

EVALUATING NAPHTHALENE SORPTION TO CEMENT-BASED
SOLIDIFICATION/STABILIZATION ADDITIVES

by

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DALHOUSIE UNIVERSITY

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DEDICATION

This work is dedicated to:

My husband, *Jason Green*,

who provided me with unlimited love, support and time.

My son, *Carter Jason Searle Green*,

who helped me prioritize what is truly important.

My parents, *Norma Searle and George Searle*,

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Abstract

Solidification/Stabilization (S/S) is a relatively low cost remedial technology that is increasingly being used with success to remediate sites that contain higher molecular weight organic compounds, leading to a need to research the interaction of organic contaminants with cement-based S/S materials. The objective of this study was to examine the sorption levels of naphthalene, an organic contaminant, to cement-based S/S materials.

Batch testing was performed with several cured, crushed cement-based S/S materials with different amounts of organic carbon present to investigate the sorption of naphthalene. It was found that actual sorption values varied, based on the S/S materials examined, but appear to be dependent on the level of organic carbon present. Dynamic leach test results, based on an abbreviated American Nuclear Society (ANS) 16.1 methodology, are presented for intact cement-based S/S materials to establish naphthalene sorption effectiveness over time. Naphthalene was not detected in the leachate generated during the test. Synthetic Precipitation Leaching Procedure (SPLP) analysis was conducted on the soil-cement mixtures. The resulting naphthalene concentrations in leachate were found to be within current applicable regulatory guidelines.

Contaminant migration modeling was performed to provide examples as to how the information obtained in the study can be used to compare the sorption capacity of cement-based S/S systems in the preliminary design stage. Considering the assumptions adopted, it was shown that well-design cement-based S/S remediation systems can provide reasonable long-term protection against naphthalene contaminant migration.

List of Abbreviations and Symbols Used

ANS: American Nuclear Society

BT: Burnside Till

BTC: Burnside till and cement

BTC-1% HA: Burnside till, cement, and 1% by weight humic acid

BTC-2% HA: Burnside till, cement, and 2% by weight humic acid

BTC-1/3 FA: Burnside till, cement, and 1/3 by weight fly ash

BTC-2/3 FA: Burnside till, cement, and 2/3 by weight fly ash

BTC-2%OC: Burnside till, cement, and 2% by weight organoclay

c: concentration at depth z and time t [ML^{-3}]

C: cement

CCME: Canadian Council of Ministers of the Environment

C_0 : the initial porewater concentration [ML^{-3}]

C_s : the equilibrium concentration of sorbate in the soil pore liquid [ML^{-3}]

C_w : the equilibrium concentration of sorbate in water [ML^{-3}]

C-S-H: Calcium silicate hydrate, or calcium silicate hydrogel

D_e : effective diffusion coefficient [L^2T^{-1}]

f_{oc} : fraction of organic carbon

FA: fly ash

HA: humic acid

i: hydraulic gradient

k: saturated hydraulic conductivity

K: kaolinite

K_d : linear distribution coefficient [M^{-1}L^3]

K_F : the Freundlich constant

K_{oc} : normalized partitioning coefficient with respect to organic carbon content [M^{-1}L^3]

K_{ow} : Octanol-water partitioning

λ : decay constant

MDL: method detection limit

n: the Freundlich exponent

n_e : effective porosity

OC: organoclay

ρ : dry density [ML^{-3}]

PAHs: polycyclic aromatic hydrocarbons

pKa: equal to $-\log_{10} K_a$, where K_a is the acid dissociation constant

R^2 : linear regression coefficient of determination

S: mass of solute removed from solution per unit mass of solute

SK: sand and kaolinite

SKC: sand, kaolinite, and cement

SKC-1% HA: sand, kaolinite, cement, and 1% by weight humic acid

SKC-2% HA: sand, kaolinite, cement, and 2% by weight humic acid

SKC-1/3 FA: sand, kaolinite, cement, and $\frac{1}{3}$ by weight fly ash

SKC-2/3 FA: sand, kaolinite, cement, and $\frac{2}{3}$ by weight fly ash

SKC-2%OC: sand, kaolinite, cement, and 2% by weight organoclay

SPLP: Synthetic Precipitation Leaching Procedure

SPME: solid phase micro extraction

S/S: solidification and stabilization

TCE: trichloroethylene

TCLP: Toxicity Characteristic Leaching Procedure

v : average groundwater velocity [LT^{-1}]

VOC: volatile organic compound

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Chapter 1 - Introduction

1.1 Introduction to Stabilization/Solidification

Solidification/stabilization (S/S) is a widely used treatment method for treatment and disposal of radioactive and hazardous wastes, including contaminated soil. S/S is a source control technology which aims to protect human health and the environment by preventing/reducing the migration of hazardous constituents from treated material. Binders such as lime, fly ash, and bitumen are sometimes used in this process but cement binders are prevalent for the technology (i.e. cement-based S/S). Cement can treat a variety of wastes by improving physical characteristics (solidification) and reducing the toxicity and mobility of contaminants (stabilization) (Batchelor, 2006). Solidification/stabilization is a relatively low cost remedial technology that has been extensively used for decades to treat soil contaminated with metals on contaminated sites. Increasingly it is being used with success to remediate sites that contain higher molecular weight organic compounds (Bates et. al., 2002). This leads to a need to research the interaction of organic contaminants with cement-based S/S materials (Paria and Yuet, 2006).

Shi and Spence (2004) explain that treatment of contaminated soils or hazardous waste via cement-based S/S involves immobilization of contaminants through both physical and chemical interactions with a cement binder (i.e. solidification and stabilization). “Solidification” refers to changes in the physical properties of the contaminated soil; an increase in compressive strength, a change in pore structure that results in a lower permeability, lower diffusivity, and the physical encapsulation of contaminated material in the soil-cement matrix (Batchelor, 2006; Bone et al., 2004). “Stabilization” refers to changes in contaminant mobility, solubility, and/or toxicity (Bone et al., 2004; Shi and Spence, 2004) and usually involves the chemical reaction of contaminated soil with the binder to produce more chemically stable and less hazardous waste forms (Paria and Yuet, 2006). The overall objective of this study was to examine the sorption of an organic compound, naphthalene, to several cement-based S/S materials.

1.2. Background

1.2.1 Cement

Prior to reviewing mechanisms responsible for the treatment of contaminants using cement-based stabilization/solidification, it is useful to understand the process of cement hydration. Cement is an inorganic, hydraulic, cementitious material obtained by grinding cement clinker to a high surface area with a defined amount of gypsum (Skalny and Daugherty, 1972). Portland cement is the most common cement mixture used. It contains predominantly tricalcium and dicalcium silicates, known as alite (Ca_3OSiO_4) and belite (Ca_2SiO_4) respectively, and smaller amounts of tricalcium aluminate ($3\text{CaOAl}_2\text{O}_3$) and calcium aluminoferrite ($\text{Ca}_2(\text{AlFe})_2\text{O}_5$). It is the hydration of the silicate and aluminate compounds with water that drives the cementing action (CAC, 2006). To regulate the rapid setting of the cement, calcium sulphate (CaSO_4) in the form of gypsum is ground and mixed in quantities of 2 to 3% SO_3 or less. The primarily exothermic reaction of cement hydration begins in the presence of water. Tricalcium aluminate and sulfates react almost immediately to form crystalline hydrates. After setting, crystalline calcium hydroxide ($\text{Ca}(\text{OH})_2$) and poorly crystallized calcium silicate hydrate, or C-S-H gel is formed. The cementitious characteristics of portland cement are attributed to the large surface area of the C-S-H gel ($300 \text{ m}^2/\text{g}$). Figure 1-1 shows the four stages of portland cement hydration.

It is the hardening/hydration action of the cement, when combined with contaminated soil that is responsible for the “solidification” in the cement-based S/S treatment technology and chemical interactions between the contaminants and the cement binder that is responsible for the “stabilization”.

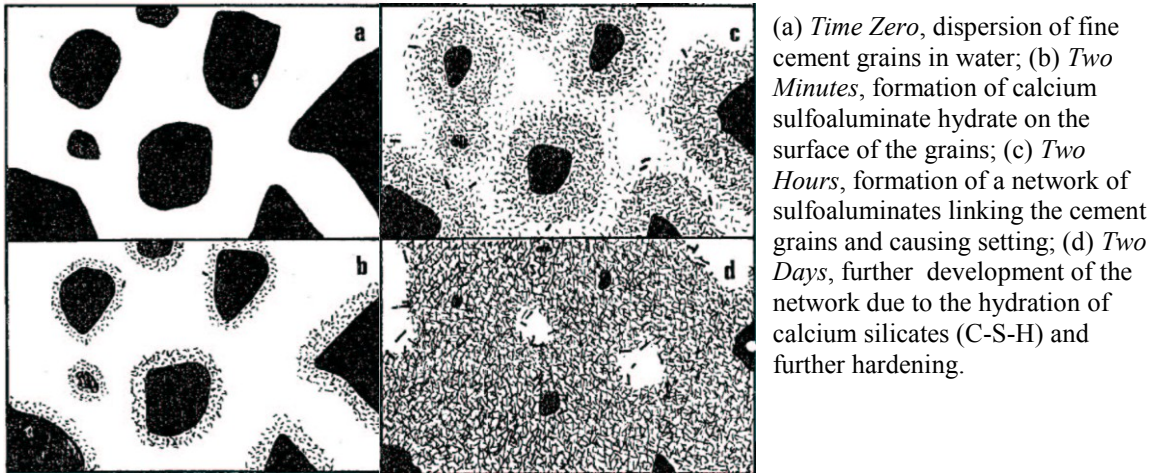


Figure 1-1 Illustration of the four time-periods in the hydration of portland cement (adapted from Skalny and Daugherty, 1972)

1.2.1.1 Solidification

With respect to “solidification”, encapsulation is generally considered to be responsible for successful treatment of waste and contaminated soil via cement-based S/S. Some contaminants are simply physically entrapped within the cement matrix once it has cured, preventing the contaminants from otherwise entering the environment (Sora et. al, 2002). This is especially true of non-polar contaminants that do not interact with the polar surfaces of cement. Organic waste constituents usually do not form the strong chemical bonds within the cement that some inorganics do. Therefore, since they are not chemically bound in the waste, their retention is strongly dependent upon the level of physical entrapment (Karamalidis et. al., 2007). However, as demonstrated by Afshar (2008), this physical entrapment may be combined with small amounts of sorption between the organic matter naturally present in the soil and the contaminant of interest. The level of physical entrapment will depend upon many factors such as the amount of cement added, the native soil being treated and the degree of mixing performed, amongst others. By adding cement, the pore structure within the contaminated soil will ideally be reduced, resulting in lower hydraulic conductivity of the soil/cement matrix as well as

lower diffusivity. The reduction in hydraulic conductivity results in less amounts of groundwater tending to pass through the waste form and also slow contaminant release. Ideally the hydraulic conductivity will be sufficiently low that contaminant transport within the waste form will be primarily by diffusion through the pores. As discussed by Batchelor (2006), a waste form with highly tortuous, unconnected pore structure will have lower hydraulic conductivity, lower diffusivity and hence leach contaminants more slowly. A secondary outcome of the solidification process is an increased strength of the waste form. This increase in strength allows for improved options for land reclamation as well as improved long term integrity. Long-term integrity is important because a waste form that degrades to small sized particles will release contaminants more rapidly. Wet-dry and freeze-thaw cycles can potentially influence this durability (Batchelor, 2006).

It should be noted that hydrated cements change their physical properties over time and wastes treated by cement-based S/S should also be expected to change in similar ways. The wide range of constituents in a waste would be expected to cause more long-term changes than are typically observed for construction materials, which are made with more clearly defined constituents. (Batchelor, 2006)

1.2.1.2 Stabilization

Unlike solidification, stabilization involves chemically altering or “binding” the contaminant present within the waste form or contaminated soil. As discussed by Batchelor (2006), depending on the contaminant and the binder used, there are several different mechanisms that can be responsible for this stabilization process:

1) *Precipitation*: results from high pH conditions of the cement which causes many metal contaminants to form hydroxide or mixed hydroxide solids, 2) *Adsorption*: the pore structure of wastes treated by cement-based S/S also provides substantial amounts of surface area to promote adsorption of contaminants. Adsorption has been shown to be an effective mechanism for a variety of contaminants on different cement minerals, 3) *Absorption*: although there are substantial amounts of surface area in wastes treated by cement-based S/S, the surfaces are often polar and are not as suitable for removal of

organics as solids with more non-polar surfaces. Activated carbon and a variety of other organic sorbents can be added to promote immobilization by absorption, 4) *Oxidation – Reduction*: oxidation–reduction reactions can be important immobilization mechanisms for those contaminants that exist in multiple redox states and have substantially different chemical or toxicological behaviours in the different redox states. Cements generally provide a moderately oxidizing environment. Furthermore, reducing agents, such as ferrous iron can be added to promote reduction of contaminants to promote immobilization.

It is the absorption mechanism that is of interest in this research.

1.2.2 S/S of Organic Contaminants

Throughout the developed world, commercial/industrial sites are impacted with contaminants at levels which trigger remedial activities. Polycyclic aromatic hydrocarbons (PAHs) represent a group of over 100 different chemical compounds of organic contaminants which can be formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat and are a group of chemicals that occur naturally in coal, crude oil and gasoline (ATSDR, 2005). Some PAHs are also manufactured and usually exist as colorless, white, or pale yellow-green solids. PAHs are found in coal tar, crude oil, creosote, and roofing tar, but some are also used in medicines or to make dyes, plastics, and pesticides. The following discussion relates to naphthalene, a specific PAH that the research presented herein focused on.

One reason that naphthalene was chosen for the work in this study is because it is one of the top ranked organic contaminants of concern on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Priority List of Hazardous Substances (ATSDR, 2007). It is also a relatively soluble PAH. Naphthalene is a PAH which at standard temperature and pressure exists as a white solid that evaporates easily. Fuels such as petroleum and coal contain naphthalene. It is also called “white tar” or “tar camphor”, and has been used in mothballs and moth flakes. It has a strong odour, commonly identified with moth balls. The major commercial use of

naphthalene is in the manufacture of polyvinyl chloride (PVC) plastics. Its major consumer use is in moth repellents and toilet deodorant blocks (ATSDR, 2005). From a human health perspective, exposure to naphthalene happens mostly from breathing air contaminated from the burning of wood, tobacco, or fossil fuels, industrial discharges, or moth repellents. Another source of naphthalene exposure is from naphthalene contaminants in the environment (i.e. direct contact with impacted soil or ingestion of impacted groundwater). Exposure to large amounts of naphthalene may damage or destroy red blood cells.

The S/S of soil or waste containing organic contaminants, such as naphthalene, presents more of a challenge, and has a shorter track record than the S/S of inorganic contaminated soils and wastes. Although unsatisfactory results have been achieved with cement alone, considerable progress has been made with the use of additives blended with the cement. A thorough scientific literature review was conducted by the United Kingdom Environmental Agency in 2004 (Bone et al., 2004). This is an excellent review and hence much of the material cited in this section was obtained from reviewing this article.

