)	98.0	97.8	98.5	31.8	75.1
Bulk density	$\rho_m$ (g/cm <sup>3</sup> )	1.27	1.24	1.24	1.32	1.19

Unlike the NY/NJ sediments, the Stavanger sediments differed in their grain size distributions and other properties. The Stavanger 19 sample contained the coarsest material of all five sediments, consisting mostly of fine to medium sands, as well as a fine fraction of silts and clays. Logically, it had the highest bulk density and specific gravity of solids. The natural organic content of Stavanger 19 sediment was comparable to the NY/NJ sediments (8.0%) while its natural moisture content was slightly lower (160%). The Stavanger 29 sample, on the other hand, had a grain size distribution in between the very

fine NY/NJ sediments and the coarse Stavanger 19 sediment. Though the majority of the Stavanger 29 material consisted of silt and clay particles, nearly a quarter of the particles were classified as fine to medium sand. The natural organic content of Stavanger 29 sediment was the highest of all five sediments (20.3%) as was its natural moisture content (326%). It is anticipated, however, that this value may have been overstated due to the treatment of supernatant during the homogenization stages of the study. In the initial and subsequent homogenization stages of the study, the supernatant (water) was mixed with the settled sediment to ensure the inclusion of all material and contaminants provided from the harbor. It is likely, however, that this excess liquid was actually a consequence of the sampling procedure, rather than representative of the natural state of the sediment.

Overall, the five sediment types provide an accurate representation of the range of dredged sediments that are typically encountered in industrial harbors: depositional material consisting of highly organic fine silts and clays, with various distributions of fine and medium sands natural to the harbor system or generated by marine activities (e.g. sandblasting the hulls of ships).

#### S/S Additives

The Portland cement used in this study was Quikrete Type I/II Portland cement, meeting ASTM C 150 Type I standards. The activated carbon used in this study was powdered activated carbon acquired from J.T. Baker. It was a solid black, odorless powder with specifications including a density of 2.0 g/cm<sup>3</sup>, 45% - 55% of particles finer than 0.044 mm (U.S. No. 325 Sieve), and 85% - 95% of particles finer than 0.149 mm (U.S. No. 100 Sieve).

### Chapter 3: Geotechnical Methods and Results

A testing matrix consisting of eight S/S mix designs was developed to meet the study's goal: to determine the impact of AC on the geotechnical properties and environmental (leaching) behavior of S/S sediments. Table 5 provides an overview of the mix designs, presented as ratios of the dry weight of binder to the wet weight of sediment.

Table 5. Experimental Mix Designs (Dry Mixing Ratios)

Mixture ID	Portland Cement, PC (% wet weight of sediment)	Activated Carbon, AC (% wet weight of sediment)
0% PC	0.0	0.0
0% PC + 1% AC	0.0	1.0
0% PC + 3% AC	0.0	3.0
4% PC	4.0	0.0
8% PC	8.0	0.0
8% PC + 1% AC	8.0	1.0
8% PC + 3% AC	8.0	3.0
12% PC	12.0	0.0

Three of the designed mixes (0% PC, 0% PC + 1% AC, and 0% PC + 3% AC) were created specifically for leachate tests, as S/S sediments containing no cementitious or pozzolanic binders are known to hold no independent strength. The environmental results for these mixes are discussed in depth in Chapter 4. This chapter focuses on the remaining five mixes, which offer insights into the strength behavior of the sediments with and without AC.

As can be seen in Table 5, only one PC dosage included AC variations, accounting for three of the five strength-tested mixes: 8% PC, 8% PC + 1% AC, and 8% PC + 3% AC. The remaining mixes of 4% PC and 12% PC were created to add to the robustness of the

study, given the abundance of Stavanger Harbor material. Due to the limited amounts of material collected for the NY/NJ sediments and their low contaminant concentrations (hence no leachate testing), only four of the total eight mixes were created for Erie Basin, Port Elizabeth, and Brooklyn Navy Yard: 0% PC, 8% PC, 8% PC + 1% AC, and 8% PC + 3% AC. Figure 10 provides a visual representation of the mixes generated for the NY/NJ sediments and Stavanger sediments, respectively. A total of 100 samples were created to conduct the strength and leaching tests required for the study.

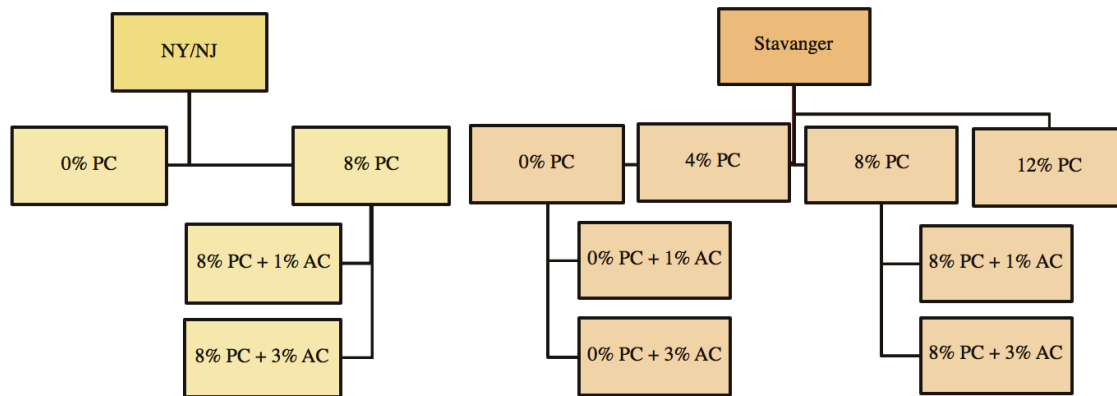


Figure 10. NY/NJ and Stavanger Sediment Experimental Mixes

The geotechnical results presented in this chapter will be separated by sediment origin location (NY/NJ sediments and Stavanger sediments, respectively) due to the difference in mixtures created for each category of materials. Chapter 5 will include a discussion of the results for all five sediments, collectively.

### Mix Creation

Sample creation for the experiment followed the procedure described by Dr. Masaki Kitazume, conforming to the Japanese Geotechnical Society Standard for making and curing stabilized soil specimens without compaction (Kitazume, 2017). Due to the high

natural moisture content of the sediment used in this experiment (typical of harbor sediments), binder was added to the sediment as a dry powder.

For mixes containing only PC, approximately 1,000 g of sediment was taken from the 12-gallon (for Stavanger sediments) and 1.5-gallon (NY/NJ sediments) storage buckets and re-homogenized using an electric stand mixer (Figure 11).



Figure 11. Stand mixer and stabilized material

The appropriate mass of PC was measured and added to the sediment while the material was mixed at a low speed. The sediment-cement mixture was then mixed at alternating medium and low speeds over one-minute intervals for a total of 5 minutes, to ensure a uniform mixture while avoiding overmixing. This procedure was kept consistent for all mixes to control the amount of mixing energy involved in the stabilization process. Laboratory measurements of the mass of sediment and cement comprising each of the PC-only mixtures are presented in Table 6.

Table 6. Laboratory Measurements for PC-only Mix Creation

Sediment	Mixture ID	Sediment (g)	PC (g)
Erie Basin	8% PC	902.1	72.1
Port Elizabeth	8% PC	899.7	71.9
Brooklyn Navy Yard	8% PC	900.1	72.0
Stavanger 19	4% PC	1141.5	45.7
Stavanger 19	8% PC	1149.8	92.0
Stavanger 19	12% PC	1129.6	135.6
Stavanger 29	4% PC	971.2	39.0
Stavanger 29	8% PC	963.1	77.1
Stavanger 29	12% PC	971.2	116.5

For mixes containing both PC and AC, an additional pre-conditioning stage was added to the beginning of the mixing process. Due to the findings of the literature review and the variety of chemical contaminants of interest, as well as a desire to mirror realistic real-world practices, a practical pre-conditioning duration of 24 hours was selected. Approximately 1,000 g of sediment was taken from the 12-gallon (for Stavanger sediments) and 1.5-gallon (NY/NJ sediments) storage buckets and re-homogenized. The appropriate mass of AC was measured, added to the sediment, and mixed at a low speed. The mixture was then placed in a 1-gallon bucket for storage and left for 24 hours. After 24 hours, the material was removed from the bucket, placed into the mixer bowl, and the above-described procedure for cement addition was followed. Laboratory measurements of the mass of sediment, activated carbon, preconditioned sediment, and cement comprising each of the AC-PC mixtures are presented in Table 7.



Table 7. Laboratory Measurements for AC-PC Mix Creation

Sediment	Mixture ID	Sediment (g)	AC (g)	Sediment + AC (g)	PC (g)
Erie Basin	8%PC + 1%AC	900.7	9.1	875.0	70.0
Erie Basin	8%PC + 3%AC	900.3	27.0	895.0	71.6
Port Elizabeth	8%PC + 1%AC	900.4	9.1	873.6	69.9
Port Elizabeth	8%PC + 3%AC	900.2	27.0	893.4	71.4
Brooklyn Navy Yard	8%PC + 1%AC	900.0	9.0	869.1	69.5
Brooklyn Navy Yard	8%PC + 3%AC	900.0	27.0	889.9	71.2
Stavanger 19	0%PC + 1%AC	1044.0	10.44	-	-
Stavanger 19	0%PC + 3%AC	1050.5	31.5	-	-
Stavanger 19	8%PC + 1%AC	1140.6	11.4	1115.6	89.3
Stavanger 19	8%PC + 3%AC	1176.8	35.2	1180.0	94.4
Stavanger 29	0%PC + 1%AC	1200.2	12.0	-	-
Stavanger 29	0%PC + 3%AC	1193.8	35.7	-	-
Stavanger 29	8%PC + 1%AC	1010.8	10.1	983.3	78.7
Stavanger 29	8%PC + 3%AC	1010.8	30.4	992.9	79.4

Moisture content samples were taken from the sediment/PC and sediment/PC/AC mixtures immediately following the mixing process (prior to filling the sample molds). The results will be discussed later in this chapter. The stabilized material was then placed into three plastic cylindrical molds (50 mm in diameter and 100 mm in height) in three stages. Due to uncertainty in the volume of materials required for evaluation by the contract laboratory for leaching tests, an additional mold was filled for each of the Stavanger sediment mixes, producing a total of four molds per mix. The cylinders were tapped lightly on the table 50 to 100 times in between filling stages to remove any existing air voids (Kitazume et al., 2015). Once filled, the tops of the samples were sealed with sheets of plastic film and rubber bands (Figure 12).



Figure 12. Sealed samples of Stavanger 19 material

### Sample Curing

The S/S samples were stored inside temperature- and humidity-controlled Thermocure II water bath curing boxes at 20° C for 28 days (Figure 13). At the end of the curing period, the samples were removed from their molds and tested for unconfined compressive strength, water content, and organic matter content.



Figure 13. Thermocure curing box

### UC Strength Testing and Results

Unconfined compressive strength ( $q_u$ ) tests were performed on triplicate samples for each mix after 28 days. The testing procedure followed ASTM D2166, and testing was conducted using an ELE Tritest50 device. The device's strain rate was set to 1% per minute

and the stress and strain data were recorded electronically using ELE software DS7.1.

Figure 14 shows a typical specimen undergoing  $q_u$  tests on the ELE device.