According to Bone et al. (2004), organic contaminants can interact with cement-based systems via the following mechanisms:

- Adsorption/Absorption
- Volatilization
- Hydrolysis
- Oxidation
- Reduction
- Salt formation

Paria and Yuet (2006) stated that cement-based S/S treatment of organic contaminants can be classified into three categories; (i) direct immobilization of organic contaminants, (ii) immobilization of organic contaminants after adsorption, and (iii) immobilization of organic contaminants using oxidizing and reducing agents. The type of reaction/immobilization will ultimately depend upon the type of organic contaminant

present in the waste form as well as the materials being utilized in the mix design for the S/S material.

Although there are substantial amounts of surface area in wastes treated by cement-based S/S, the surfaces are generally polar and are not as suitable for removal of non-polar organics (Batchelor, 2006). It has been suggested by Trussell and Spence, (1994), Bone et al. (2004) and Batchelor (2006), that organic waste constituents usually do not form the strong chemical bonds within the cement that some inorganic contaminants do and therefore these organic constituents are not chemically bound in the waste and their retention is strongly dependent upon physical entrapment. Compounds that are retained purely by physical mechanisms may leach from the waste form more readily, since their entrainment depends on the physical characteristics of the solid. This situation is exacerbated if the organic contaminant is soluble in water and/or has a low acid dissociation constant (pKa), which suggests that transformation to a water soluble species would occur at the pH of the cementitious system.

Many authors have reported difficulty with cement or lime alone in the treatment of organics contaminants (USEPA, 1993). Karamalidis et al., (2007) also highlighted that the presence of significant levels of organic material can cause retarding of setting or hardening of cement. This is because many organic compounds interfere with the hydration of cement/lime, resulting in retardation of set and a reduction in strength. If organics are admixed with cement, they would affect the cement hydration kinetics by retarding the reactions through the formation of a protective film around the cement grain, hindering the formation of calcium hydroxide, and accelerating the reaction of modification of the C-S-H gel precipitated at very early stages around the cement grains (Botta et al., 2004 and Gussoni, et al., 2004). Karamalidis et al. (2007) restated the Nestle et al. (2001) conclusion that while non-polar organic compounds only lead to a minor delay and qualitatively to the same hydration kinetics compared to the uncontaminated cement mixture, the polar solvents lead to much more pronounced delays in the hydration kinetics. Sora et al. (2002) found that the addition of consistent amounts of a water-methanol-organic contaminant solution to cement pastes retarded the setting and hardening by some days and slowed down the overall process for many weeks.

However, the usual reactions do not seem to be altered, as suggested by the X-ray diffraction analysis on mature samples. The results of the Sora et. al. study confirm the potential requirement of using sorbents to capture organic contaminants, as they are not firmly immobilised in the cement paste.

1.2.2.1 Additives Used in S/S to Improve Sorption of Organic Contaminants

To improve on the “immobilization” of organic contaminants in S/S materials, various materials have been added to waste forms in combination with the binder. Most of these additives (e.g. fly ash, organoclay, activated carbon, zeolites, fly ash, organic polymers) consist of sources of organic matter, either natural or synthetic, that improves the adsorption/absorption interaction with the organic contaminant in the mixture.

(Conner and Hoeffner, 1998, Paria and Yuet, 2006)

Cote et al., (1990) developed a method to differentiate between the physical and chemical components of containment for different contaminants in cement-based waste forms. The method was demonstrated using seven mixtures containing three aromatic organic compounds. Additives evaluated included activated carbon, hydrated lime, silica fume and fly ash. The authors concluded that activated carbon was the best additive for chemical containment, and that silica fume was the best additive for improving the physical containment of the contaminants studied. However, they also concluded that the dosage of activated carbon used in preparing the formulation was unlikely to be cost effective in practice.

Additives such as activated carbon can be used as part of a binder mixture in S/S contaminated material or as a pre-solidification adsorbent, where, the activated carbon is mixed with the contaminated material prior to the addition of binders. Arafat et al. (1999) reported that reactivated carbon was a promising additive, and that the capacity of the virgin and the less expensive reactivated forms of the carbon were comparable. Franz et al. (2000) found that reactivated carbon could also be used in the successful immobilization of naphthalene.

Recognizing that the use of hydraulic binders (e.g. cements) alone is insufficient for the chemical immobilization of PAHs, Mulder et al., (2001) examined the possibility

of utilizing cement-based S/S treatment for a range of PAHs in order to produce a material suitable for use as road-base construction material. Ten PAHs were evaluated in this study, with varying water solubilities, with the two end members being naphthalene (most soluble) and indeno[123-cd]pyrene (least soluble). The authors considered two proprietary additives – a clay modifier and an adsorbent (no details were provided on these materials). The adsorbent was able to bind the PAHs in such a way that the leaching was largely reduced and the product was solidified with a hydraulic binder. The leaching of the lighter (and more water-soluble) PAHs was especially improved in this way.

At a contaminated wood preserving site where naphthalene was a contaminant of concern, several reagents were tested for their naphthalene attenuation effectiveness. The reagents included portland cement, Class C fly ash, Class F fly ash, rice hull ash, powdered activated carbon, calcium oxide, organoclay (Biomin EC-100) and montmorillite (e.g. kitty litter). Various reagent/soil addition levels were made for each reagent system. Only formulations containing powdered activated carbon were effective in attaining naphthalene leachability target through Synthetic Precipitation Leaching Procedure (SPLP) analysis. (Shaw Technology, 2004)

It has been shown that fly ash can be a potentially effective sorbent for organic contaminants in S/S systems. A recent study by Leonard and Stegemann (2010) showed the beneficial effects of fly ash in the leaching performance of S/S mixtures to a wide variety of organic contaminants found in acid tar sludge. Afshar (2008) showed the beneficial effects of fly ash in sorbing several volatile organic compounds (VOCs) in cement-based S/S mixtures. However it was also shown that the presence of cement can potentially decrease the amount of sorption in the fly ash material. The sorption capacities of fly ashes appear to depend significantly on the carbon content of the fly ash. Banerjee et al. (1995) studied the sorptive aspects of fly ash in the context of wastewater treatment and found that the higher carbon content fly ash was shown to have higher adsorption capacity and thus higher removal rates. Mott and Weber (1992) suggest that solute migration through soil-bentonite barriers by molecular diffusion can be significant and that the addition of a sorbent phase such as fly ash to soil-bentonite mixtures can

markedly improve the performance of such barriers with respect to retardation of organic contaminant migration.

The use of absorbent soil materials has shown promise in solidifying organic wastes. These materials can absorb organic wastes and can be successfully incorporated in the structure of binders (Wiles, 1987). The result of this phenomenon is the organics absorbed onto these compounds may be microencapsulated by the binder reducing their leachability. The most promising of these additives have been organoclays. Results demonstrating reduced organic waste leachability from wastes solidified with organoclays have been reported (Faschan, 1992). Organoclays are clays manufactured to possess a high organic matter content and a high potential to absorb nonionic organic compounds. The clays typically consist of bentonite or attapulgite clays treated by exchanging all the cation exchange sites on the clay surface with organic quaternary ammonium compounds. Several authors have stated organoclays may be beneficially used as an additive in the solidification of organic wastes (Faschan, 1993). The success of the organoclays for these utilizations is dependent on their ability to absorb organic compounds.

There are a number of compliance tests used in the S/S industry to evaluate the “success” of S/S mix designs to attenuate contaminants of concern. The SPLP test mentioned above is an overestimate of contaminant migration potential which utilizes a physically altered S/S sample (crushed) and an aggressive leachant (nitric/sulfuric acid). The dynamic leach test developed by the American Nuclear Society (ANS) method 16.1 is more representative of in-situ S/S conditions, using an intact S/S sample and distilled water as a leachant. However, the ANS16.1 is deemed to be a long-term test that occurs over 90 days, which is not long-term when relatively compared to the anticipated design life of S/S treated soil.

1.2.2.2 Literature Review Observations

The literature review presented above has highlighted several issues with respect to treatment of organic contaminants with S/S materials:

- There is a perception that treatment of organics via S/S may not be effective. This is based on scientific rationale related to the “non-interaction” of non-polar organic compounds with polar surfaces found in S/S mixtures. One aspect that was discovered was that there is also a perception that the technology “will” or “will not” work, as opposed to quantifying how effective or non-effective the technology will be. The reason for this is that the performance criterion for the S/S technology always involves a leach test which is associated with a regulatory limit on the leaching observed. Unfortunately, this approach does not quantify the level of sorption of organics to S/S materials nor does it often consider that S/S materials will be intact as opposed to crushed in a Toxicity Characteristic Leaching Procedure (TCLP) or SPLP test.
- There has been little focus on the level of organic matter native to the contaminated soil and its role in the immobilization of organic compounds. More importantly, this level of sorption has not been quantified in detail.
- Many additives have been used in cement-based S/S mixtures and assessed with respect to effectiveness of immobilizing S/S materials but few studies, if any, have examined the role of cement in the interaction with the additive.

1.3 Objectives

The main hypothesis of this research was that naphthalene sorption could be improved in cement-based S/S mixtures using common additives containing organic matter. This hypothesis was evaluated using the following tasks:

- Task 1: To establish the level of sorption of naphthalene, if any, to materials used in cement-based S/S, but without cement, via batch testing (i.e. humic acid, natural soil, fly ash, organoclay).

- Task 2: To establish the level of sorption of naphthalene, if any, to materials used in cement-based S/S, with cement, via batch testing (i.e. humic acid, natural soil, fly ash, organoclay).
- Task 3: To compare the sorption found from batch testing with several different standard leach tests used in practice.
- Task 4: To use the quantitative numbers found in this study to demonstrate potential implications of the work in the context of contaminant migration from cement-based S/S treatments.

1.4 Thesis Organization

Following this introductory chapter, Chapter 2 focuses on the results of the three laboratory tests conducted in support of this research, specifically 1) sorption batch testing of soil cement components and mixtures, 2) dynamic leach testing, and 3) a standard, single-batch agitated extraction compliance test. Chapter 3 contains an exploration of the implications of the results of the laboratory sorption testing through modelled S/S remediation of contaminated site scenarios. Chapter 4 presents the summary, conclusions and recommendations developed from this work.

1.5 Originality of Research

Previous studies have focused primarily on the use of S/S as a remedial technology for inorganic contaminants. Significantly less work has been conducted on the effectiveness of S/S as an organic contaminant remedial solution. Even though organic contaminants have been inadvertently remediated using S/S technology, the process through which organic contaminants are “treated” by S/S has only recently been explored. The current study attempts to quantify the level of sorption of a common organic contaminant, naphthalene, to several cement-based S/S materials and examine the influence of various additives and the cement on this level of sorption.

Chapter 2 – Laboratory Studies

2.1 Introduction

As described in Chapter 1, the objective of this thesis is to examine the ability of different materials to sorb an organic contaminant, naphthalene, when used in cement-based S/S treatments. To carry out this objective, a series of laboratory tests were conducted in support of this research:

- Batch testing experiments – performed to evaluate the level of sorption of naphthalene to soil-cement materials,
- Dynamic leach tests – conducted to determine the extent of naphthalene migration from intact cement-based S/S samples containing various materials utilized in the batch testing experiments (Burnside till, fly ash, organoclay, and cement), over time, and,
- Synthetic Precipitation Leaching Procedure (SPLP) – conducted to determine the extent of naphthalene migration from crushed cement-based S/S samples, simulating a worst case scenario for naphthalene impacted soil treated with S/S.

The intent of this chapter is to provide details on the materials utilized for testing, the procedures used to perform the testing, as well as presentation and discussion of the results obtained.

2.1.1 Materials Utilized

A variety of individual solids were used to represent the various parts of the soil-cement system. Specifically, the solids utilized included:

- Sand and Kaolinite
- Humic Acid
- Cement (Type 10 portland)
- Fly ash (Class F)
- Burnside Till (silt)
- Organoclay (PM-199™)

A LECO induction furnace and Orsat gasometric analyzer at the Minerals Engineering Center, Dalhousie University, were used to determine the organic carbon content of sand, kaolinite, humic acid, cement, fly ash, and Burnside till (silt) as shown in Table 2-1.

Table 2-1 Results of organic carbon analysis in various solids tested in this research study (modified from Afshar, 2008)

	Sand	Kaolinite	Humic Acid	Uncured Type 10 "Portland" Cement	Class "F" Fly Ash	Burnside Till	Organo-clay (PM-199™)
% Organic Carbon	0.031	0.401	39.50	0.27	2.99	0.55	19.8

Silica sand samples obtained from Shaw Resources (Nova Scotia) were blended with kaolinite clay samples obtained from Quality China Clay in Imerys, England to create a "surrogate" soil sample for testing. For blending purposes, the sand and kaolinite materials were mixed at percentages of 75% and 25% by weight, respectively. The reason for creating a 'surrogate' was to compare with a naturally occurring silt material and to provide a measure of laboratory control. Figure 2-1 shows the grain size distribution for the sand kaolinite mixture. The grain size indicates a clayey sand 'soil'.

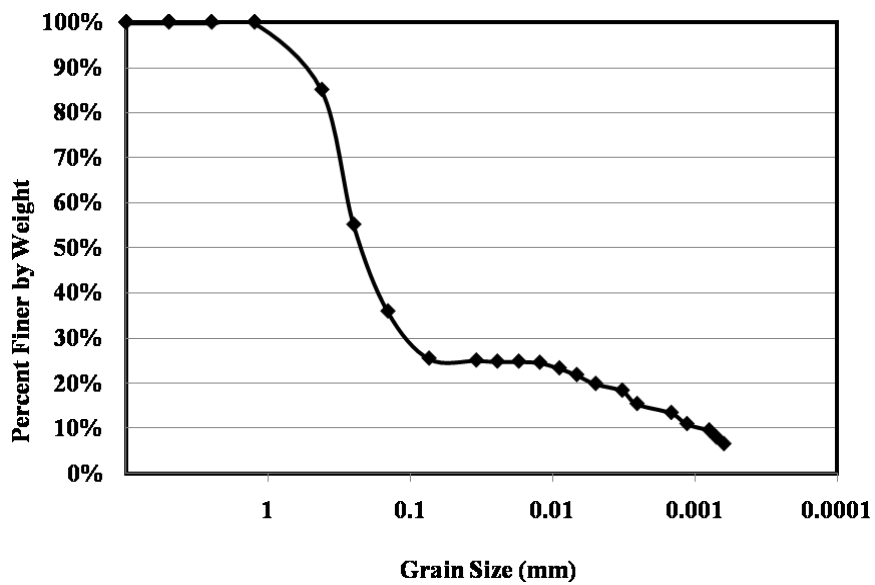


Figure 2-1 Combined grain size distribution curve for the sand and kaolinite mixture (from Afshar, 2008).

Humic acid was added to the sand and kaolinite mixtures in controlled quantities. Humic acid was added in amounts of either 1% or 2% by weight. These values were chosen to be similar to the range of 0.06% to 6.0% soil organic matter found in natural soil (Domenico and Schwartz, 1998). The humic acid used in the laboratory tests was purchased from Sigma Aldrich (Product No. 53680, Fluka). This is the same product used by Afshar (2008).

Burnside till (silty sand with gravel) obtained from a native site location in Dartmouth, Nova Scotia, was used in laboratory testing as a ‘natural’ soil. The Burnside till material sieved at through a 0.075 mm (No. 200 sieve) was utilized for use in the soil cement mixtures. Figure 2-2 shows the grain size distribution for the silt portion of the soil. As stated in Table 2-1, the organic carbon content of the silt fraction of the Burnside till was measured as 0.55%.

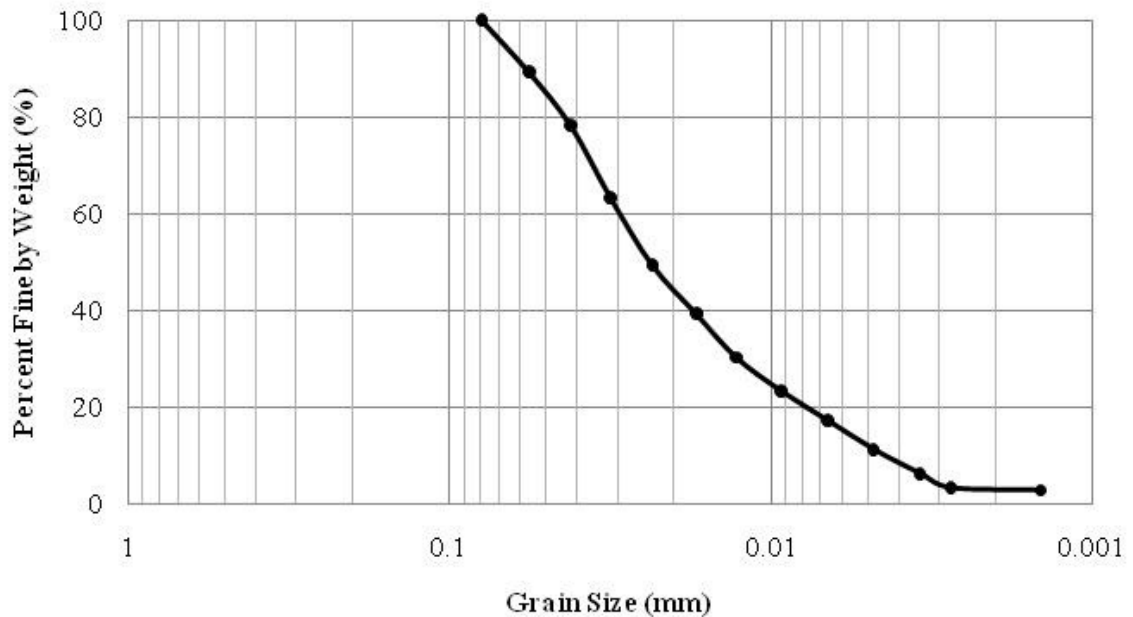


Figure 2-2 Grain size distribution curve for the Burnside Till utilized in this research

Type 10 Portland cement, donated by St. Lawrence Cement, was utilized in all testing performed in this thesis. Cement was used to mix with the surrogate and natural soils. The samples utilizing cement that were tested in this research were added to soil mixtures in grout form (2:1 water to cement ratio).

Fly ash is commonly used in concrete mix designs to improve hydraulic conductivity and freeze-thaw durability (CAC, 2006). Class F Fly Ash (derived from burning coal at a Cape Breton location of Nova Scotia Power) was utilized for all laboratory testing performed in this research. Before utilized for testing, fly ash was sieved through a No. 200 sieve before it was added, in dry form, to cement grout mixtures.

A sample of commercially available organoclay (PM-199™) was obtained from Colloid Environmental Technologies Company (CETCO) for use in testing performed in this thesis. Organoclay is an engineered material synthesized by exchanging a clay mineral's naturally occurring inorganic cations with organic cations, providing improved sorption properties of non-polar organics compared to the original clay (Lake and Rowe, 2005). The contents of the organoclay utilized are proprietary. The organoclay was not physically or chemically altered prior to use in the laboratory testing.

2.2 Soil/Binder Mixtures Utilized for Testing

To address the objectives set out in Chapter 1, various mixtures of the sand/kaolinite soil, humic acid, Burnside till, cement, fly ash and/or organoclay were utilized. Below is a brief description of the various mixtures utilized for testing as well as any unique details associated with any of the mixtures tested. The composition of each mixture, as mass of each solid in grams, is summarized in Table 2-2. It should be noted that these mixtures were cured for 14 days and then pulverized using a ceramic mortar and pestle. All samples were sieved through a 2.00 mm (No. 10 sieve) and oven dried at 50°C prior to testing.

Table 2-2 Summary of the composition of the mixtures prepared and utilized in this research

	Dry Weight (g)						
	Sand	Kaolinite	Humic acid	Cement	Fly ash	Burnside Till	Organo-clay
BT	---	---	---	---	---	3.000	---
FA	---	---	---	---	3.000	---	---
OC	---	---	---	---	---	---	3.000
BT-2%OC	---	---	---	---	---	2.940	0.060
SKC(10%)	2.025	0.675	---	0.300	---	---	---
SKC-1% HA	2.005	0.668	0.027	0.300	---	---	---
SKC-2% HA	1.985	0.662	0.054	0.300	---	---	---
SKC-1/3 FA	2.025	0.675	---	0.200	0.100	---	---
SKC-2/3 FA	2.025	0.675	---	0.100	0.200	---	---
BTC(10%)	---	---	---	0.300	---	2.700	---
BTC-1/3 FA	---	---	---	0.200	0.100	2.700	---
BTC-2/3 FA	---	---	---	0.100	0.200	2.700	---
SKC-2%OC	2.025	0.675	---	0.240	---	---	0.060
BTC-2%OC	---	---	---	0.240	---	2.700	0.060

Notes: Total weight of all mixtures = 3.000 g.
 BT = Burnside Till; FA = fly ash (alone or as $\frac{1}{3}$ or $\frac{2}{3}$ of binder); OC= organoclay (alone or 2% by weight);
 SKC = sand, kaolinite, and cement; HA= humic acid (1% or 2% by weight); BTC = Burnside Till and cement

2.2.1 Mixtures of Kaolinite/Sand Soil and Humic Acid with Cement

The sand/kaolinite was mixed with 10% by weight cement in grout form (2:1 water to cement ratio). These samples are referred to as “SKC(10%)”. To establish the influence of humic acid on sorption, 1% and 2% of humic acid by weight was added to the sand/kaolinite soil and then mixed with 10% by weight cement (2:1 water to cement ratio). These 1% and 2% humic acid samples mixed with cement are referred to as “SKC-1% HA” and “SKC-2% HA”, respectively. Distilled water was added to the sand/kaolinite soil prior to cement addition such that the water content was 13% (the optimum water content for this soil, as determined by a standard proctor test conducted by Afshar, 2008).

2.2.2 Mixtures of Fly Ash and Cement

Fly ash was mixed with cement at dry mass ratios of $\frac{1}{3}$ fly ash and $\frac{2}{3}$ cement (referred to as “SKC-1/3 FA”) and $\frac{2}{3}$ fly ash and $\frac{1}{3}$ cement (referred to as “SKC-2/3 FA”) while the total percentage weight of cement and fly ash were kept at 10% of the total weight of the mixture. The sand/kaolinite surrogate soil moisture content was kept at 13% and cement and fly ash were added as a grout mixture of 2:1 water to cement-fly ash. For comparison purposes, fly ash was tested in isolation (i.e. 100% by weight) and referred to as “FA”.

2.2.3 Mixtures of Burnside Till and Cement

Burnside till was mixed with 10% cement in grout form (2:1 water to cement ratio). These samples are referred to as “BTC(10%)” in this thesis. As stated in Section 2.2, the organic content of the Burnside till was determined to be 0.55% by weight (Minerals Engineering Center, Dalhousie University). For comparison purposes, Burnside till was tested in isolation (i.e. 100% by weight) and referred to as “BT”.

Additionally, batch testing was completed on the Burnside till with varying quantities of fly ash and cement as binders. Like the sand/kaolinite soil, fly ash was mixed with cement at dry mass ratios of $\frac{1}{3}$ fly ash and $\frac{2}{3}$ cement (referred to as “BTC-1/3 FA”) and $\frac{2}{3}$ fly ash and $\frac{1}{3}$ cement (referred to as “BTC-2/3 FA”) while the total percentage weight of cement and fly ash was kept at 10% of the total weight of the mixture.

2.2.4 Mixtures of Organoclay and Cement

Organoclay was mixed with cement at 2% organoclay and 8% cement in soil cement mixtures with both surrogate and natural soils (referred to as “SKC-2%OC” and “BTC-2%OC”, respectively) while the total percentage weight of cement and organoclay were kept at 10% of the total weight of the mixture. Cement and organoclay were added as a grout mixture of 2:1 water to cement-organoclay. For comparison purposes, organoclay was tested in isolation (i.e. 100% by weight) and referred to as “OC”.

2.3 Naphthalene Solutions

Naphthalene is a polycyclic aromatic hydrocarbon with two (2) fused benzene rings, as shown in Figure 2-3. Specific physical and chemical properties of naphthalene are summarized in Table 2-3.

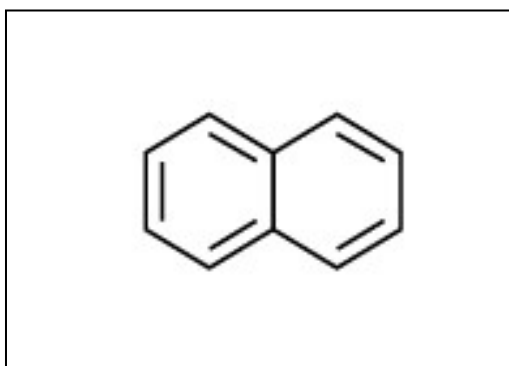


Figure 2-3 Chemical structure of the hydrophobic organic compound naphthalene

Table 2-3 Summary of physical and chemical properties of naphthalene

	MW ¹ (g/mol)	T _b ² (°C)	Log C _{sat} ³ (mol/L)	Log K _{ow} ⁴	Dielectric constant ⁵
Naphthalene	128.2	218	3.6	3.36	2.5 (90)

¹Molecular Weight (Schwarzenbach et al., 2003).

²Normal Boiling Point (Schwarzenbach et al., 2003).

³Solubility (Schwarzenbach et al., 2003).

⁴Octanol-Water partition coefficient (Schwarzenbach et al., 2003).

⁵The number in the parentheses is the temperatures, in °C, at which the dielectric constant was measured (ASI Instrument Inc., 2008)

The low dielectric constant presented in Table 2-3 demonstrates that the non-polar naphthalene is slightly soluble to insoluble (3 mg/100 mL) in polar water (dielectric constant of ~ 80). Temperature, pressure, and presence of other chemicals (inorganic and/or other organic compounds) influence this solubility (Schwarzenbach et al., 2003). Relative to VOCs such as trichloroethylene (TCE), and benzene, naphthalene has a fairly high octanol-water partitioning coefficient (K_{ow}) value.

Batch testing was performed with naphthalene solutions at concentrations less than 1 mg/L to maintain a concentration well within the solubility limits of naphthalene.

2.4 Laboratory Testing Methodologies

2.4.1 Batch Testing Methodology

Batch test procedures were performed similar to that described by Afshar (2008), but will be described here for completeness. Sorption batch tests were performed in 50 mL centrifuge tubes (PYREX[®]) with open-top caps lined with Teflon[®] septa.

Prior to batch tests, all glass centrifuge tubes and caps were thoroughly cleansed with soap and hot water, rinsed with tap water, further rinsed with Milli-Q[®] water, and oven dried at 150°C. Teflon[®] septa were placed in the open top caps and assembled onto the centrifuge tubes after drying. The tubes were then numbered and divided into five groups of two with each group representing duplicate measurements for each naphthalene concentration level of 0.05, 0.1, 0.25, 0.5, and 1.0 mg/L. The concentrations selected for analysis in the batch testing were based on the low solubility of naphthalene as well as non-linear adsorption of naphthalene at higher concentrations, as shown by Winkler et al. (2007).

Three grams (3.000 g) of the various mixtures was weighed and placed in the tubes, and all were then filled with Milli-Q[®] water until the headspace was minimized. The mass at each of these steps was recorded to the nearest 0.0001 g.

To achieve desired initial concentrations in each centrifuge tube, a methanol stock solution containing naphthalene was prepared, and stored at room temperature at least one hour prior to use in an amber 125 mL Boston bottle (Wheaton). Injections were made into the centrifuge tubes using a Hamilton gastight syringe and the centrifuge tubes were then capped. The centrifuge tubes remained closed for the remaining period of the batch tests. The volume and the mass of each injection were recorded for each tube. All water used for cleaning and in the batch tests was obtained from a Milli-Q[®] filter system.

After each centrifuge tube was prepared, the tubes were mechanically agitated for 24±2 hours (at 22 ± 2 °C). Solids and solution were separated using Thermo IEC Centra GP8R centrifuge at 2500 rpm for 30 to 60 minutes. Two 0.8 mL aliquots were taken from each tube and separately placed in 2 mL gas chromatograph auto sampler vials for gas chromatography analysis. The concentrations of solutes in solution were determined

using a 3800 Varian gas chromatograph with a DB-5 column (30 m x 0.25 mm x 1.0 µm). Injections were performed with a Varian 8400 AutoSampler equipped with a solid phase micro extraction (SPME) polydimethylsiloxane (100 µm) fibre. Headspace analyses of the 2 mL auto sampler vials were performed with a fibre adsorption time of analytes for 5 minutes, followed by a desorption time of 1 minute with injector temperature at 220-250°C. The oven temperature programming used for naphthalene had an initial column temperature of 80°C, followed by a temperature ramp to 200°C at a rate of 50°C/min, and a final temperature ramp to 250°C at a rate of 10°C/min which was held for 6 minutes. The compounds were detected using a Flame Ionization Detector (FID) at 280-325°C. Peak integration of the analyses was performed using Varian Star (v. 6.20) software. The method detection limit (MDL) for the was determined to be 0.004 mg/L based on an analytical detection limit guidance published by the Wisconsin Department of Natural Resources (1996).

Quantification of naphthalene was obtained using prior calibration of external standards using the following concentrations: 0.05, 0.1, 0.25, 0.5, and 1.0 mg/L. The amount of the compound sorbed was calculated as the difference between the initial concentration in the centrifuge tubes based on the actual amount of naphthalene-methanol stock solution added to each tube, which was assumed to represent the concentrations at the beginning of the test, and those measured at the end of the test by gas chromatography.