Figure 14. ELE Tritest50 device for  $q_u$  tests

As was discussed previously, samples containing 0% Portland cement were unable to be tested for unconfined compressive strength due to their inability to hold shape outside of the plastic mold structure. Figure 15 presents photographs of this material. The samples were still useful in providing controlled information on the water content, organic content, and leaching behavior of the sediments without the influence of Portland cement.

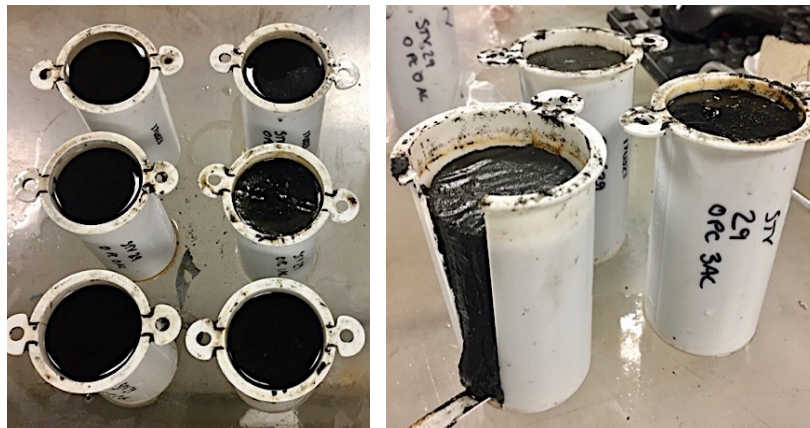


Figure 15. Samples containing 0% PC after 28 days of curing

The remaining samples, consisting of 4% PC, 8% PC, 8% PC + 1% AC, 8% PC + 3% AC, and 12% PC, were successfully tested for unconfined compressive strength. Figure 16 presents a triplicate series of samples prior to being removed from the mold (left), prior to testing (center), and after testing (right).

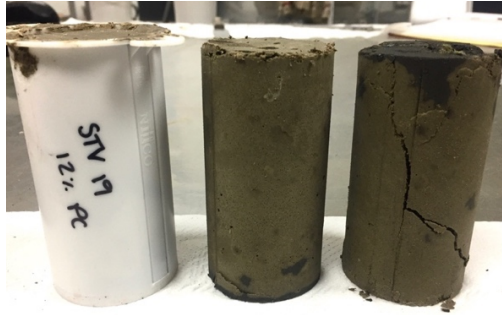


Figure 16. Triplicate samples for  $q_u$  tests

#### *NY/NJ Harbor Strength Results*

Figure 17 presents the unconfined compressive (UC) strength results for the NY/NJ Harbor sediments after 28 days.

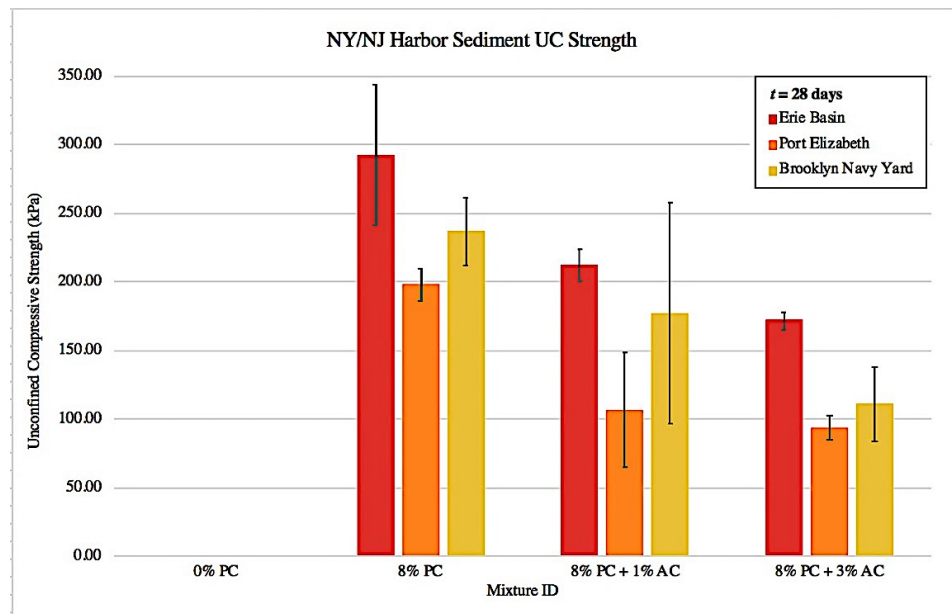


Figure 17. 28-day UC Strength Results for NY/NJ Sediments

As can be seen in Figure 17, reductions in the average UC strength of the stabilized material were observed with the addition of AC. Erie Basin sediment had a 27% reduction in average strength from 8% PC to 8% PC + 1% AC and a 41% reduction from 8% PC to 8% PC + 3% AC. Port Elizabeth sediment had a 46% reduction in average strength from 8% PC to 8% PC + 1% AC and a 53% reduction from 8% PC to 8% PC + 3% AC. Brooklyn Navy Yard sediment had a 25% reduction in average strength from 8% PC to 8% PC + 1% AC and a 53% reduction from 8% PC to 8% PC + 3% AC. However, due to the large standard deviations among the samples, a statistical test was required to determine whether or not the various mixtures produced significant differences in UC strength.

The Kruskal-Wallis test by ranks (a one-way analysis of variance on ranks) was used to statistically determine whether or not a difference in AC (0%, 1%, or 3%) in the S/S mixture significantly affected the UC strength of the material. The results of the Kruskal-Wallis test for the NY/NJ sediments are presented in Table 8.

Table 8. Kruskal-Wallis Test for NY/NJ Sediments

Sediment	Degrees of Freedom, df	Test Statistic, H	P-value, p	Level of Significance, $\alpha$	Significant Difference in $q_u$
Erie Basin	2	9.200	0.010	0.05	Yes
Port Elizabeth	2	8.711	0.013	0.05	Yes
Brooklyn Navy Yard	2	7.067	0.029	0.05	Yes

As can be seen in Table 8, all three sediments showed significant differences in UC strength with various doses of AC at 95% confidence ( $\alpha = 0.05$ ). This indicates that the observed

reductions in UC strength with AC can and should be considered adverse effects of the addition of AC for S/S treatment of soft NY/NJ harbor sediments.

### *Stavanger Harbor Strength Results*

Figure 18 presents the unconfined compressive strength results for the NY/NJ Harbor sediments after 28 days.

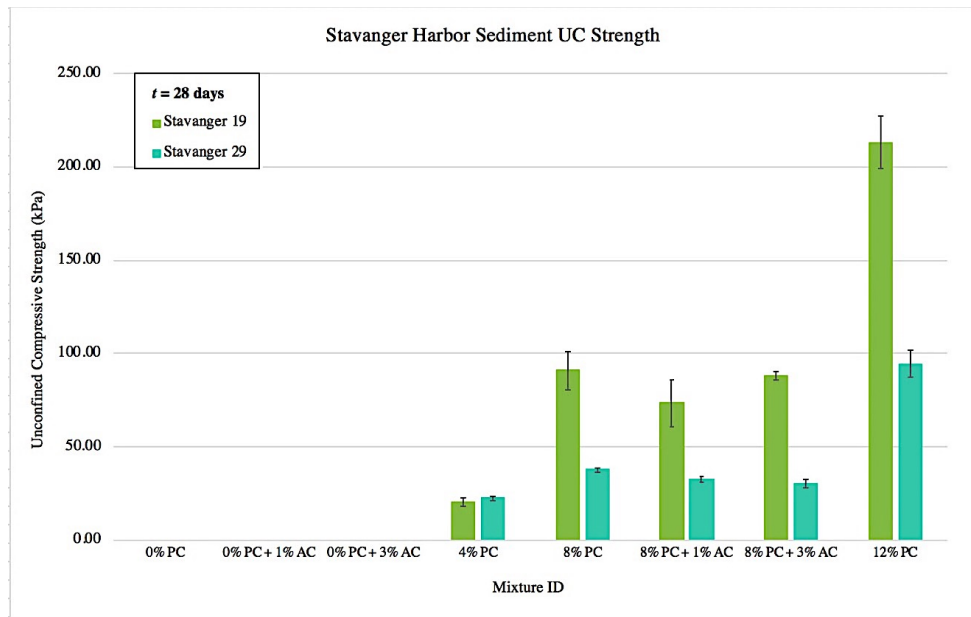


Figure 18. 28-day UC Strength Results for Stavanger Sediments

It is anticipated that the high moisture content of the Stavanger 29 sediment (naturally 326%) contributed to the samples' extremely low observed  $q_u$  values after 28 days. Figure 19 shows excess moisture beading and leaking from a low-cement Stavanger 29 sample undergoing the  $q_u$  test.



Figure 19. Moisture around 4% PC Stavanger 29 sample

While reductions in average UC strength were again visible for the Stavanger sediments, only Stavanger 29 sediment showed the same trend of increasingly reduced strength with AC, with a 13% reduction in average strength from 8% PC to 8% PC + 1% AC and a 19% reduction from 8% PC to 8% PC + 3% AC. Stavanger 19 sediment, on the other hand, had a 19% reduction in average strength from 8% PC to 8% PC + 1% AC and only a 3% reduction from 8% PC to 8% PC + 3% AC. This inconsistent pattern in strength reduction, as well as large standard deviations among samples, necessitated a statistical test to determine whether or not the various mixtures produced significant differences in UC strength.

The Kruskal-Wallis test by ranks was again used to statistically determine whether or not a difference in AC in the S/S mixture significantly affected the UC strength of the material. The results of the Kruskal-Wallis test for the Stavanger sediments are presented in Table 9.

Table 9. Kruskal-Wallis Test for Stavanger Sediments

Sediment	Degrees of Freedom, df	Test Statistic, H	P-value, p	Level of Significance, $\alpha$	Significant Difference in $q_u$ ?
Stavanger 19	2	4.756	0.093	0.05	No
Stavanger 29	2	7.956	0.019	0.05	Yes

As can be seen in Table 9, the Stavanger 29 sediment showed a significant difference in UC strength with various doses of AC at 95% confidence ( $\alpha = 0.05$ ) while the Stavanger 19 sediment did not. However, at a lower confidence level of 90% ( $\alpha = 0.10$ ) the Stavanger 19 sediment did show a significant difference. This indicates that a reduction in UC strength can be considered an adverse effect of the addition of AC for S/S treatment of Stavanger harbor sediments, with an increased likelihood of occurrence for softer, finer sediments akin to Stavanger 29 than for sandy material similar to Stavanger 19.

#### Water Content

Water content samples were taken immediately following the addition of cement (curing time  $t = 0$  days), and immediately following the  $q_u$  tests ( $t = 28$  days). Water content was calculated as the mass of water present in the sample over the mass of dry solids. The procedure followed ASTM D2216-10, where samples consisting of at least 10 grams of material were removed from the broken cores, weighed (to determine the moist weight) and then oven-dried at 105° C for 24 hours and weighed again (to determine the dry weight).



Figures 20 and 21 present the moisture content data for NY/NJ and Stavanger sediment samples, respectively, immediately after mixing ( $t = 0$  days) and after the  $q_u$  tests ( $t = 28$  days). The values presented for 0% PC at  $t = 0$  represent the natural moisture content of the material.