To compare the results obtained from the batch isotherm experiments, the linear form of the Freundlich adsorption isotherm (Schwarzenbach et al., 2003) was used. The isotherm is mathematically described as:

$$S = K_F \cdot C_w^n \quad \text{[Equation 2-1]}$$

Where

S = the total concentration of the sorbate,

C_w = the concentration of sorbate in solution,

K_F = the Freundlich constant,

n = the Freundlich exponent.

The linear form of the isotherm is described when $n=1$ (Schwarzenbach et al., 2003):

$$S = K_d C_w \quad \text{[Equation 2-2]}$$

Where

K_d = the linear distribution coefficient (L^3/M).

2.4.2 Dynamic Leach Test Methodology - ANS16.1

ANS16.1 is a dynamic serial batch test developed by the American Nuclear Society (ANS) where the temporal release of leachable constituents can be inferred by constructing an extraction profile of the data. The following discussion is a summary of the ANS 16.1 methodology as presented by Conner (1990). The test uses a solid monolith of the waste form with a known initial quantity of the contaminant submersed in water. The leachant is completely replaced after specified leaching periods. This allows an estimation of an apparent diffusion coefficient using Fick's Second Law.

Dynamic leach testing was conducted on five (5) S/S mixtures containing Burnside till according to an abbreviated ANS 16.1 test procedure (Connor, 1990). The S/S mixtures subjected to the dynamic leaching testing included:

- Burnside Till + 10% cement
- Burnside Till + 25% cement
- Burnside Till + binder ($1/3$ fly ash, $2/3$ cement)
- Burnside Till + binder ($2/3$ fly ash, $1/3$ cement)
- Burnside Till + cement + 2% organoclay

For consistency, the same S/S mixtures were subjected to SPLP testing as described in Section 2.4.3.

The Burnside till soil cement mixtures were prepared similarly to those prepared for the batch testing, detailed in Section 2.2.3. The specific amounts of materials used in each solidified sample are showed in Table 2-4.

Table 2-4 Summary of the composition (g) of the mixtures prepared and utilized in the dynamic leach testing

	Burnside Till	Cement	Fly Ash	Organoclay	Total Weight
BTC(10%)	90.0	10.0	---	---	100.0
BTC(25%)	75.0	25.0	---	---	100.0
BTC-1/3FA	75.0	16.7	8.3	---	100.0
BTC-2/3FA	75.0	8.3	16.7	---	100.0
BTC-2%OC	75.0	23.0	---	2.0	100.0

To simulate mixing soil with cement, as in a cement-based S/S treatment, the surrogate soil was mixed with cement in grout form (2:1 water to cement ratio). The water added to the soil cement mixture was ‘contaminated’ with 40 µg of dissolved naphthalene added as 20 mL of MilliQ[®] water spiked with 2 mg/L of naphthalene. Duplicate solidified samples of each mixture were made. The soil cement was allowed to cure for 14 days and the solidified sample was then inserted into the dynamic leach testing apparatus. The solidified samples were cylindrical, measuring 3 cm high and 5 cm in diameter.

The apparatus used for the dynamic leach test included a glass jar as the leach test vessel. A 2 mm diameter stainless steel wire was used to form a simple basket which suspended the solidified sample in the leachant solution. After removal of the solidified sample from the curing container and prior to immersion in the leachant solution, the solidified sample was rinsed by immersion in distilled water for 30 seconds. The leach test vessel was also rinsed with distilled water.

The leachant solution consisted of distilled water. As per the ANS 16.1 methodology, the leachant solution was a demineralized water. The solidified sample was suspended in 500 mL of leachant solution such that it was surrounded on all sides. At the end of each leaching interval, the solidified sample was removed from the leachant solution which was poured into a sterile sample container. “Fresh” distilled water was poured into the leach test vessel, and the solidified sample was re-submerged.

Two (2) 0.8 mL aliquot of the leachate from each leaching interval was taken and analysed in the 3800 Varian gas chromatograph as described in Section 2.4.1. The leachate was sampled and completely replaced after cumulative leach times of two (2), seven (7) and 24 hours from the initiation of the test, then at 24-hour intervals for the next four (4) days. One additional sample was obtained 14 days later (19 days after the initiation of the test). Due to time restrictions, the ANS16.1 methodology was abbreviated and the sampling events at 47 and 90 days after test initiation were not completed. The leachate samples were analyzed in duplicate and the results are presented in Section 2.5.2.

2.4.3 Synthetic Precipitation Leaching Procedure (SPLP)

The Synthetic Precipitation Leaching Procedure (SPLP) is a standard, single-batch agitated extraction compliance test that was developed as an alternative to the Toxicity Characteristic Leaching Procedure (TCLP) which uses an aggressive leachant to simulate landfill leachate. The following discussion is a summary of the SPLP methodology (USEPA, 1996) as presented by Spence & Shi (2004). The SPLP specifies a crushed sample (i.e., is capable of passing through a 9.5 mm standard sieve) to minimize physical barriers to mass transport, thereby simulating a worst-case scenario for a S/S monolith. The SPLP uses an acid mix containing sulphuric/nitric acid (60/40 w/w) for an initial leachant pH of 4.2 or 5 at a liquid to solid ratio of 20:1, for 18 hours. The SPLP procedure is useful in those situations where a determination must be made if a potentially contaminated material, left in-situ, will leach toxic substances when degraded due to normal weathering. The concentrations of pollutants in SPLP leachate can be measured and compared to groundwater quality criteria to determine if groundwater contamination is likely. The SPLP methodology is known as Method 1312 and is detailed in the document *Test Methods for Evaluating Solid Waste - Physical/Chemical Methods (SW-846)* (USEPA, 1996).

A set of solidified soil samples with the same properties as those utilized in the dynamic leach testing (i.e. BTC(10%), BTC(25%), BTC-1/3FA, BTC-2/3FA and BTC-2%OC) were submitted to AGAT Laboratories in Dartmouth, Nova Scotia for SPLP

analysis. Table 2-4 in Section 2.4.2 provides the composition of the specific soil cement mixtures.

2.5 Laboratory Testing Results

2.5.1 Batch Testing Results

This section provides results of the batch tests performed. Each individual point shown on the isotherm plots represents the average result of two gas chromatography analyses for one centrifuge tube. To establish the sorption coefficient values, K_d , shown on the graphs, linear regression analyses were performed for the batch test results assuming an intercept through the origin. On each of these isotherms, the linear regression lines are represented as a solid line. For each test performed, the K_d value and R^2 value as obtained from the regression analyses are tabulated in Table 2-5 and discussed in more detail in the following sections.

Table 2-5 K_d and R squared values (R^2) for naphthalene sorption to various solids and mixtures

	K_d (L/kg)	R^2
BT	6.9	0.9
FA	NC	NC
OC	NC	NC
BT-2%OC	109.4	1.0
SKC(10%)	0.4	0.1
SKC-1% HA	3.3	0.9
SKC-2% HA	3.5	1.0
SKC-1/3FA	1.3	0.3
SKC-2/3FA	9.3	0.7
BTC(10%)	1.4	0.7
BTC-1/3FA	4.6	0.9
BTC-2/3FA	5.4	0.8
SKC-2%OC	62.1	1.0
BTC-2%OC	59.2	1.0

NC = not calculated as measured naphthalene concentrations were below the laboratory method detection limit.

2.5.1.1 Soil Materials, Without Cement

2.5.1.1.1 Burnside Till, Fly Ash and Organoclay

The results for naphthalene sorption onto Burnside till, are presented in Figure 2-4. Sorption testing using similar masses of organoclay and fly ash used for the other batch tests (3 g), resulted in concentration of naphthalene below the MDL (<0.004 mg/L) in batch vial solutions. This suggests that sorptive uptake to both fly ash and organoclay is high for naphthalene. This was not unexpected as both materials are known to be excellent sorbents to higher molecular weight organic compounds (Lake and Rowe, 2005).

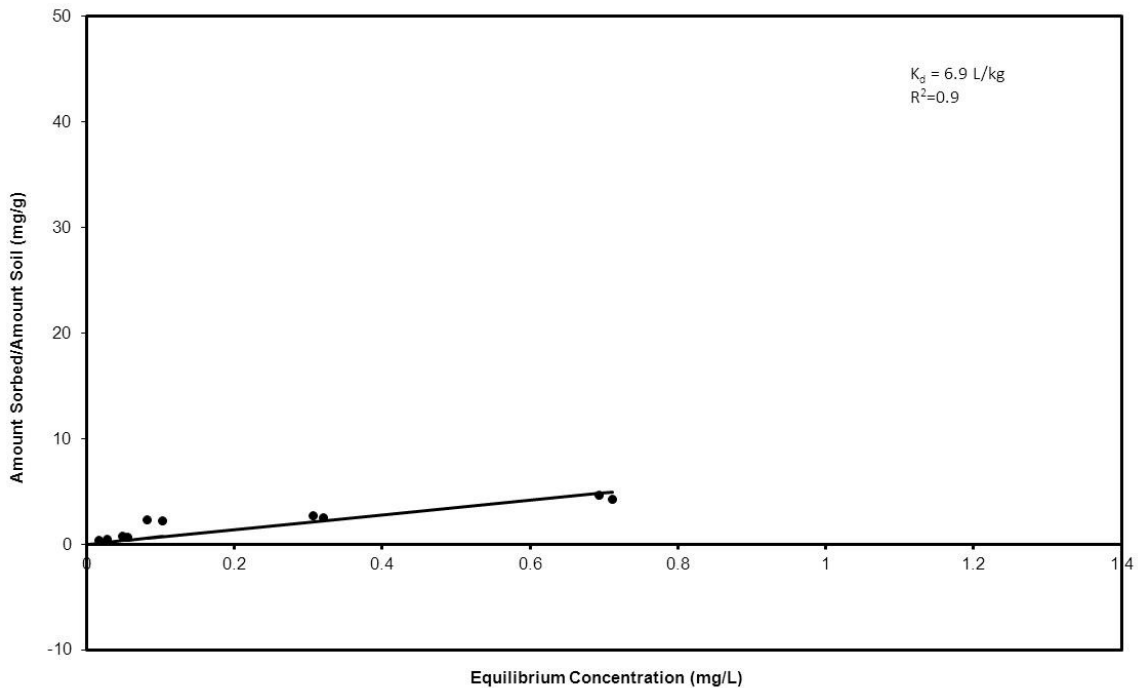


Figure 2-4 Batch test results for naphthalene sorption to Burnside Till

2.5.1.1.2 Burnside Till Mixed with 2% Organoclay

For comparison purposes, the sorption of naphthalene to natural soil (Burnside till) amended with 2% (by weight) organoclay is presented in Figure 2-5. The lower amount of organoclay in the mixture allowed for detectable levels of naphthalene in the

solutions after mixing. When organoclay was tested in isolation, 100% of the naphthalene was absorbed. However with only 2% by weight organoclay was mixed with the Burnside till, 100% naphthalene sorption was not achieved. It is clearly shown in Figure 2-5 that the addition of the small percentage of organoclay improved the sorption capacity of the natural Burnside till soil. It is also noted that the sorption response is linear as denoted by the high R^2 value obtained from the regression analysis.

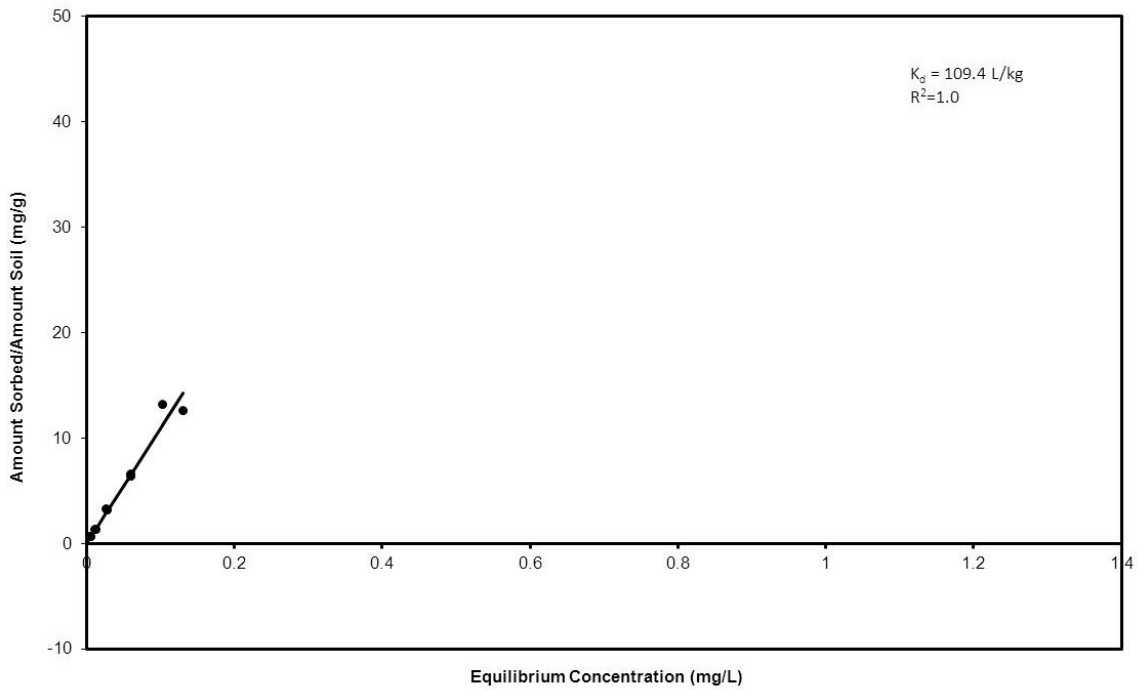


Figure 2-5 Batch test results for naphthalene sorption to Burnside Till + Organoclay (PM-199™)

2.5.1.2 Soil Materials, With Cement

2.5.1.2.1 Mixtures of Cement with Sand, Kaolinite, Humic Acid

As shown in Figure 2-6, sorption to the SKC(10%) mixture was found to be essentially zero. Figure 2-7 shows that the level of naphthalene sorption increases to a K_d of 3.3 L/kg as 1% humic acid was added to the sand kaolinite mixture prior to mixing and curing with cement. The addition of 2% humic acid for the SKC-2%HA samples (see

Figure 2-8) did increase the level of naphthalene sorption marginally. This same observation was observed by Afshar (2008) in similar soil mixtures tested with three different VOCs (i.e. no increase in sorption when twice the amount of humic acid is utilized).