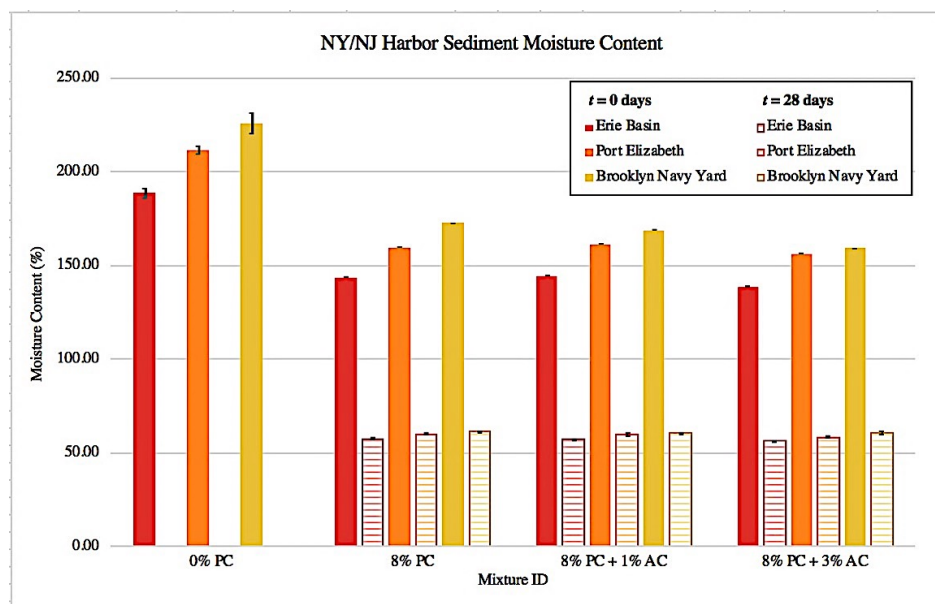


Figure 20. Water Content Comparison for NY/NJ Sediments

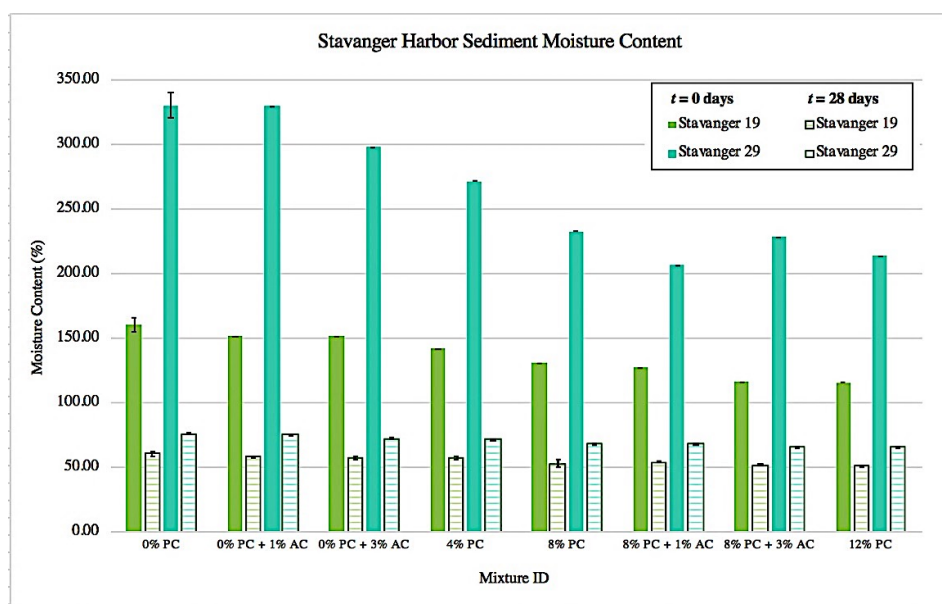


Figure 21. Water Content Comparison for Stavanger Sediments

The decrease in moisture content at  $t = 0$  days between the natural NY/NJ sediments (0% PC) and stabilized NY/NJ sediments (8% PC, 8% PC + 1% AC, and 8% PC + 3% AC) can be explained by the addition of dry material (PC and/or AC) to the wet sediments. Erie Basin sediment had 23.8%, 23.4%, and 26.5% decreases in average water content from 0% PC to 8% PC, 0% PC to 8% PC + 1% AC, and 0% PC to 8% PC + 3% AC, respectively, at  $t = 0$  days. Port Elizabeth sediment had 24.4%, 23.7%, and 26.0% decreases in average water content for the same respective mixes, while Brooklyn Navy Yard sediment had 23.5%, 25.1%, and 29.5% decreases. In general, the Stavanger sediments also had decreasing water content with increasing PC/AC content at  $t = 0$  days: Stavanger 19 sediment had a 5.4% reduction in average water content from 0% PC to 0% PC + 1% AC, 5.3% from 0% PC to 0% PC + 3% AC, 11.5% from 0% PC to 4% PC, 18.4% from 0% PC to 8% PC, 20.7% from 0% PC to 8% PC + 1% AC, 27.3% from 0% PC to 8% PC + 3% AC, and 27.9% from 0% PC to 12% PC. Stavanger 29 sediment had reductions of 0.1%, 9.8%, 17.7%, 29.5%, 37.4%, 30.9%, and 35.2% for the same respective mixes.

The decrease in moisture content between the stabilized sediments at  $t = 0$  days and  $t = 28$  days, on the other hand, can be explained by the chemical binding of water in the cement hydration reactions, as well as its evaporation due to the exothermic reaction of Portland cement. This results in a much larger reduction of water content for each sample than the initial addition of dry material and is reflected in the percent decreases for each mix. Erie Basin sediment had 59.8%, 60.1%, and 59.2% decreases in average water content for 8% PC, 8% PC + 1% AC, and 8% PC + 3% AC mixes, respectively, from  $t = 0$  days to  $t = 28$  days. Port Elizabeth sediment had 62.4%, 62.8%, and 62.5% decreases for the same respective mixes, while Brooklyn Navy Yard sediment had 64.3%, 63.9%, and 61.9%

decreases. Stavanger 19 sediment had 61.4%, 62.0%, 59.5%, 59.3%, 57.5%, 55.4%, and 55.6% decreases in average water content for 0% PC + 1% AC, 0% PC + 3% AC, 4% PC, 8% PC, 8% PC + 1% AC, 8% PC + 3% AC, and 12% PC mixes, respectively, from  $t = 0$  days to  $t = 28$  days. Stavanger 29 sediment had reductions of 77.1%, 75.7%, 73.6%, 70.6%, 67.1%, 71.0%, and 69.3% for the same respective mixes.

The relative magnitudes of the sediments' water content reductions mirrored those of their natural water contents. Stavanger 29 sediment had the highest natural water content (326%) as well as the highest reduction in water content for stabilized material (between 67.1% and 77.1% from  $t = 0$  days to  $t = 28$  days). Brooklyn Navy Yard sediment had the second highest natural water content (237%) and second highest reduction in water content (between 61.9% and 64.3%). Port Elizabeth sediment had the third highest natural water content (213%) and the third highest reduction in water content (between 62.4% and 62.8%). Erie Basin sediment had the second lowest natural water content (187%) and the second lowest reduction in water content (between 59.2% and 60.1%). Finally, Stavanger 19 sediment had the lowest natural water content (160%) and the lowest reduction in water content (between 55.4% and 62.0%). The discussion in Chapter 5 will provide further explanation for these observations.

### Organic Content

Organic content was determined by performing loss on ignition tests on the oven-dried specimens generated by the water content tests. The ash content of each sample was determined to be the mass of sample remaining at the end of the loss on ignition test, divided by the mass of the initial oven-dried test specimen. The organic matter content was then determined to be 100% minus the ash content (expressed as a percentage). Figure 22

provides pictures of the test specimens before (left) and after (right) the loss on ignition test. The change in color of the specimens from dark brown and black to rusty brown and orange is a consequence of the combustion of organic constituents – as the organic matter is burnt off, the specimens appear more similar to the silt and clay particles from which they are formed. The gray colored specimens indicate a high composition of PC.



Figure 22. Organic content test specimens before (left) and after ignition (right)

Figures 23 and 24 present the organic content data for NY/NJ and Stavanger sediment samples, respectively, immediately after mixing ( $t = 0$  days) and after breaking the sample cores ( $t = 28$  days). The values presented for 0% PC at  $t = 0$  days represent the natural organic content of the material. The values presented at  $t = 28$  days are average values determined from the three oven dried samples taken from each broken core following the  $q_u$  tests.

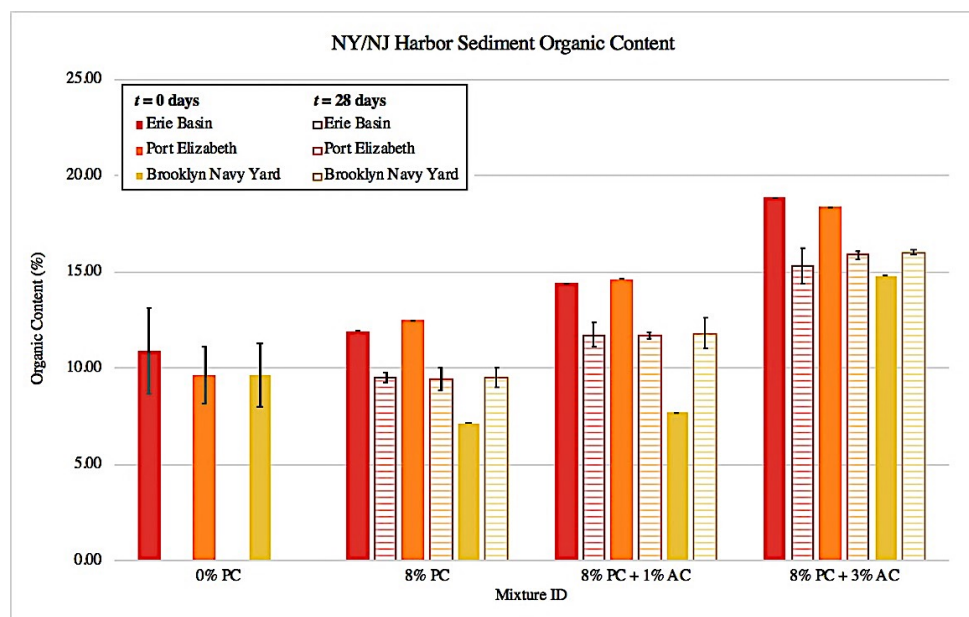


Figure 23. Organic Content Comparison for NY/NJ Sediments

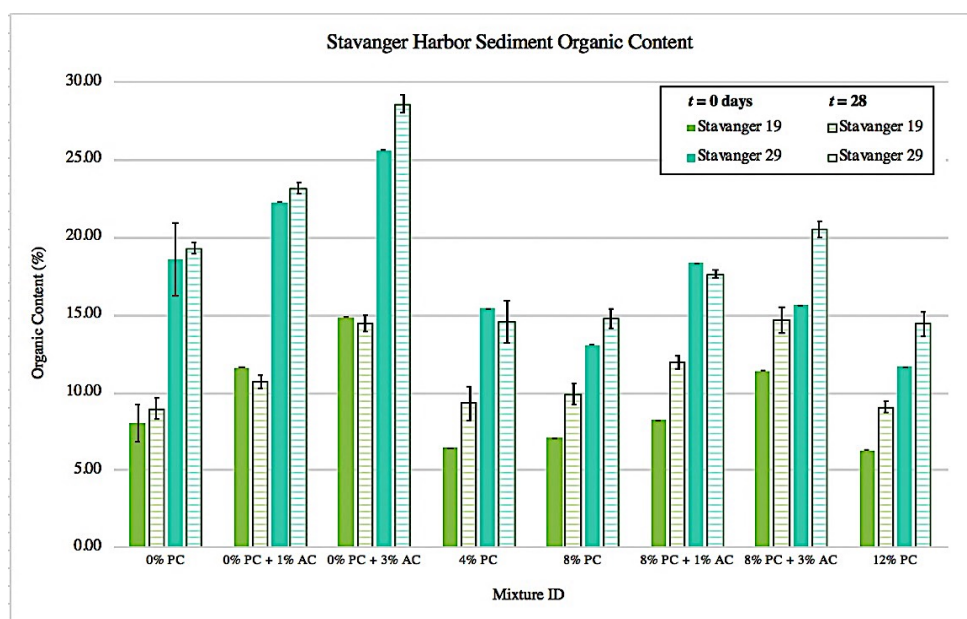


Figure 24. Organic Content Comparison for Stavanger Sediments

The organic content results are most useful from a quality assurance standpoint, to compare between the various mixes including and excluding AC rather than comparing the mixes over time. The observed increases in organic content with increasing AC dosage at