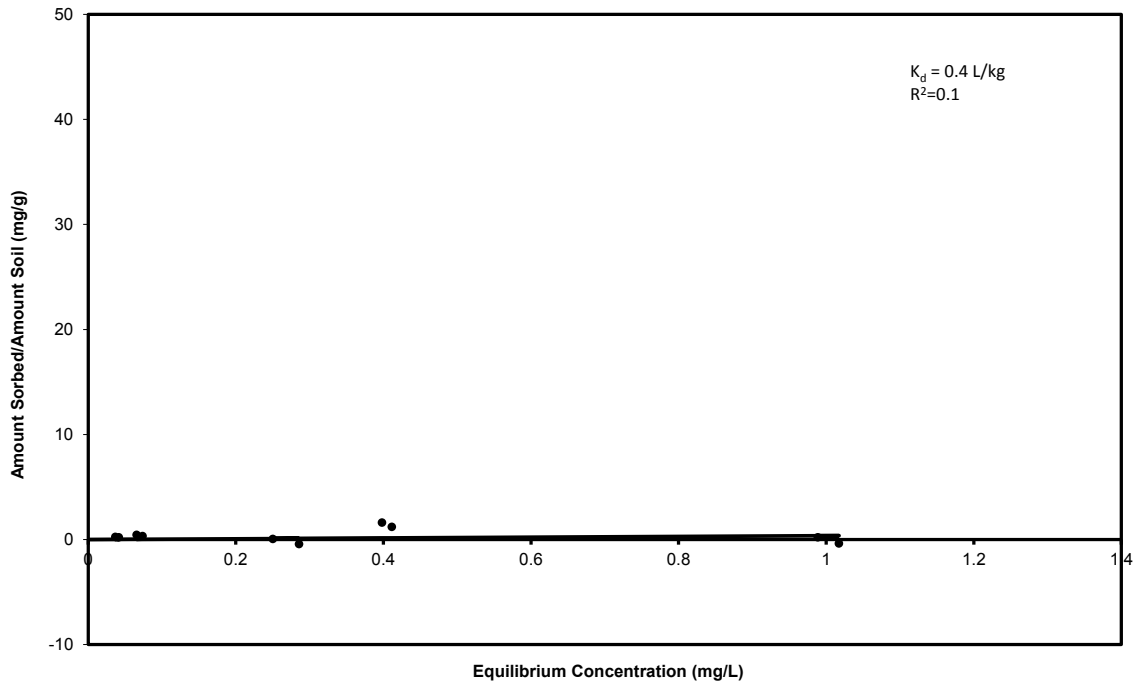


Figure 2-6 Batch test results for naphthalene sorption to SKC(10%) mixture

As expected, due to the very low amounts of organic matter, naphthalene sorption was shown to be significantly lower in SKC(10%) compared to the SKC-1% HA and SKC-2% HA mixtures. This is inherently due to the increased level of organic matter. The marginal increase in K_d observed for twice the amount of organic matter in SKC-2% HA relative to SKC-1% HA is likely due to physical coating of the organic matter in the sample by the cement. Afshar (2008) found that sorption of TCE, benzene and ethylbenzene was also influenced by the presence of cured cement.

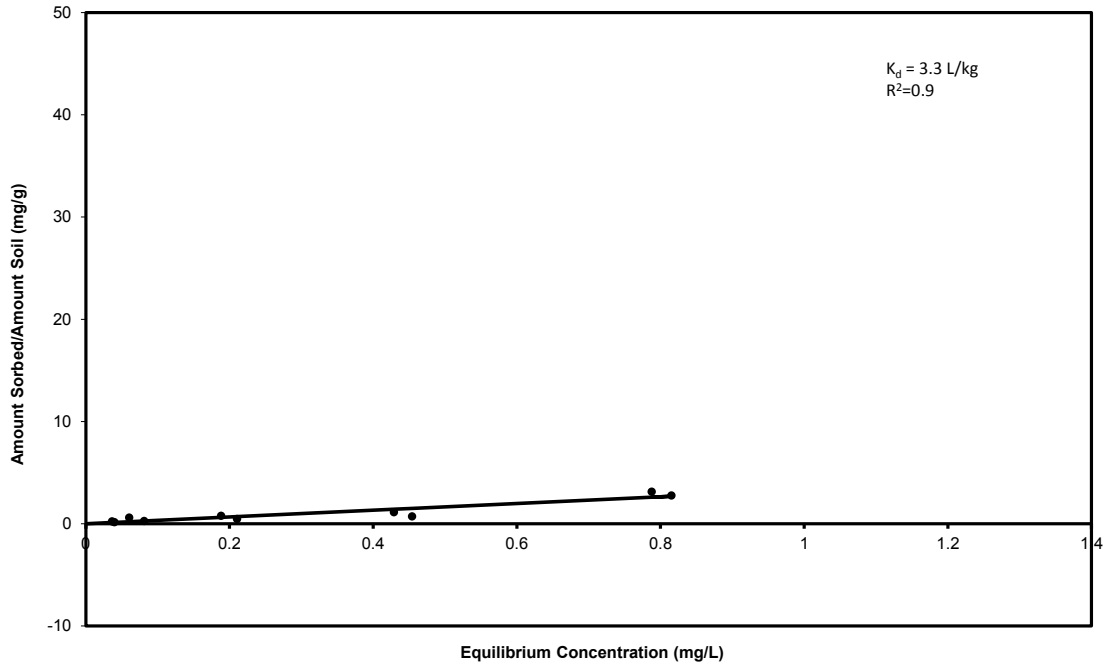


Figure 2-7 Batch test results for naphthalene sorption to SKC-1%HA mixture

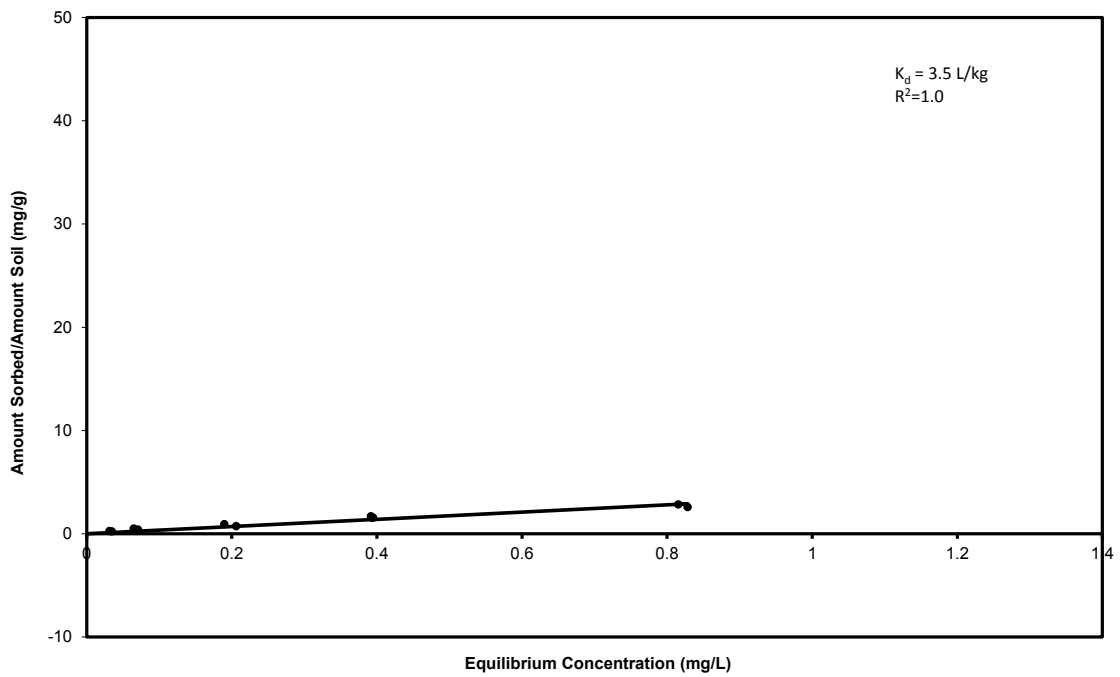


Figure 2-8 Batch test results for naphthalene sorption to SKC-2%HA mixtures

2.5.1.2.2 Mixture of Cement with Fly Ash

The fly ash utilized in this research contributes a 3% organic carbon content to the mixture. As such, this resulted in non-detect naphthalene concentrations in the sorption to fly ash alone. K_d values for cured mixtures of cement and fly ash (i.e. SKC-1/3 FA and SKC-2/3 FA) were measurable and hence reduced from the non-detect values obtained from the unaltered fly ash (FA) sample, as shown in Figures 2-9 and 2-10, respectively. Similar to the SKC-HA results, this is likely due to the coating of sorption surfaces by the cement and changes in the fly ash structure from pozzolanic activity. However it is noted that the sorption afforded by the SKC-2/3 FA mixture is much higher than that of the SKC-1/3FA mixture. It does appear that at these fly ash contents, sorption is non-linear (as indicated by the lower R^2 values) and hence simple comparisons with K_d values may not be adequate. Non-linear curve-fitting could be used to attempt to compare this set of results.

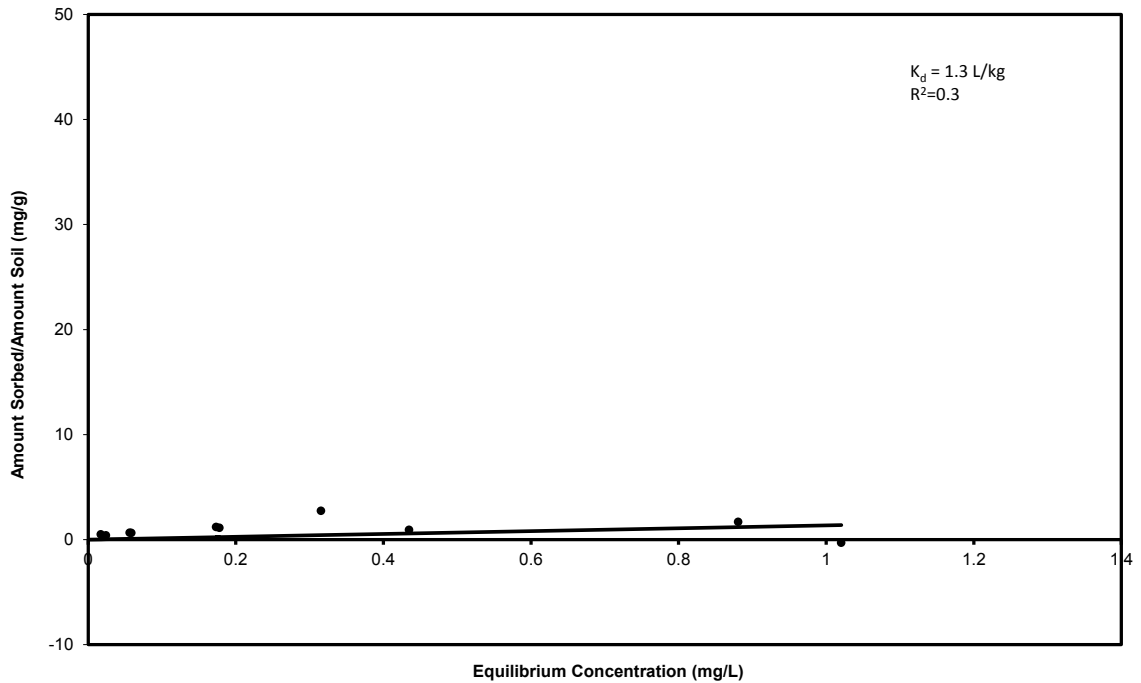


Figure 2-9 Batch test results for naphthalene sorption to SKC-1/3 FA mixtures

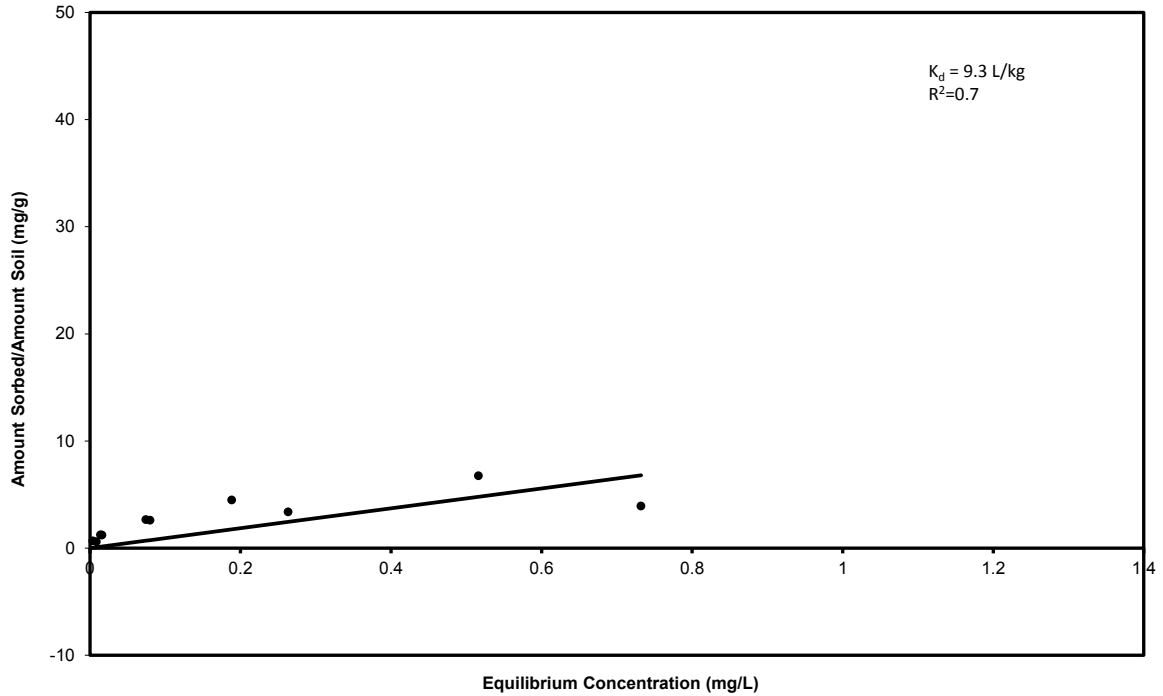


Figure 2-10 Batch test results for naphthalene sorption to SKC-2/3 FA mixtures

2.5.1.2.3 Mixtures of Cement with Burnside Till

Similar to the SKC(10%) results, naphthalene showed somewhat lower sorption to BTC(10%) relative to the Burnside till alone. This is most likely due to the cement making the sorption sites inaccessible for naphthalene partitioning onto the soil organic matter. As shown in Figures 2-11, 2-12, and 2-13, the replacement of portions of the cement with fly ash significantly increased the sorption of naphthalene to the mixture. Also of note is the higher sorption of the naphthalene at the 1/3 fly ash content (BTC-1/3FA) compared to SKC-1/3FA. Given the higher organic carbon content of the Burnside till relative to the sand/kaolinite mixture, it is likely that this is responsible for the higher sorption relative to SKC-1/3FA.

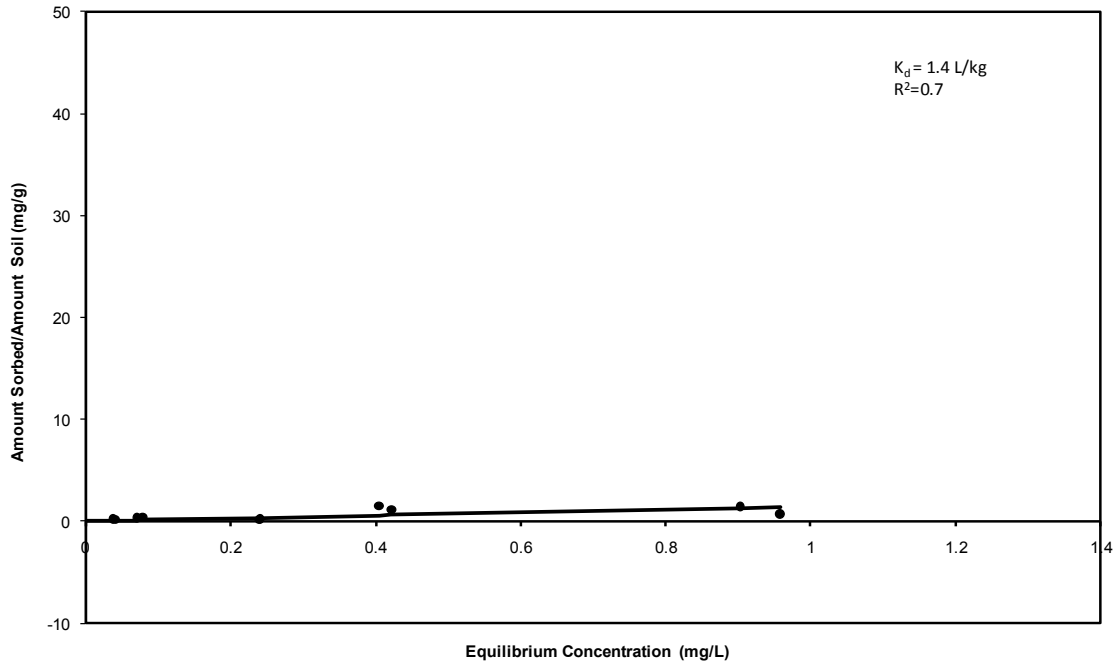


Figure 2-11 Batch test results for naphthalene sorption to BTC(10%) mixtures

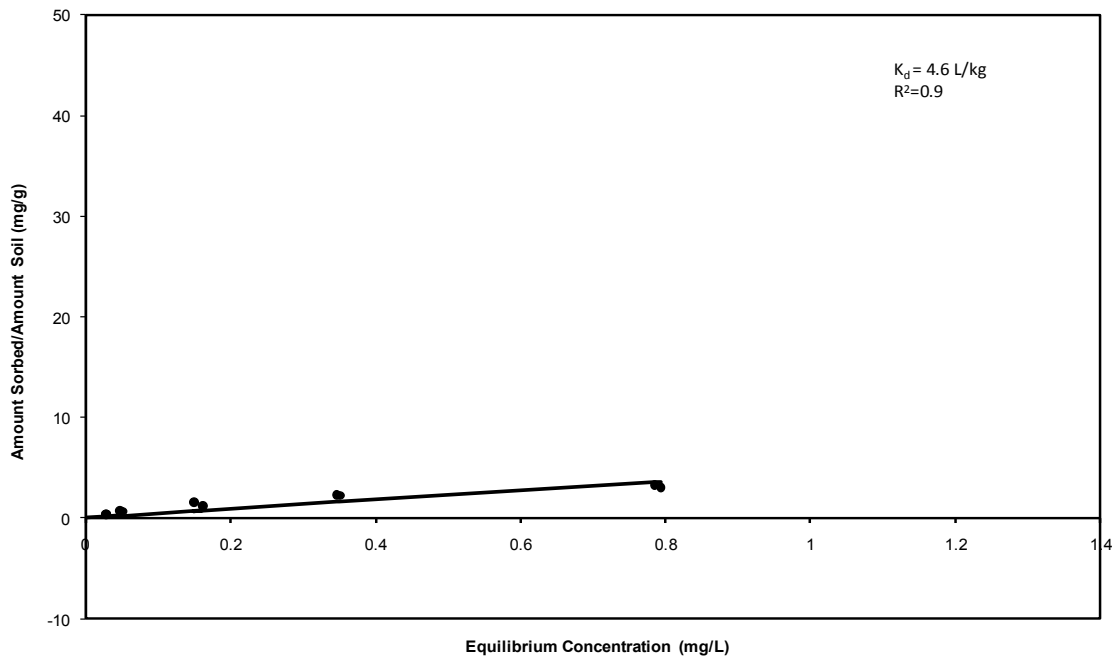


Figure 2-12 Batch test results for naphthalene sorption to BTC-1/3 FA mixtures

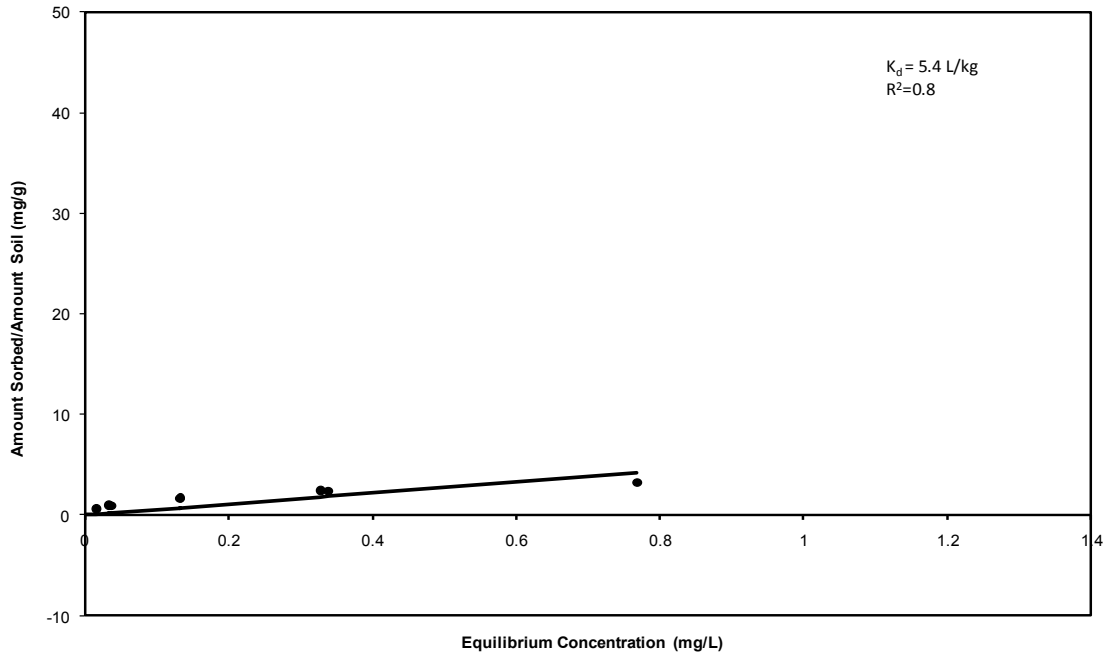


Figure 2-13 Batch test results for naphthalene sorption to BTC-2/3 FA mixtures

2.5.1.2.4 Mixtures of Cement with Organoclay

In soil cement mixtures amended with organoclay, naphthalene showed a high sorption to all mixtures as demonstrated by Figures 2-14 and 2-15. Comparing the SKC-2%OC and BTC-2%OC mixtures, naphthalene showed very similar sorption to both soil cement mixtures.

Similar to soil cement mixtures containing fly ash, K_d values for cured mixtures of cement and organoclay (i.e. SKC-2%OC and BTC-2%OC) were observed to be significantly reduced when compared to organoclay alone or the Burnside till amended with organoclay. This is most likely due to the coating of sorption surfaces by the cement and changes in the fly ash structure from pozzolanic activity.

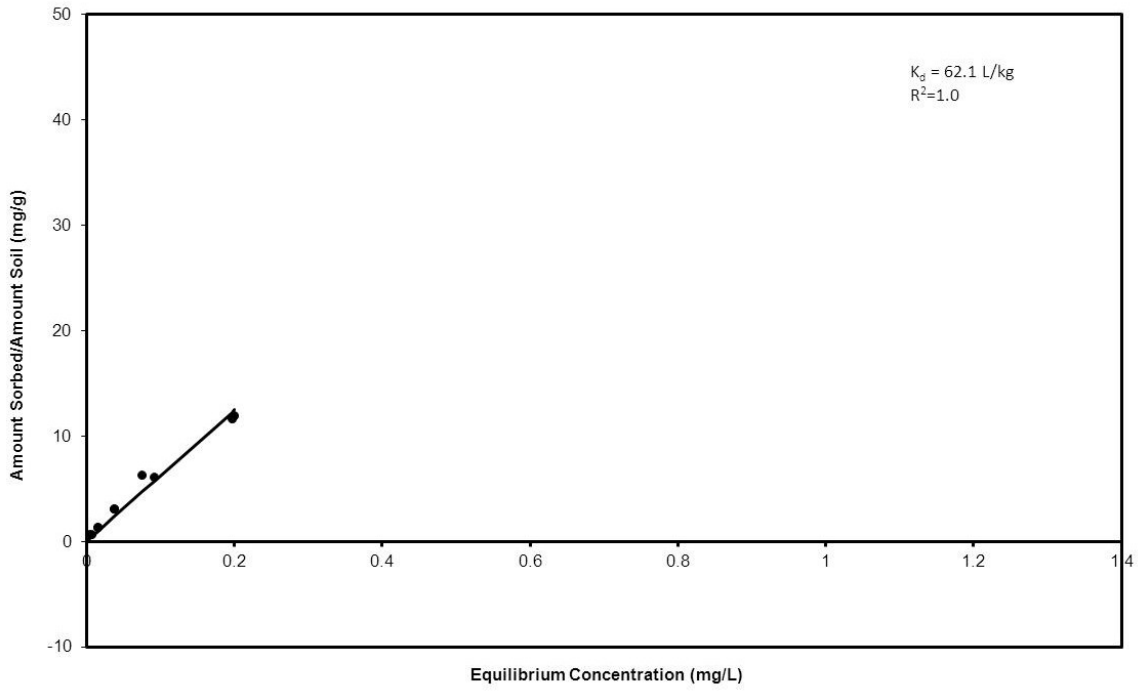


Figure 2-14 Batch test results for naphthalene sorption to SKC-2%OC mixtures

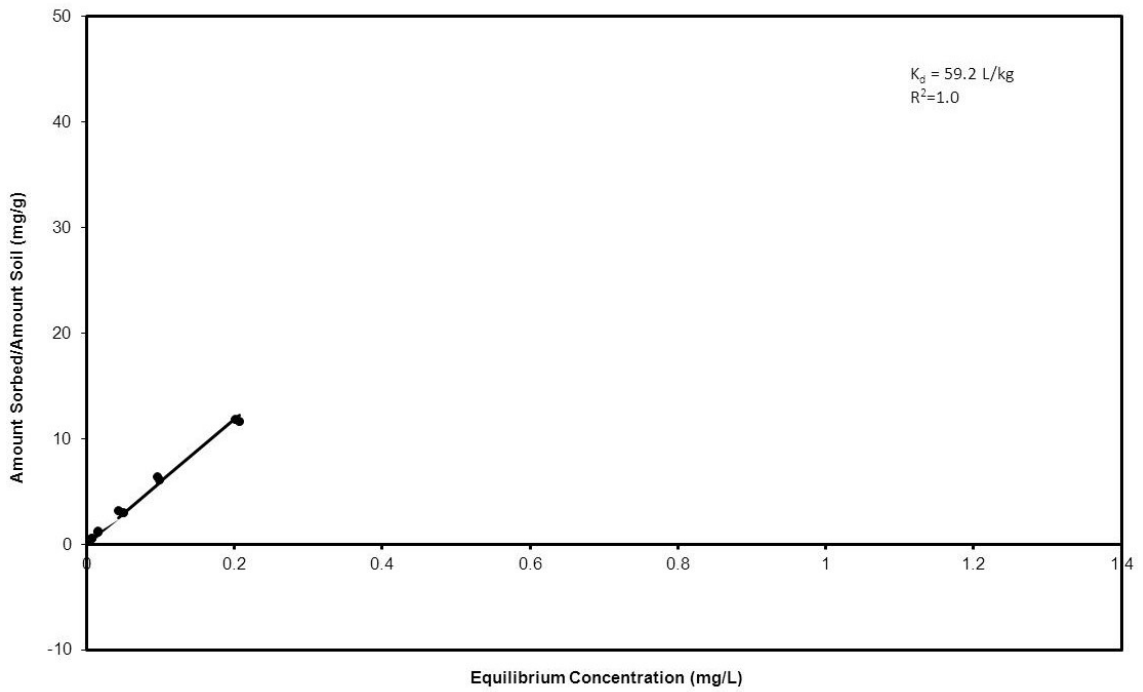


Figure 2-15 Batch test results for naphthalene sorption to BTC-2%OC mixtures

2.5.2 Dynamic Leach Test Results

The results of the abbreviated Dynamic Leaching Testing are displayed in Table 2-6.

Table 2-6 Summary of dynamic leach testing results (mg/L)

Leach Period	BTC(10%)	BTC(25%)	BTC-1/3 FA	BTC-2/3 FA	BTC+2%OC
2 hours	<0.004	<0.004	<0.004	---	<0.004
7 hours	<0.004	<0.004	<0.004	---	<0.004
24 hours (1 day)	<0.004	<0.004	<0.004	---	<0.004
48 hours (2 days)	<0.004	<0.004	<0.004	---	<0.004
72 hours (3 days)	<0.004	<0.004	<0.004	---	<0.004
96 hours (4 days)	<0.004	<0.004	<0.004	---	<0.004
120 hours (5 days)	<0.004	<0.004	<0.004	---	<0.004
14 days	<0.004	<0.004	<0.004	<0.004 ¹	<0.004

Note: '---' solidified sample could not be removed intact from leaching test vessel.

¹Leachant sample collected and analyzed after 5+14 days.

Based on the analytical results of the abbreviated ANS 16.1 testing, the cumulative fraction of the naphthalene released during the test is not calculable during the time periods tested.

2.5.3 SPLP Results

Naphthalene was detected in all five (5) SPLP analysis as outlined in Table 2-7. The results for all five soil-cement mixtures showed a naphthalene leachate concentration of less than 1 µg/L.

Table 2-7 Summary of SPLP results

	Naphthalene Leachate (µg/L)
BTC(10%)	0.54
BTC(25%)	0.27
BTC-1/3FA	0.45
BTC-2/3FA	0.06
BTC+2%OC	0.73

The solidified sample with 25% cement generated a lower concentration of naphthalene in leachate than the solidified sample with 10% cement, which was unexpected since a higher cement content will facilitate greater micro-encapsulation. Since fly ash was added prior to cement curing, the sorption capacity of the greater amount of fly ash ($\frac{2}{3}$ versus $\frac{1}{3}$) is evident in the significantly lower naphthalene concentration in leachate. It is notable that the soil cement mixture containing $\frac{1}{3}$ fly ash had a comparable sorption capacity to the soil treated with cement only. Somewhat surprisingly, the greatest naphthalene leachate concentration was derived from the soil-cement sample containing the 2% organoclay. This is contrary to the results from the batch testing as discussed in Section 2.5.1.2. It is possible that the mixture of sulfuric and nitric acids used to digest the sample could consume part of the organoclay, causing a release of the naphthalene sorbed to it.