$t = 28$  days, in particular, verify that the expected quantities of AC were present in the samples as they were tested for UC strength. At  $t = 28$  days, the average organic content of Erie Basin sediment increased from 9.5% (for 8% PC samples) to 11.7% and 15.3% (for 8% PC + 1% AC and 8% PC + 3% AC samples, respectively). The average organic content of Brooklyn Navy Yard sediment increased from 9.5% to 11.8% and 16.0% for the same respective mixes, while the average organic content of Port Elizabeth sediment increased from 9.4% to 11.7% and 15.9%. The average organic content of Stavanger 19 sediment increased from 9.9% (for 8% PC samples) to 11.9% and 14.6% (for 8% PC + 1% AC and 8% PC + 3% AC samples, respectively) and from 8.9% (for 0% PC) to 10.7% and 14.4% (for 0% PC, 0% PC + 1% AC, and 0% PC + 3% AC samples, respectively). The average organic content of Stavanger 29 sediment increased from 14.8% to 17.6% and 20.5% and from 19.3% to 23.1% and 28.5% for the same respective mixes. Ultimately, mixtures with intended doses of 1% AC had an average increase in organic content of 2.6% while mixtures with intended doses of 3% AC had an average increase in organic content of 5.5%. This is presumably due to the incineration of activated carbon during the loss on ignition tests for organic content.

## Chapter 4: Environmental Methods and Results

Following the unconfined compressive strength tests described in Chapter 3, broken test specimens were stored at 4° C awaiting laboratory analysis. Samples were submitted to Alpha Analytical Labs in Massachusetts, USA for total solids concentration analysis and Synthetic Precipitate Leaching Procedure (SPLP) extraction. Due to the experimental requirements for high contaminant concentrations discussed in detail in Chapter 2, only samples consisting of Stavanger Harbor sediments were submitted for chemical analysis at Alpha Analytical Labs. The chemicals evaluated included US EPA TAL Metals, PAHs, and tributyltin. Descriptions of the test methods and detailed results for these analyses will be discussed in this chapter. First, however, a brief discussion of the contaminants of interest will be provided to give context to the environmental results.

### Contaminant Overview

#### *Target Analyte List (TAL) Metals*

US EPA Target Analyte Lists (TALs) are subsets of chemicals found in the US EPA Priority Pollutant List, originally consisting of 129 toxic pollutants identified by the Clean Water Act. These pollutants are regulated by the EPA and have published, associated analytical test methods. The heavy metals and organic compounds included in these lists have been prioritized due to their frequent discovery in wastewater and their individual toxicity characteristics, including the specific toxicity and persistence of the pollutant and the nature and extent of impacts on affected organisms (NJDEP, 2014). Heavy metals are of particular concern for their known toxicities, accretion with sediment, and classification by the US EPA and International Agency for Research on Cancer as known or probable

human carcinogens (Tchounwou, Yediou, Patlolla, & Sutton, 2012). The US EPA Metals TAL includes the following compounds: aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, thallium, vanadium, and zinc. While these metals occur naturally in the environment at trace or background concentrations, anthropogenic sources are the largest contributors to environmental contamination due to the widespread use of heavy metals in industrial, domestic, and agricultural activities (Tchounwou et al., 2012).

#### *Polycyclic Aromatic Hydrocarbons (PAHs)*

Polycyclic aromatic hydrocarbons (PAHs) are semivolatile organic pollutants that are also persistent in the environment, hydrophobic, and potentially carcinogenic. PAHs are often released into the environment by anthropogenic sources, including the spill or release of petroleum products and the incomplete combustion of fossil fuels, wood, garbage, or other organic materials (ATSDR, 1995). In general, PAHs are found in the environment as complex mixtures rather than as individual compounds, often including the following compounds: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(j)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene, and pyrene. As they do not dissolve easily in water, PAHs are generally present in a vapor or solid form, either in the air or stuck to the surface of dust or small soil particles (ATSDR, 1995). As a result, they are often found sorbed to sediments in areas prone to deposition such as urban streams or harbors.



### *Tributyltin (TBT)*

Tributyltin (TBT) has been identified as an emerging contaminant of concern, with few sediment- or stabilization-related studies conducted within the United States or the New York/New Jersey Harbor region (Yan, Subramanian, Tyagi, Surampalli, & Zhang, 2009). It is a synthetic organotin compound with widespread historical use as a biocide and has been found to have acute toxicological effects as well as adverse ecological impacts on the marine environment (Antizar-Ladislao, 2008). Historical use of TBT has included antifouling paints for boats, preservatives for wood and textiles, slimicides for masonry and industrial processes, and molluscicides (Danish Environmental Protection Agency, 2013). TBT is released into the environment from anthropogenic sources and is found most highly concentrated near marinas, or in areas with frequent boat activity, due to its use as hull paint (Danish Environmental Protection Agency, 2013). It is a persistent and pervasive compound with an affinity for adsorption to suspended particles and dissolved organic matter, which results in the majority of TBT in the natural environment found bound to sediment (ATSDR, 2005). A review of existing literature found favorable results for TBT removal from wastewater and marine sediment via sorption to activated carbon, indicating that it would be a good additional target compound for observation in this experiment (Brändli, Breedveld, & Cornelissen, 2009; Ayanda, Fatoki, Adekola, Ximba, & Petrik, 2015).

### Total Concentration of Contaminants

In order to verify that the material being tested for leaching potential contained the anticipated (detectable) values of contaminants, eight samples were tested for total concentrations of metals, PAHs, and tributyltin. Untreated (raw) material from sampling

site Stavanger 29 was tested for total concentrations of metals and PAHs. Raw material from sampling site Stavanger 19 was tested for total concentration of tributyltin. Similarly, Stavanger 29 material stabilized with 8% (by wet weight) Portland cement was tested for total concentrations of metals and PAHs, while 8% stabilized Stavanger 19 material was tested for tributyltin. These correlations remained the same for the subsequent SPLP analyses and are summarized in Table 10. The selection of Stavanger 29 samples for PAH and metals analysis and Stavanger 19 samples for tributyltin analysis are justified by the preliminary concentration values reported in Chapter 2.

Table 10. Correlation of Source Material and Assessed Contaminants

Contaminant Category	Source Material
PAHs	Stavanger 29
TAL Metals	Stavanger 29
Tributyltin	Stavanger 19

The results of the total concentration analyses are presented for PAHs in Table 11 and for metals and tributyltin in Table 12. Overall, concentrations in the raw sediments (0% PC) were found to be similar to those reported in the preliminary chemical assessments. Concentrations in the 8% PC stabilized sediments were used as supplementary data for analysis of the SPLP results, to verify that any non-detectable or unexpectedly low leaching concentrations could not be attributed to a lack of contaminant present in the material.

Table 11. Total Concentrations of Semivolatile Organics in Stavanger Sediments

Chemical Compound	Concentration (mg/kg)			
	0% PC		8% PC	
	Sample 1	Sample 2	Sample 1	Sample 2
<b>Semivolatile Organics</b>				
Acenaphthene	208	184	635	364
Acenaphthylene	226	253	229	368
Anthracene	1,550	649	2,060	1,110
Benzo(a)anthracene	2,360	2,660	3,760	2,350
Benzo(a)pyrene	3,560	3,830	4,300	3,330
Benzo(b)fluoranthene	3,420	3,630	3,850	3,110
Benzo(g,h,i)perylene	2,480	2,620	2,740	2,140
Benzo(k)fluoranthene	2,890	3,090	3,350	2,430
Chrysene	2,510	2,730	3,630	2,350
Dibenz(a,h)anthracene	690	743	736	586
Fluoranthene	5,630	6,110	10,100	5,940
Fluorene	293	224	848	465
Indeno(1,2,3-cd)pyrene	2,550	2,700	2,710	2,150
Naphthalene	208	265	1,080	278
Phenanthrene	2,440	2,320	6,420	3,660
Pyrene	5,270	5,650	8,070	5,140

Table 12. Total Concentrations of Metals and Organometallics in Stavanger Sediments

Chemical Compound	Concentration (mg/kg)			
	0% PC		8% PC	
	Sample 1	Sample 2	Sample 1	Sample 2
<b>Metals</b>				
Aluminum	8,960	7,890	11,800	11,500
Antimony	7.11	3.98	3.80	4.64
Arsenic	40.7	34.4	30.2	27.9
Barium	232	198	235	189
Beryllium	0.574	0.471	0.532	0.543
Cadmium	2.67	3.10	1.95	2.01
Calcium	19,400	13,400	121,000	130,000
Chromium	51.8	47.4	93.7	92.5
Cobalt	11.3	8.23	7.76	7.57
Copper	466	409	314	315
Iron	50,600	38,000	34,600	34,600
Lead	931	838	657	663
Magnesium	10,800	9,520	13,500	13,700
Manganese	385	309	605	608
Mercury	6.09	7.68	4.66	4.73
Nickel	39.9	28.9	35.7	35.7
Potassium	3,240	3,050	4,050	4,250
Selenium	5.26	3.88	3.19	3.82
Silver	1.05	0.889	1.16	1.04
Sodium	33,800	32,000	21,700	24,600
Thallium	0.599	0.510	0.440	0.574
Vanadium	100	86.0	96.5	97.0
Zinc	1,060	937	853	874
<b>Organometallics</b>				
Tributyltin	1.50	2.80	0.608	3.10

## Synthetic Precipitation Leaching Procedure (SPLP)

SPLP is a single extraction “batch” test for leaching that is advantageous for several reasons, discussed in the literature review in Chapter 1.

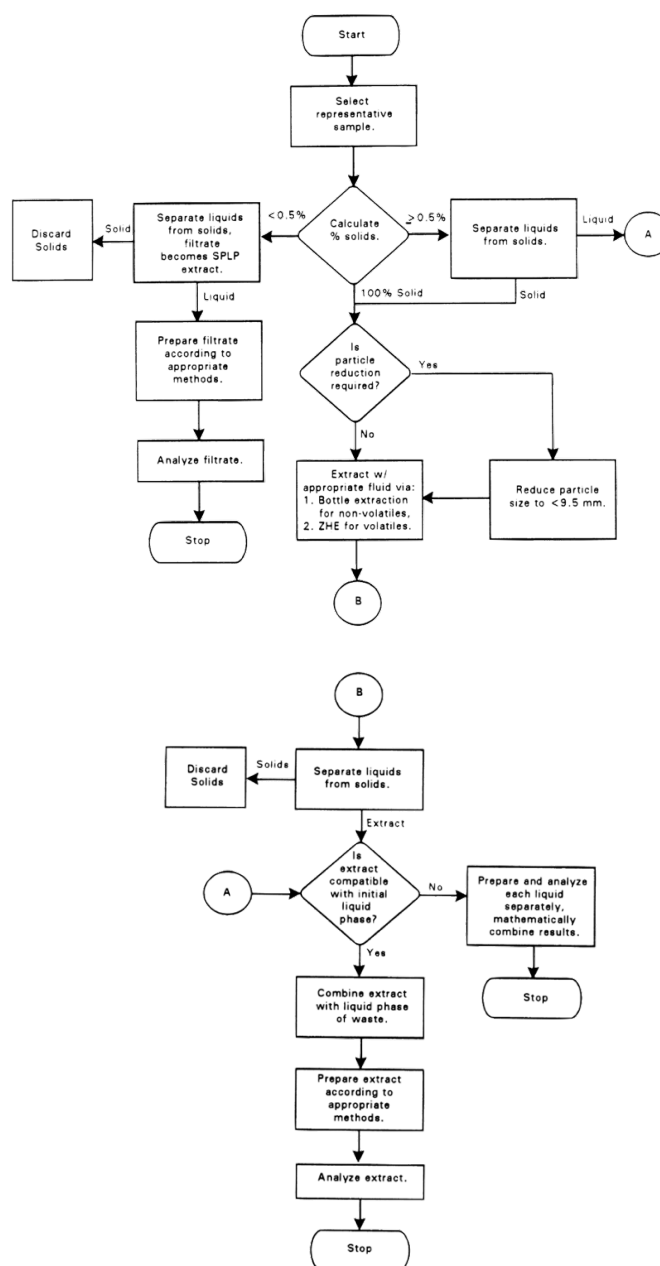


Figure 25. SPLP Process Diagram

(USEPA, 1994)

SPLP was selected for use in this experiment due to the time-efficiency of tests (allowing dozens of samples to be tested for comparison within a reasonable timeframe), the availability of laboratory expertise due to its use in compliance regulations, and the availability of associated standards for a meaningful comparison of leachate concentrations. However, it is important to note that SPLP is purely an assessment of the potential leachate concentration that can be generated from a particular material subjected to the test and that it is only an assessment of S/S treatments' chemical stabilization potential. The procedure does not represent the combined effects of stabilization and solidification, as the samples must be crushed in order to conduct the test and thus do not behave as solid monoliths. Standard practice involves comparing the leachate concentrations to the appropriate groundwater water quality standards. If a concentration is in excess of the standard, the potential transport of contaminants through the solidified soil matrix can be modelled using both the hydraulic conductivity of the material (on the order of  $10^{-6}$  cm/s for cement-stabilized material) and the SPLP concentration results to better understand the associated risk of leaching. For this study, SPLP concentration values were compared to New Jersey Specific Ground Water Quality Criteria.

Minor adjustments were made to the laboratory-reported SPLP concentration values to correct for uncertainty due to the joint SPLP treatment of water and sediment phases. Whereas samples that were stabilized using Portland cement contained no free water, the 0% PC (raw material), 0% PC + 1% AC, and 0% PC + 3% AC samples contained visible free water after 28 days of curing. The SPLP procedure, which specifies a mass of sediment solids and a volume of acidic solution, was performed identically in both cases by the laboratory. This produced inconsistencies in the amount of material available for

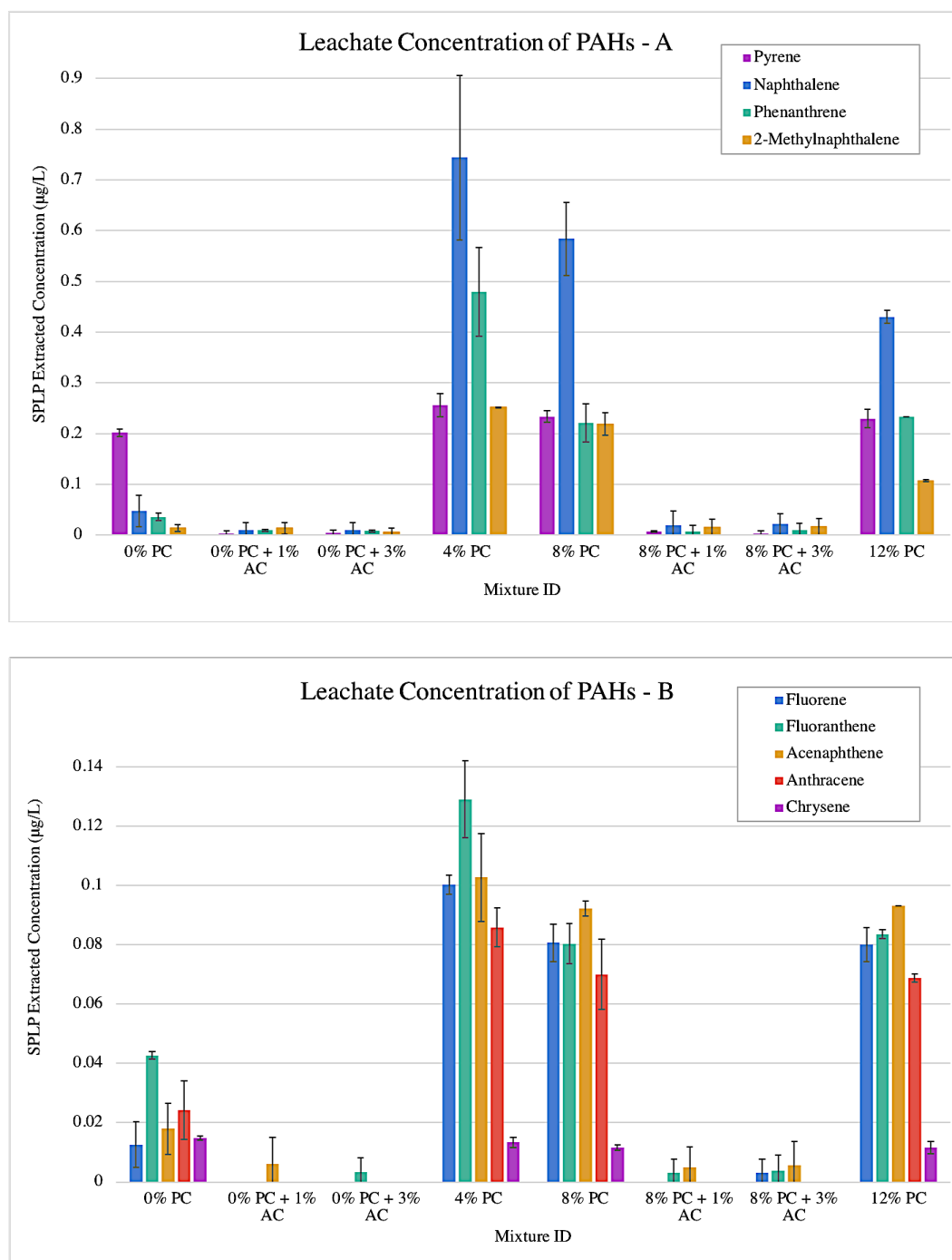
extraction and made it difficult to accurately compare the leaching performance of the mixtures to each other. To correct for the differences in the amount of solid material tested, the reported SPLP concentration values were normalized to the percent solids contained in each sample, producing leachate concentrations *per dry solids*. Values for percent solids (or percent dry matter) were calculated as 100% minus the percent moisture (discussed in Chapter 3). Reported concentration values were divided by the percent solids present in the sample to produce the corrected (*per dry solids*) concentration values. Table 13 presents the correction factors utilized to generate the results portrayed in the following figures.

Table 13. Percent Solids Correction Factors for SPLP Concentrations

Mixture ID	Stavanger 29 (PAHs and TAL Metals)	STV 19 (Tributyltin)
Raw material	0.24	0.39
0%PC + 1%AC	0.25	0.42
0%PC + 3%AC	0.28	0.42
4% PC	0.28	0.43
8% PC	0.32	0.47
8%PC + 1%AC	0.32	0.46
8%PC + 3%AC	0.34	0.48
12% PC	0.34	0.49

### SPLP Leaching Results: Semivolatile Organics

Figure 26 presents the SPLP leachate concentrations (*per dry solids*) for PAHs observed during this study.





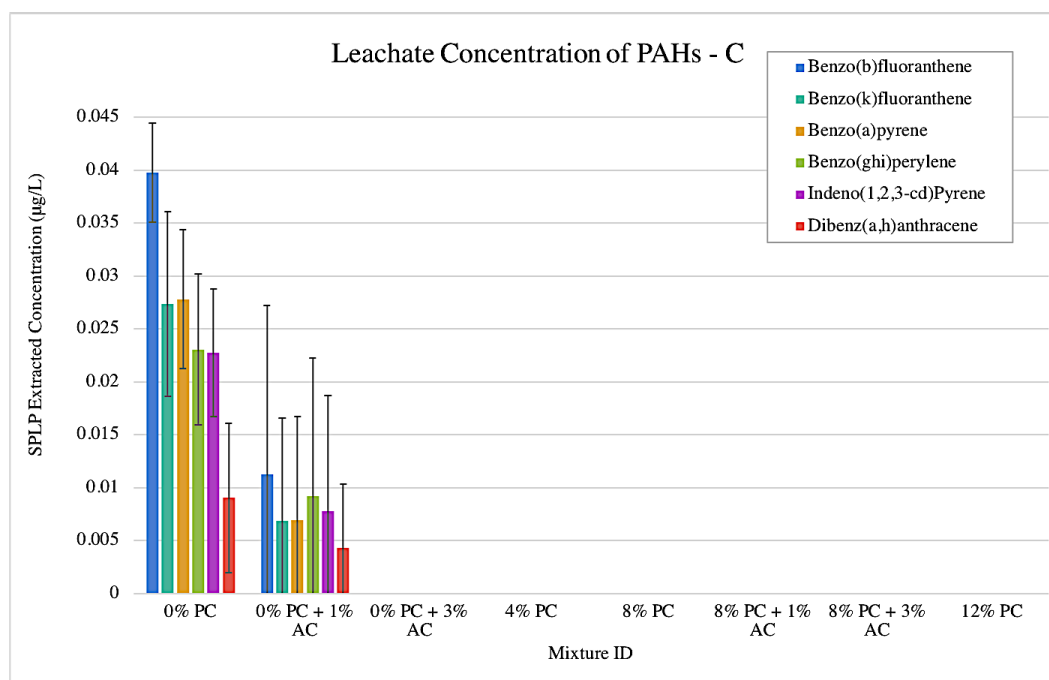


Figure 26. Leachate Concentrations (*per dry solids*) for PAHs – A, B, and C

Two common behavioral trends were apparent in the leachate concentrations of PAHs: the first, visible in Figure 26 – A and B, is a nearly complete reduction in detected PAH concentration for all mixes containing activated carbon. Though detectable values were still present for PC-only mixes (some compounds displaying decreasing trends with increasing cement dosages, others remaining approximately constant), powdered activated carbon was clearly successful at binding and limiting the transport of PAHs in cement-stabilized sediment. The second trend, visible in Figure 26 – C, is the complete non-detection of compounds for all treatments more aggressive than 0% PC + 1% AC. This result indicates that while Portland cement alone is successful at stabilizing the contaminants at various ratios, the same effect may be achieved with moderate to high doses of activated carbon alone, or minimal carbon-cement mixtures.