2.5.4 Discussion of Results

From the batch tests performed, it was generally observed that the level of organic carbon had a significant effect on the performance of the contaminant to the solids tested. Figure 2-16 summarize the K_d sorption values for all soil components and mixtures calculated from all the batch tests performed.

Comparing all the batch test results, it is clear that organoclay and fly ash contribute the most significantly to the capacity of soil cement mixtures to sorb naphthalene.

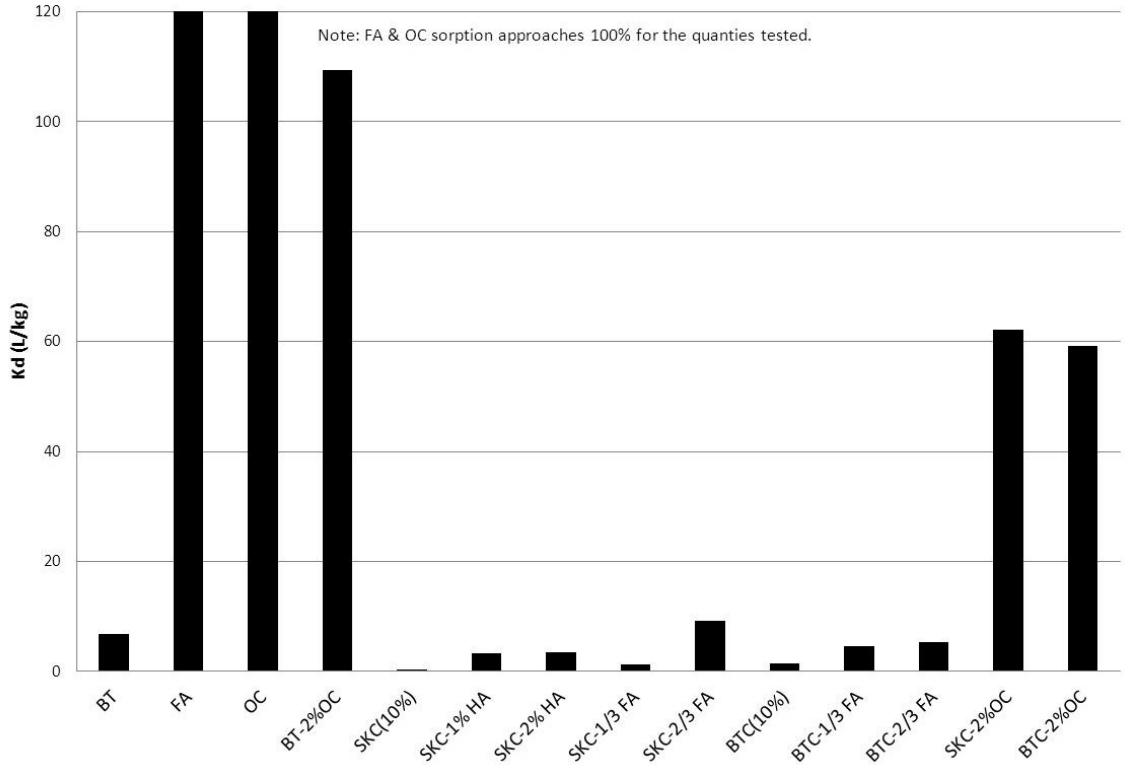


Figure 2-16 K_d values for naphthalene sorption to various solids and mixtures

A compound's K_d value can be normalized with respect to the fraction of organic matter (f_{oc}) in the soil, i.e. the mass of organic carbon per total mass of sorbent, to produce what is called the organic carbon-water partition coefficient, K_{oc} (Karickhoff et al., 1979; Schwarzenbach et al., 2003):

$$K_{oc} = \frac{K_d}{f_{oc}} \quad \text{[Equation 2-3]}$$

This normalization allows comparison of each sorbent used in terms of its relative “efficiency” of naphthalene sorption. K_d values obtained from each of the batch tests were normalized with respect to the fraction of organic carbon to yield K_{oc} values shown in Table 2-8. For comparison, the empirical log K_{oc} value for naphthalene derived for natural soil organic matter is 3.15, as estimated from Karickhoff et al (1979).

Table 2-8 Log K_{oc} values for the mixture and contaminants tested in batch tests in this study

Soil Cement Components & Mixtures	f_{oc}	Log K_{oc}	Soil Cement Components & Mixtures	f_{oc}	Log K_{oc}
BT	0.00550	3.098	SKC-1/3 FA	0.00229	2.754
FA	0.02990	NC	SKC-2/3 FA	0.00319	3.464
OC	0.198	NC	BTC(10%)	0.00522	2.428
BT-2%OC	0.00935	4.068	BTC-1/3 FA	0.00613	2.876
SKC(10%)	0.00138	2.462	BTC-2/3 FA	0.00703	2.885
SKC-1% HA	0.00492	2.826	SKC-2%OC	0.00529	4.070
SKC-2% HA	0.00847	2.616	BTC-2%OC	0.00913	3.812

NC = not calculated a measured naphthalene concentrations were below the laboratory method detection limit.

The log K_{oc} values for naphthalene obtained from the batch test data generated in this study were found to be similar to the log K_{oc} calculated from Karickhoff et. al. (1979). Karickhoff et al. (1979) developed empirical correlations to predict K_{oc} values for a particular organic compound (for soil with natural organic matter) based on the octanol–water partition coefficient, K_{ow} :

$$\log K_{oc} = \log K_{ow} - 1.21 \quad \text{[Equation 2-4]}$$

The advantage of simple, though approximate, relationships such as Equation 2-4 is that the K_d value of an organic contaminant with soil organic matter can be estimated by using published values of K_{ow} and measured values of f_{oc} .

The experimental log K_{oc} values were generally higher than the calculated log K_{oc} of 3.15 for both of the individual soil-cement additives, i.e. fly ash and organoclay. The experimental log K_{oc} values are generally lower than the log K_{oc} of 3.15 for all of the soil cement mixtures with the exception of the SKC-2/3FA and those containing organoclay. This reduced sorption may be due to interactions (physical and/or chemical) between the cement and the organic matter. Since the batch tests were performed by adding contaminant to cured cement, the presence of the cured cement appears to be influencing the sorption efficiency of the soil-cement mixture. Organoclay mixtures, with and without cement, showed higher sorption efficiency relative to the natural soil as calculated by Karickhoff et. al. (1979).

2.5.4.1 Regulatory Framework

There are several environmental guidelines in effect in Canada with respect to naphthalene in various media. Table 2-10 lists the most common guidelines applied when dealing with contaminated sites.

Table 2-9 Canadian Environmental Quality Guidelines for naphthalene

Media	Guideline (units)	Protective of:
Water (Fresh) ¹	1.1 µg/L	Freshwater aquatic life
Water (Marine) ¹	1.4 µg/L	Marine aquatic life
Sediment ¹	34.6 µg/kg (interim sediment quality guideline) 391 µg/kg (probable effects level)	Freshwater & marine aquatic life
Soil ¹	0.1 mg/kg 0.6 mg/kg 22 mg/kg	Agricultural land use Residential/parkland Land use Commercial/industrial land use
Soil/Solid Waste ²	10 mg/kg individual PAHs (Naphthalene) 50 mg/kg total PAHs	Landfill leachate generation.
Water (Leachate) ²	0.01 mg/L based on TCLP analysis	Landfill leachate generation.

¹(CCME, 2010)

²(NSDE, 1994)

The results from the dynamic leach test (ANS 16.1) were below the MDL, which is elevated above the freshwater aquatic life guidelines. The SPLP analysis of Burnside till based soil cement samples indicated a leachate concentration of less than 1 µg/L from all five (5) soil-cement mixtures analyzed, as shown in Table 2-7, in Section 2.5.3. Conservatively comparing these concentrations to the CCME freshwater aquatic life guidelines for surface water (assuming a complete pathway of groundwater discharge to surface water) show that the naphthalene concentrations leaching from S/S treated material would be acceptable based on this regulatory standard.

Although there is no current guideline for the leachate generation potential of S/S treated material in Nova Scotia, a project-specific guideline has been developed for the Sydney Tar Ponds remediation project being conducted in Sydney, NS using cement-

based S/S remedial technology. The compliance objective set for the project for naphthalene is 50 mg/L (adopted from MCP, 2010) based on a modified SPLP analysis. Although it is noted that the compliance objective is greater than the solubility of naphthalene in water, the results of the SPLP analysis conducted on the soil cement mixtures containing Burnside till demonstrated that all five (5) of the soil cement mixtures would be considered acceptable as a remedial technology under this project-specific compliance criterion.

3.1.1 Assumptions Adopted for Examples

Below are the assumptions used for the examples in this chapter unless indicated otherwise:

- The potential for contaminant migration is only lateral (i.e. one dimensional) and hence the depth of the contaminated soil is considered infinite for modeling purposes.
- The contaminated site consists of a sandy silt material with a hydraulic conductivity, k , of 1×10^{-4} cm/s and a 1% gradient, i , horizontally. It is assumed this gradient remains constant for all examples, for comparison purposes. The groundwater flow direction is as shown in Figure 3-1.
- A cross-section of the site is shown in Figure 3-1. There is approximately 2 m of uncontaminated soil (sandy silt; 1×10^{-4} cm/s) separating the contaminated soil from the property boundary with a minimal naphthalene sorption capacity of 0.1 L/kg, based on the sorption derived by Afshar (2008) for simulated soil comprised of sand and kaolinite (SK). The soil is considered saturated for comparison purposes.
- The site is contaminated with dissolved naphthalene porewater concentrations of 1 mg/L. It is assumed the source of contamination is constant and that the properties of the soil beyond the property line (i.e. to the right in Figure 3-1) are infinite in extent. The initial pore water concentration of 1 mg/L is assumed to also be present in the porewater after cement-based S/S treatment. It is assumed in the modeling that there is no degradation or transformation of contaminants.
- The service life of the cement-based S/S is at least 500 years.

The contaminant migration modeling parameters used in this chapter are as provided in Table 3-1.

3.1.2 Modelled Examples

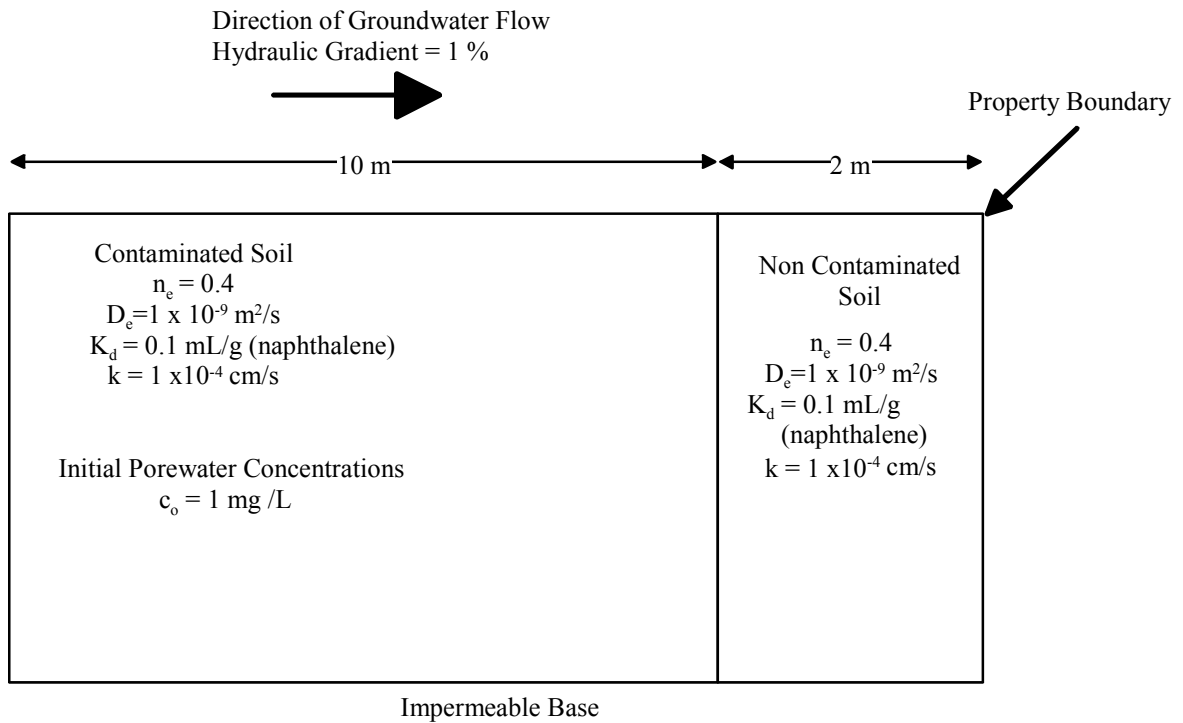


Figure 3-1 Cross-section of hypothetical contaminated site used in the modeling exercises (Case 1)

Example 1: The contaminated site shown on Figure 3-1 is being considered for a cement-based S/S treatment approach (Figure 3-2). The naphthalene sorption values were set at 0.1 L/kg for the untreated soil after Afshar’s (2008) results for SK, and 9.3 L/kg from the results for SKC-2/3FA representing “moderate” sorption from a S/S treated soil, as presented in Chapter 2. A K_d value of 0.1 mL/g was also used for the uncontaminated soil. Diffusion coefficients and porosities for the cement-based S/S material were estimated from Goreham et al. (2010).

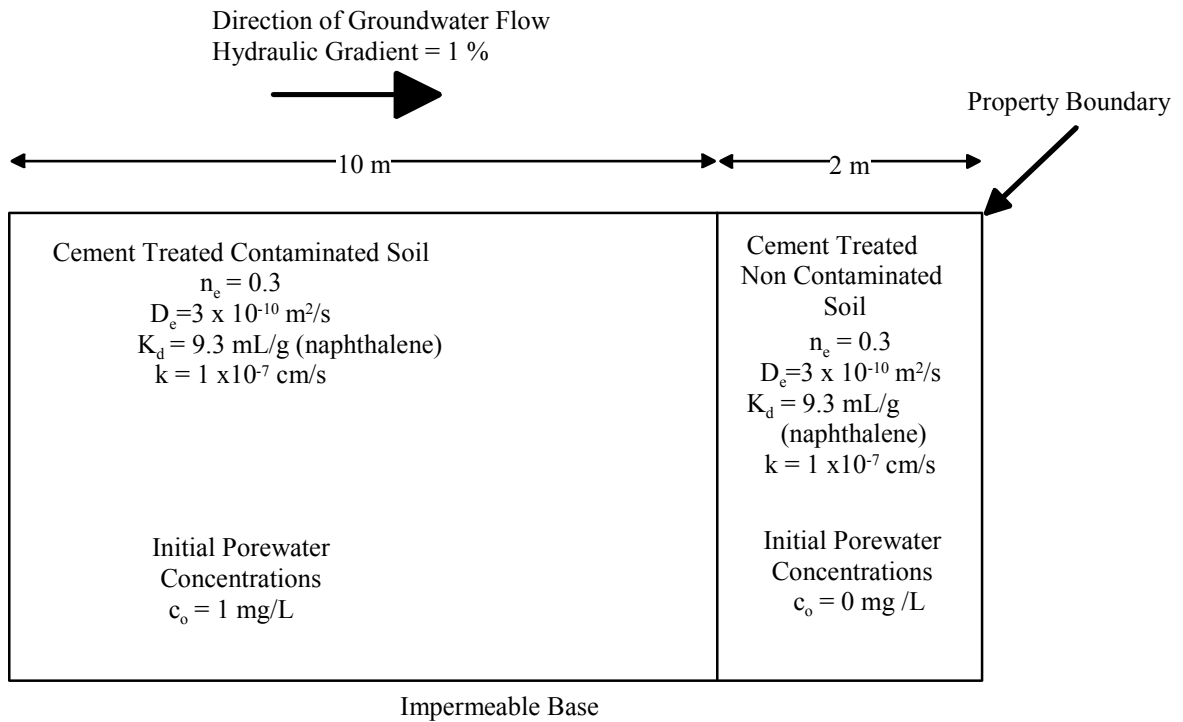


Figure 3-2 Hypothetical contaminated site used for Example 1, with cement-based S/S treatment (Case 2).