A better understanding of these two trends is achieved by considering the specific compounds involved. The PAH compounds that displayed complete non-detection with PC alone as well as with AC-PC doses (Figure 26 – C) included benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene. All six of these compounds are longer chain PAHs (with relatively heavy molecular weights between 252 and 278 g/mol), for which S/S with PC is a well-documented, successful technique (Bates & Hills, 2015). The remaining PAH compounds (pyrene, naphthalene, phenanthrene, 2-methylnaphthalene, fluorene, fluoranthene, acenaphthene, anthracene, and chrysene) are less suitable for stabilization with PC alone due to their relatively smaller, lighter chemical structures (molecular weights between 128 and 228 g/mol). As Figure 26 – A and B shows, however, these compounds can be successfully treated using modified binders, such as those including AC (Bates & Hills, 2015).

The method of correcting SPLP concentrations per dry solids was useful for comparing leaching performance among the samples. However, the non-corrected (laboratory-reported) concentrations were required in order to accurately compare each of the observed leaching values to the relevant standards. The *as-reported* average leachate concentrations for all mixtures except the raw material (0% PC) were compared to NJ Class II-A Ground Water standards, the maximum values of which are presented in Table 14 alongside their corresponding criterion. As can be seen in Table 14, none of the as-reported leachate concentrations for PAH compounds were in exceedance of NJ standards for this study.

Table 14. Comparison of (*as-reported*) PAH Leachate Concentrations to NJ Standards

Chemical compound	Maximum Average <i>As-Reported</i> Leachate Concentration (µg/L)	NJ Class II-A Ground Water Criterion (µg/L)
2-Chloronaphthalene	0.005	600
2-Methylnaphthalene	0.07	30
Acenaphthene	0.03	400
Acenaphthylene	0.009	-
Anthracene	0.02	2,000
Benz(a)anthracene	0.004	0.05
Benzo(a)pyrene	0.002	0.005
Benzo(b)fluoranthene	0.003	0.05
Benzo(ghi)perylene	0.002	-
Benzo(k)fluoranthene	0.002	0.5
Chrysene	0.004	5
Dibenz(a,h)anthracene	0.001	0.005
Fluoranthene	0.04	300
Fluorene	0.03	300
Indeno(1,2,3-cd)pyrene	0.002	0.05
Naphthalene	0.2	300
Phenanthrene	0.1	-
Pyrene	0.08	200

### *SPLP Leaching Results: Tributyltin (TBT)*

Figure 27 presents the SPLP leachate concentrations (*per dry solids*) for tributyltin (TBT) observed during this study:

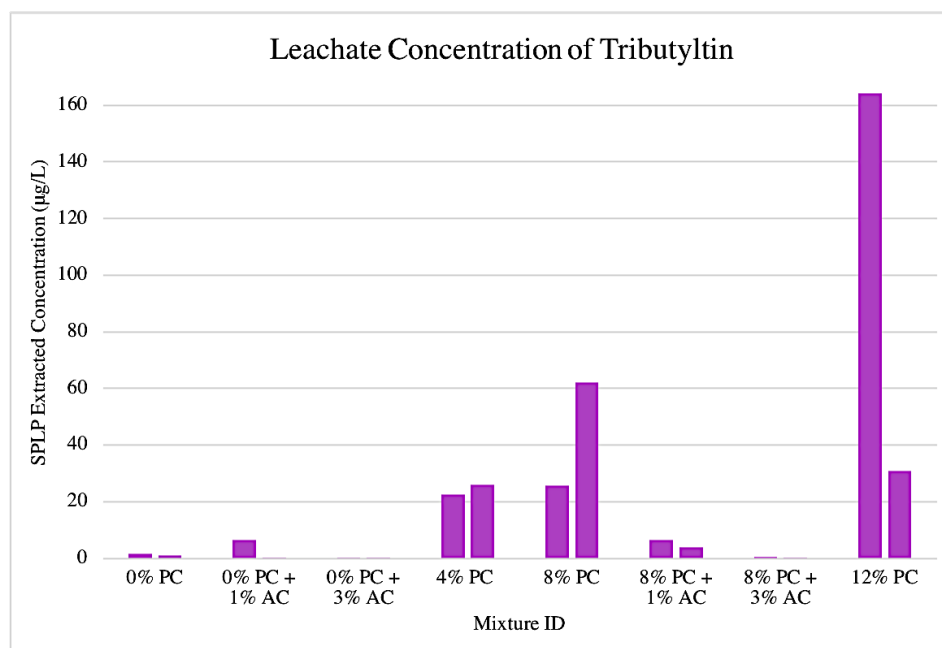


Figure 27. Leachate Concentrations (*per dry solids*) for Tributyltin (TBT)

The leachate concentration of TBT appears to increase with increasing cement content (presumably due to the associated increase in pH) from an average of 1.3 µg/L (0% PC) to an average of 97.5 µg/L (12% PC), however there is a fair amount of variation among the samples. The first sample tested for 12% PC, in particular, is a suspected outlier (though this cannot be statistically confirmed due to the small sample size of the study). When activated carbon is introduced into the stabilized mixture, the leachate concentration decreases on orders of magnitude: from an average of 43.9 µg/L (8% PC) to 5.2 µg/L (8% PC + 1% AC) to 0.31 µg/L (8% PC + 3% AC).

Tributyltin's observed leaching behavior can be explained by its aqueous solubility and affinity for particulate matter. While both salinity and pH are known to influence TBT

partitioning between sediment and water, pH has the greatest impact on TBT mobility in the case of sediment stabilization. Figure 28 shows the effect of pH on TBT partitioning in seawater and sediment, reported by Langston and Pope in 1995. Under neutral conditions ( $\text{pH} \approx 6.0 - 8.0$ ), TBT tends to sorb to the sediment rather than dissolve into seawater. However, under more extreme acidic or alkaline conditions ( $\text{pH} < 6.0$  or  $\text{pH} > 8.0$ ), TBT favors the liquid phase over the solid phase.

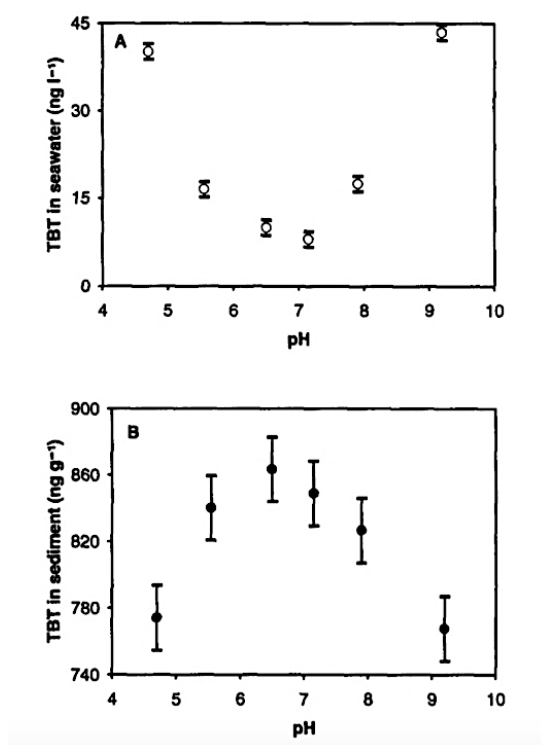


Figure 28. Effect of pH on TBT partitioning in water (A) and in sediment (B)  
(Langston & Pope, 1995)

This behavior has direct implications on the stabilization of TBT-contaminated sediment, as the addition of Portland cement or other pozzolanic amendments results in a significantly increased (alkaline) pH. Under these circumstances, TBT becomes more mobile and thus available for transport through groundwater movement rather than trapped

as a solid particulate. The addition of activated carbon to the stabilization/solidification process, however, has the potential to strip TBT from this mobile phase, and thus reduce the concentration available for leaching.

As TBT has not yet been included in New Jersey standards, the leachate concentration values generated by this study could not be compared to the appropriate groundwater criterion at this time. However, several studies that report seawater TBT concentrations in port areas (ASTDR, 2005; Batiuk, 1987) indicate that the leachate concentrations found in this study are less than typical seawater concentrations, meaning that the leachate from this material would have little to no effect on the surface water concentration of TBT. It is also important to note that while the potential leachate concentration is higher at greater binder addition rates, the hydraulic conductivity also decreases significantly at these rates, which would eventually be considered when determining the actual leaching potential of the stabilized material.

*SPLP Leaching Results: Metals*

Unlike PAHs and tributyltin, US EPA Target Analyte List (TAL) metals did not exhibit common or singular behavioral trends in leaching during this study. Many of the observed values can be attributed to the presence of trace metals within Portland cement, their roles in cement hydration reactions, and their respective pH-dependent solubilities. Several of the TAL metals produced non-detectable leachate concentrations for all mixes, including the raw material. These metals include: beryllium, cadmium, manganese, mercury, selenium, silver, thallium, and zinc. However, not all of the metals' leachate concentrations fell below NJ ground water standards. The remaining discussion in this section will focus on the metals whose leachate concentrations exceeded the groundwater standards.

The *as-reported* average leachate concentrations for all mixtures except the raw material (0% PC) were compared to NJ Class II-A Ground Water standards, the maximum values of which are presented in Table 15 alongside their corresponding criterion. As can be seen in Table 15, five metals were found to be in exceedance of NJ standards: aluminum, antimony, arsenic, lead, and sodium.

Table 15. Comparison of (*as-reported*) Metal Leachate Concentrations to NJ Standards

Chemical compound	Maximum Average <i>As-Reported</i> Leachate Concentration (µg/L)	NJ Class II-A Ground Water Criterion (µg/L)
<b>Aluminum</b>	<b>1070</b>	<b>200</b>
<b>Antimony</b>	<b>12</b>	<b>6</b>
<b>Arsenic</b>	<b>6</b>	<b>0.02</b>
Barium	180	6,000
Beryllium	ND	1
Cadmium	ND	4
Calcium	336,000	-
Chromium	9	70
Cobalt	4	100
Copper	240	1,300
Iron	110	300
<b>Lead</b>	<b>11</b>	<b>5</b>
Magnesium	30,000	-
Manganese	ND	5
Mercury	ND	2
Nickel	41	100
Potassium	54,000	-
Selenium	ND	40
Silver	ND	40
<b>Sodium</b>	<b>308,000</b>	<b>50,000</b>
Thallium	ND	0.5
Vanadium	45	60
Zinc	ND	2,000



Figure 29 presents the SPLP leachate concentrations (*per dry solids*) for the five metals that exceeded NJ groundwater standards:

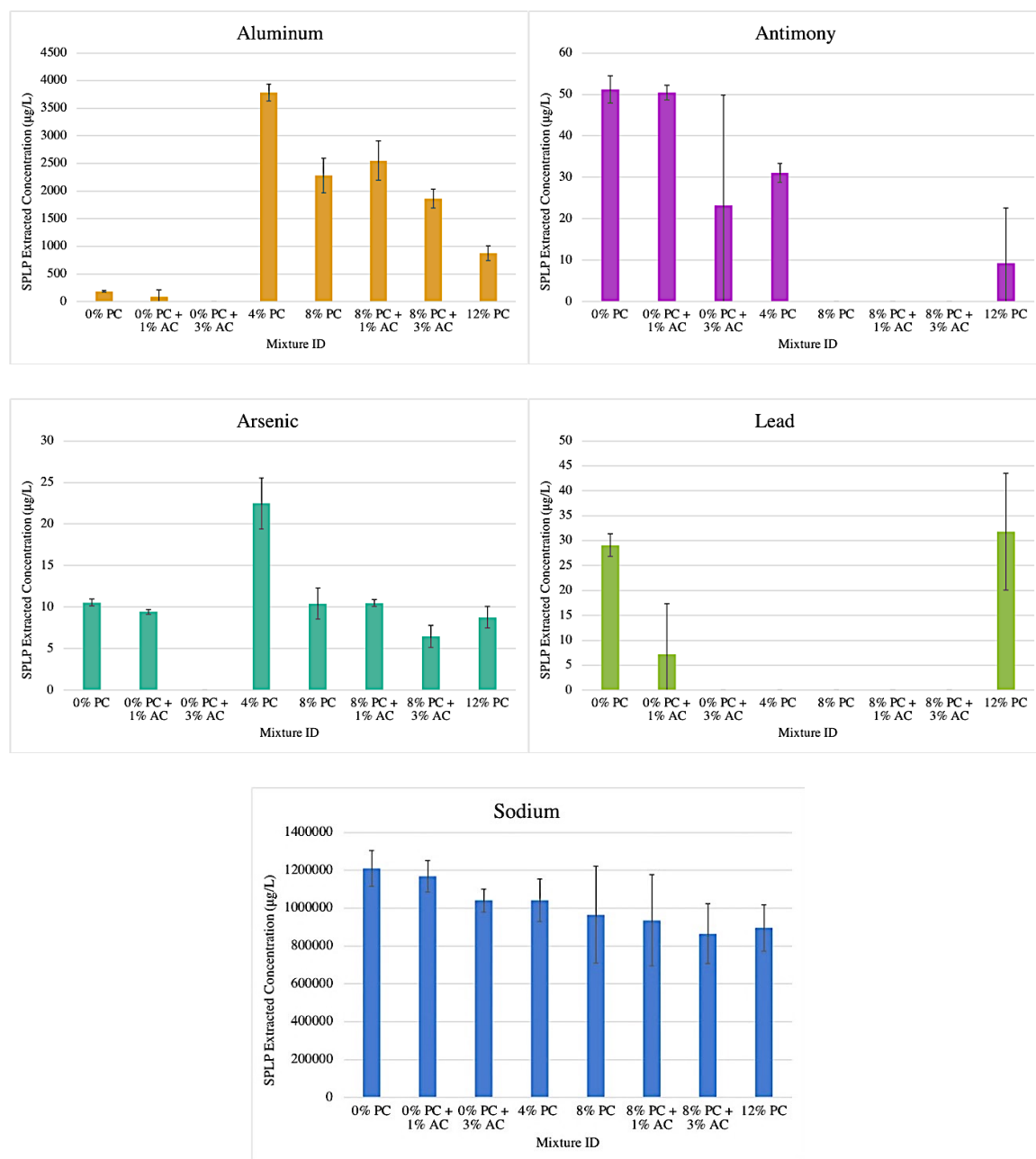


Figure 29. Leachate Concentrations (*per dry solids*) for TAL Metals

The exceptionally high leachate concentrations of sodium compared to the NJ criterion are no cause for concern, as they merely indicate the marine environment from

which the sediment originated. Similarly, the elevated concentrations of aluminum for mixtures containing Portland cement highlight the alumina content of the cement itself.

Both arsenic and antimony demonstrate the effectiveness of Portland cement stabilization: antimony falls beneath the standard value for all treatments more aggressive than 4% PC (including joint carbon-cement treatments with 8% PC), while arsenic tapers toward the standard with increasing PC content without quite reaching it. It is important to note, however, that the solubility and speciation of arsenic is complex and highly dependent on pH, much like TBT, with increased solubility known to occur with increased alkalinity (Papassiopi, Virčíková, Nenov, Kontopoulos, & Molnár, 1996; Masscheleyn, Delaune, & Patrick, 1991). Lead also shows promise for stabilization with cement and carbon, though apparent anomalies within the results make it difficult to reach firm conclusions.

## **Chapter 5: Conclusions and Recommendations for Future Work**

The results of this study suggest that powdered activated carbon can aid in the effectiveness of Portland cement solidification/stabilization to treat uniquely challenging contaminants; it is particularly effective in reducing the leaching potential of PAHs and TBT. However, it may also produce a significant reduction in the strength gain of the stabilized material, especially for fine sediments. This chapter will provide a broader discussion of the results of the study and their implications for the future of AC-PC S/S applications for sediment management.

### Discussion of Strength Results

As was discussed in Chapter 3, additional mixes were created for the 28-day strength analysis of Stavanger Harbor sediments but not for the New York/New Jersey sediments, and samples from both locations consisting of 0% Portland cement (with and without activated carbon) were too weak to be successfully removed from their molds and tested. Therefore, a specific comparison of strength results among all five sediment types is only possible for samples consisting of 8% PC with 0, 1, and 3% AC. Figure 30 presents a comparison of the average UC strength results for all five sediments at these three mixing conditions.

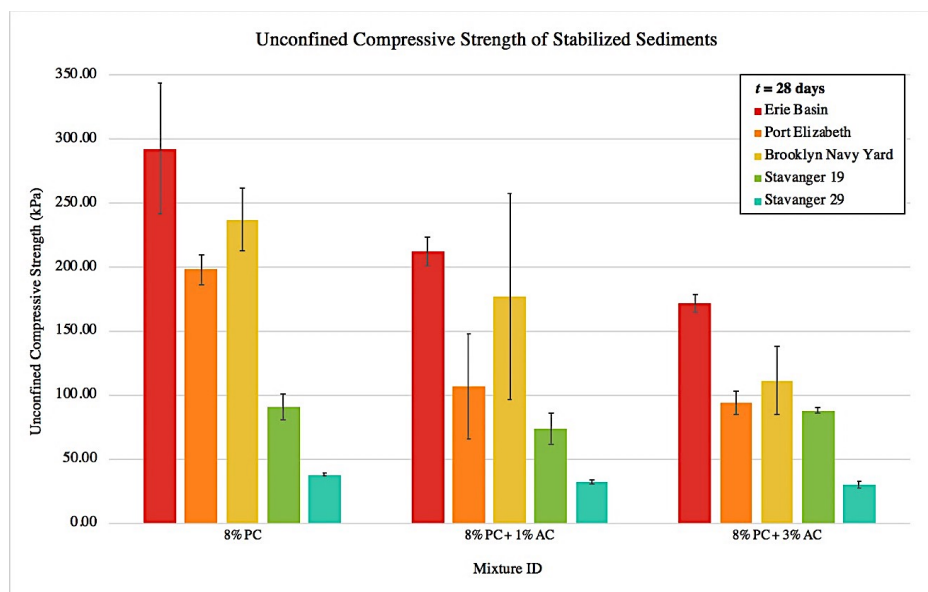


Figure 30. Unconfined Compressive Strength of Stabilized Sediments

In general, the Stavanger sediments were weaker than the NY/NJ sediments – while the average strength values for NY/NJ sediments’ 8% PC mixes ranged from 198 kPa to 293 kPa, Stavanger sediments were limited to 38 kPa to 91 kPa. For 8% PC + 1% AC mixes, NY/NJ sediments ranged between 107 kPa and 212 kPa and Stavanger sediments remained between 33 kPa and 74 kPa. For 8% PC + 3% AC mixes, NY/NJ sediments’ average strength values were between 94 kPa and 172 kPa, while Stavanger sediments ranged from 30 kPa to 88 kPa. From these values and the statistical analyses performed in Chapter 3, it is clear that while the NY/NJ sediments’ strength values visibly decreased with the addition of AC, the Stavanger sediments’ strength values remained more or less consistent.

The behavior of the individual sediment types and their observed strength gains can be best understood within the context of the natural properties of the sediments; that is, their moisture contents, organic contents, and grain size distributions. Table 16 presents a summary of these properties, previously discussed in Chapter 2.

Table 16. Properties Influencing the Strength of Stabilized Sediment

Source Material	Natural moisture content, $w_n$ (%)	Natural organic content, $OM$ (%)	Sand (%)	Silt and Clay (%)
Erie Basin	187	9.5	2.0	98.0
Port Elizabeth	213	8.9	2.2	97.8
Brooklyn Navy Yard	237	9.2	1.5	98.5
Stavanger 19	160	8.0	62.9	31.8
Stavanger 29	326	20.3	23.7	75.1

Figure 31 presents a comparison of the average moisture content results for all five sediments at the three comparable mixing conditions at  $t = 28$  days. As was addressed in Chapter 3, the Stavanger 29 sediment had the highest natural moisture content and the highest reduction in moisture content of all five sediments. Stavanger 29 samples also had the highest average moisture content at  $t = 28$  days (between 66.2% and 68.5%) and the lowest observed UC strength (between 30 and 37 kPa).

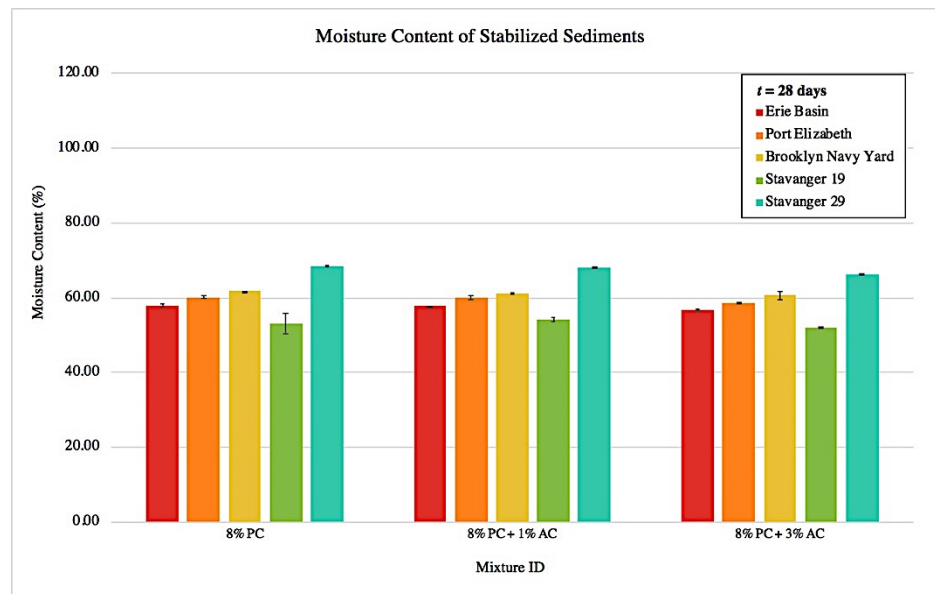


Figure 31. Moisture Content of Stabilized Sediments

The relationship between moisture content and S/S material strength has been explored in depth by previous S/S studies, the results of which suggest that the unfavorable initial moisture content of the Stavanger 29 material hindered the mechanism of cement stabilization. Cement stabilization occurs via four consecutive steps: the reduction of water content, the improvement of soil physical properties, cement hydration and hardening, and pozzolanic reaction hardening (Kitazume, 2017).

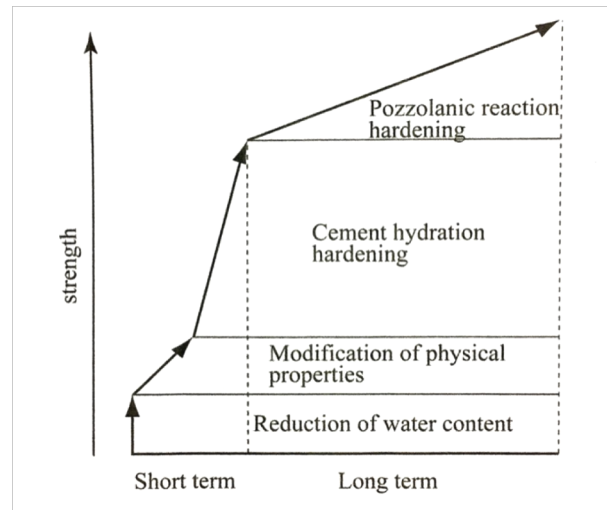


Figure 32. Mechanism of Cement Stabilization

(Kitazume, 2017)

If the initial moisture content of the sediment is excessively high, the first stage of the cement stabilization process can be prolonged and delay or prevent the ultimate strength gain of the material (Figure 32). It is expected that this was the case for the Stavanger 29 material.

Considering only the moisture content of the sediments would suggest that Stavanger 19 sediment, with the lowest natural moisture content and lowest reduction in moisture content of all five sediments, would have the lowest average moisture content at  $t = 28$  days and the highest observed UC strength. While the Stavanger 19 sediment did

have the lowest average moisture content at  $t = 28$  days (between 52.0% and 54.1%) it actually had the second lowest observed UC strength, suggesting the influence of additional factors on the cement-stabilized sediment's strength gain. In this case, it is likely that the grain size of the material combined with its moisture content contributed to the low strength gain. From Table 16 it can be seen that Stavanger 19 material consisted primarily of sand (62.9%) while the other four sediments consisted primarily of silt and clay particles. The large surface areas of clay and silt particles allow such soils to retain more water than larger sand particles, resulting in typically higher natural moisture contents. While it is not uncommon for clayey, silty, and organic sediments to have moisture contents that exceed 100%, it is unusual for sandy sediments to have such high moisture contents. It is anticipated, therefore, that the Stavanger 19 sediment's significant separate phase of water hindered the mechanism of cement stabilization in a similar way to the Stavanger 29 sediment. By the same token, the superior strength results of the NY/NJ sediments could be attributed to their more reasonable natural moisture contents and unhindered cement stabilization.

Following the conclusion of the study, additional UC strength tests were performed on the Stavanger sediments to better understand their potential strength gain. Sediment samples were decanted to produce lower moisture contents, then mixed with doses of 20% PC, cured for 28 days, and tested for  $q_u$ . The rating curves shown in Figure 33 present the results of these tests, as well as the previous mixes' strength results, and demonstrate the water and cement contents required for the sediments to reach strength-related performance goals. Water-cement ratio ( $W/C$ ) values were calculated using the mass of cement added in the mixing stage and the amount of water present in the sediment at that time (determined

from the mass of the sample and the measured water content). Presenting the data as UC strength versus  $W/C$  allows for a direct comparison of all samples generated during the study. The curves predict the  $q_u$  performance of various mixtures of sediment with cement and water and fit the typical power equation relationship described by Dr. Masaki Kitazume:  $q_u = a(W/C)^b$  (Kitazume, 2017). Two power relationships were fit using the strength data generated by this study: one for all tested mixtures, including both cement-only and carbon-cement combinations, and one for the Portland cement mixtures only (4%, 8%, 12%, and 20% PC).

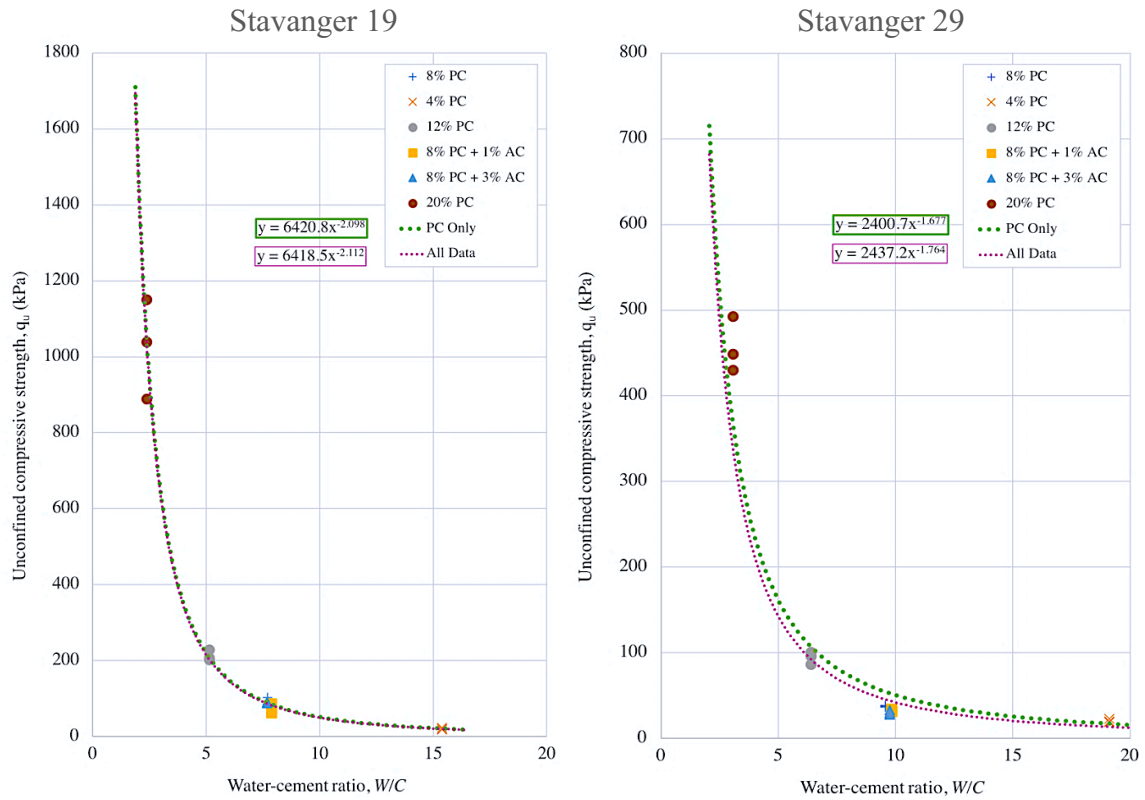


Figure 33. Strength- $W/C$  curves for Stavanger sediments based on 28-day  $q_u$  data

From the curves presented in Figure 33, it is clear that the initial low strength results for the Stavanger sediments were, in fact, due to their very high moisture contents. Changes



such as a reduction in water content or an increase in cement content have the ability to produce the lower  $W/C$  values associated with the sediments' higher strength regions, resulting in more useful unconfined compressive strength values. The Stavanger 19 sediment maintained its higher strength relative to the Stavanger 29 sediment for all  $W/C$  values, presumably due to its coarser grain size and the higher strength (and uniformity of mixing) associated with sandy silts, as opposed to silty clays (Bates & Hills, 2015). As a result, strength values comparable to the NY/NJ sediments (around 200 kPa) could be achieved for the Stavanger 19 sediment with a  $W/C$  value around 5.0, whereas the Stavanger 29 sediment would require a  $W/C$  value around 4.0.

#### Discussion of Leaching Results

The leaching results from this study suggest that powdered activated carbon has the potential to aid in the effectiveness of Portland cement solidification/stabilization to treat uniquely challenging contaminants. It is particularly effective in cases where Portland cement alone is unsuccessful, such as in reducing the leaching potential of certain PAHs and TBT. Several contaminants, including pyrene, naphthalene, phenanthrene, 2-methylnaphthalene, fluorene, fluoranthene, acenaphthene, anthracene, chrysene, and TBT had complete or nearly complete reductions in leaching concentrations even without the addition of Portland cement – doses of 1% and 3% AC were just as effective with and without 8% PC. The leaching concentrations of other PAH compounds, including benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene, were reduced to non-detectable values for doses of 3% AC without PC as well as all of the more aggressive PC and AC-PC mixes (4% PC, 8% PC, 8% PC + 1% AC, 8% PC + 3% AC, and 12% PC). The leaching

behavior of metals with the addition of AC was less conclusive, due in part to the well-documented effectiveness of PC alone in stabilizing metals in S/S applications.

#### Recommendations for Future Work

Additional laboratory testing would be beneficial to confirm whether or not the observations made in this study are consistent for similar sediment types at higher and lower ratios of Portland cement with activated carbon. While this study focused on the 8% binder ratio for PC, industry standard PC doses for SS sediment range from 4% to 12%, all of which could be amended by the addition of AC. In addition, a plethora of emerging contaminants of concern and other environmental pollutants exist that, assuming the appropriate chemical analysis methodologies have been verified, could be assessed using the procedure described in this study. This study focused on metals, PAHs, and tributyltin because they were the categories of contaminants historically present in the sediment at the available sampling locations and pose known threats to human and environmental health. Local discretion should be used when proposing similar studies, to identify the contaminants of interest and evaluate them as necessary.

A value engineering assessment would also be useful to determine the benefit of joint AC-PC treatment on a specific project basis, in addition to more exhaustive bench-scale laboratory assessments to identify the optimized AC-PC mix based on beneficial use performance goals. Overall, large S/S sediment volumes can be beneficially used for a variety of purposes, including as structural fill for port expansions, filling behind bulkheads, the remediation of already contaminated GreenPorts and brownfields, transportation highway projects, and coastal resiliency protection. A promising outlook is demonstrated by projects such as the upgrade of the Port of St Sampsons in Guernsey,

where 25,000 m<sup>3</sup> of sediment with similar characteristics to those evaluated in this study (low organic sand with high TBT concentrations and concern for groundwater leaching) was stabilized using ordinary Portland cement and biochar and utilized during the port's expansion (Bates & Hills, 2015).

Ultimately, the results of this study indicate that AC can be useful in sediment S/S applications, but that the exact ratios of AC and PC required to produce materials with the optimal strength and leaching characteristics will be defined by the sediment type, target contaminants, and beneficial end use. Continued research into the feasibility of joint AC-PC sediment S/S will enhance the understanding of these specifications and enable practical sediment management applications for the betterment of human and environmental health.

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