Table 3-1 Summary of parameters used in Example 1

	Case 1 No Treatment	Case 2 Cement Based S/S Treatment
Contaminated Soil		
Thickness	10 m	10 m (treated with cement)
Hydraulic Conductivity	$1 \times 10^{-4} \text{ cm/s}$	$1 \times 10^{-7} \text{ cm/s}$ (treated with cement)
Effective Porosity, n_e	0.4	0.3 (treated with cement)
Sorption Coefficient, K_d	0.1 L/kg	9.3 L/kg (SKC-2/3FA)
Effective Diffusion Coefficient, D_e	$1 \times 10^{-9} \text{ m}^2/\text{s}$	$3 \times 10^{-10} \text{ m}^2/\text{s}$ (treated with cement)
Initial Porewater Concentration	1 mg/L	1 mg/L
Uncontaminated Soil		
Thickness	2 m	2 m (treated with cement)
Hydraulic Conductivity	$1 \times 10^{-4} \text{ cm/s}$	$1 \times 10^{-7} \text{ cm/s}$ (treated with cement)
Effective Porosity, n_e	0.4	0.3 (treated with cement)
Sorption Coefficient, K_d	0.1 L/kg	9.3 L/kg (SKC-2/3FA)
Effective Diffusion Coefficient, D_e	$1 \times 10^{-9} \text{ m}^2/\text{s}$	$3 \times 10^{-10} \text{ m}^2/\text{s}$ (treated with cement)
Initial Porewater Concentration	0 mg/L	0 mg/L

The results obtained from contaminant migration modeling of Example 1 for naphthalene are shown in Figure 3-3. The results are shown for porewater concentrations immediately adjacent to the property boundary (i.e. 0.1 m to the right of the property boundary shown on Figure 3-1). The plot shows the development of naphthalene concentration at this location over a period of 500 years for Cases 1 and 2. For example, in Case 1, where no remedial action is taken, the naphthalene concentrations develop adjacent to the property boundary at a time within 1 year, approaching 100% of initial porewater concentrations (1 mg/L) at approximately 10 years. Since it is assumed there is a constant source concentration for the contaminated site, the concentration remains at 1 mg/L, from 10 to 500 years. This would be considered an unacceptable option in most jurisdictions.

For Case 2 (cement-based S/S treatment), a significantly different result is obtained. The naphthalene concentrations at the adjacent site are only 0.0001% of initial source concentrations (i.e. 0.000001 mg/L) at 500 years based on 2 m clean soil next to S/S. This improved performance is due to slow, diffusion-controlled movement of naphthalene from the cement-based S/S treated mass, to the adjacent site, as well as due to a lowering of the hydraulic conductivity of the treated contaminated soil and addition of fly ash into the mixture (i.e. higher sorption).

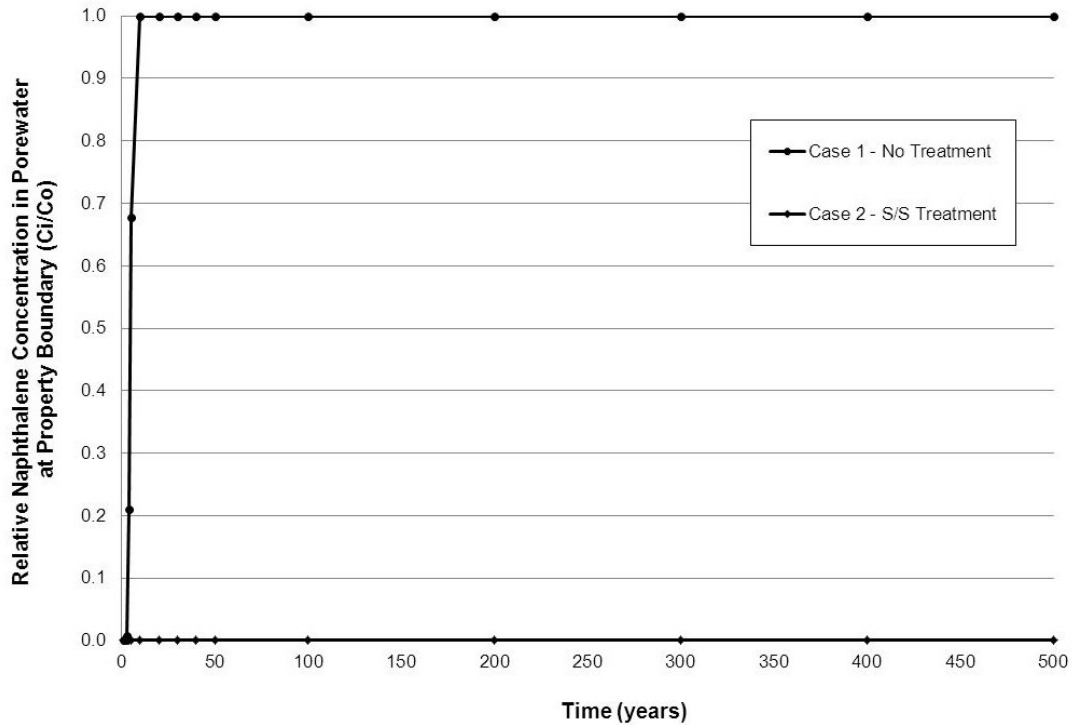


Figure 3-3 Contaminant migration modeling results for Example 1

Example 2: For Example 2, the results of Case 2 and the laboratory results for sorption of naphthalene are used to further demonstrate the influence of sorption for a given mix design. Two additional hypothetical mix designs are considered in this example. A summary of sorption properties are provided in Table 3-2. All properties other than K_d are the same as provided for Case 2 in Table 3-1. Case 3 would represent a mix with lower sorption than Case 2, while Case 4 would represent a mix design with higher sorption than Case 2. These three cases represent the range of values obtained from batch testing in Chapter 2. As with Example 1, the model was run to predict porewater concentrations 0.1 m away from the property boundary.

Table 3-2 Summary of K_d values used in Example 2

	Case 2 Moderate Sorption	Case 3 Low Sorption	Case 4 High Sorption
Partitioning Coefficient, K_d	9.3 mL/g	0.4 mL/g	62.1 mL/g
Representative S/S Mix	SKC-2/3FA	SKC(10%)	SKC-2%OC

As shown on Figure 3-4, Case 3 (lower sorption) exhibits porewater concentrations approaching 7% of the initial source concentrations at 500 years. This is a significant increase relative to Case 2 (also plotted on Figure 3-5 for comparison) indicating the influence of sorption on results. For Case 4 (higher sorption), the porewater concentrations adjacent to the property line are indistinguishable from Case 2 at 500 years. Subsequent modeling shows that appreciable leaching in Case 2 at the property line occurs between 500 and 1000 years, while in Case 4 it doesn't occur until between 3000 and 4000 years. This implies mixtures with a higher sorption capacity are desired to minimize the transport of contaminants, such as naphthalene, by diffusive transport.

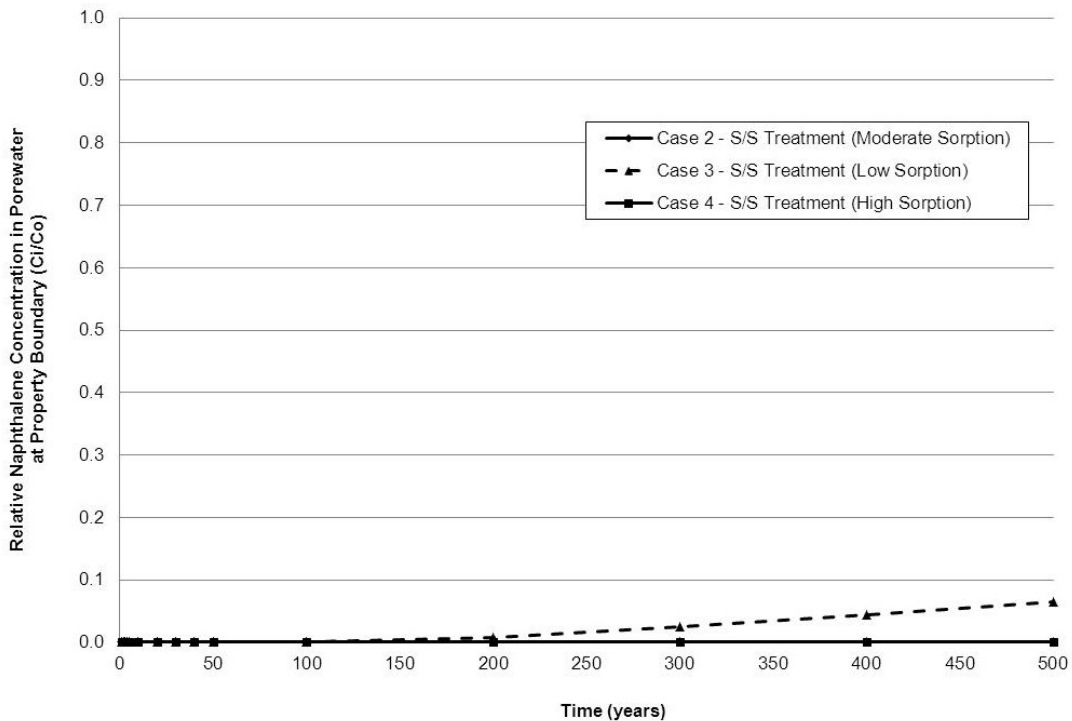


Figure 3-4 Contaminant migration modeling results for Example 2

The following assumptions used during the modeling exercise require further consideration:

- The contaminant source is not infinite which would reduce the amount of leachate generated than predicted.
- The initial source concentration in S/S treated soil-cement mixtures will be less than that in untreated soils, depending on the soil cement mixture utilized. The specification of the same initial source concentration in modelled Case 2 that was used in Case 1 is an over-estimate.
- Organic contaminants will biodegrade over time, which may reduce the amount of leachate generated, however, the degradation products may not, and in fact will not likely, respond to the sorption capacity of the soil-cement mixture in the same way. This process should be understood prior to implementing an S/S treatment for organic contaminants.
- The sorption capacity of the soil-cement components and mixtures is not infinite and the initial contaminant concentration may “overwhelm” the S/S treatment, which would increase the amount of leachate generated than predicted.

3.1.3 Summary and Conclusions

The results obtained from the two examples presented in the previous sections are limited to the assumptions adopted. However, some general observations can be made based on this work.

- 1) A cement-based S/S monolith with low hydraulic conductivity and diffusion coefficient results in significantly less transport of naphthalene from a contaminated site than untreated soil. The main reason for these results is the treatment of the entire contaminated mass which results in a thick barrier system for transport.

- 2) Higher sorption capacity S/S cement mixes are desirable for limiting transport of naphthalene for the time frames examined. It is hypothesized that this will be accentuated the less sorption the contaminant undergoes with the cement-based S/S material.
- 3) For the modeling performed in Case 4 utilizing 2% organoclay, the transport of naphthalene was found to be negligible over a period of 500 years. This is due to the significant sorption that was assumed for the naphthalene in the analysis.

These modeling exercises demonstrate that, with all other things being equal, sorption can have a significant effect on contaminant migration through soil-cement barrier systems.

3.2 Cost Implications of S/S Additives to Treat Organic Contaminants

Current market prices for the PM-199TM organoclay, Type 10 portland cement and Class F fly ash and utilized in this research are approximately \$3,100, \$150 and \$10 per metric tonne, respectively. Based on the Burnside till S/S design mixes utilized in this research, the cost comparison for remediating a small 100 m² site with a treated soil thickness of 2 m (i.e. total treated volume is 20,000 m³) is presented in Table 3-3.

Table 3-3 Cost Comparison of S/S Additives

Soil Cement Mixtures	BTC(10%)	BTC-1/3FA	BTC-2/3FA	BTC-2%OC
K_d (L/kg)	1.4	4.6	5.4	59.2
Cement (metric tonnes) <i>Bulk Density = 1,506 kg/m³</i>	3,102	5,045	2,485	7,379
Fly Ash (metric tonnes) <i>Bulk Density = 960 kg/m³</i>	---	1,584	3,216	---
Organoclay (metric tonnes) <i>Bulk Density = 801 kg/m³</i>	---	---	---	80
Cost/m³ of S/S Treated Soil	\$22.59	\$38.63	\$20.24	\$67.76
Cost/Site	\$451,800	\$772,605	\$404,895	\$1,355,196
Cost/ Naphthalene Sorption Capacity	\$16.14	\$8.40	\$3.75	\$1.14

Assuming all four (4) mix designs provide adequate naphthalene sorption, the most economical mix design is BTC-2/3FA. However, when the total cost per site is normalized with respect to the amount of sorption each S/S design mix affords, it is clear that the most cost effective mix design with respect to the retention of naphthalene is BTC-2%OC, based on the findings of this research. It should be noted that the addition of 2% organoclay provided significantly more sorption than the other three (3) mix designs, and it is likely that a reduced quantity of organoclay would be sufficient to achieve the required naphthalene sorption, thereby reducing the total cost of the remediation project.

Chapter 4 - Conclusions

4.1 Summary

As discussed in the Chapter 1, the main hypothesis of this research was that naphthalene sorption could be improved in cement-based S/S mixtures using common cement additives containing organic matter. To assess this hypothesis, the following tasks were carried out:

- Task 1: To establish the level of sorption of naphthalene, if any, to materials used in cement-based S/S, but without cement via batch testing (i.e. humic acid, natural soil, fly ash, organoclay).
- Task 2: To establish the level of sorption of naphthalene, if any, to materials used in cement-based S/S, with cement via batch testing (i.e. humic acid, natural soil, fly ash, organoclay).
- Task 3: To compare the sorption found from batch testing with several different leaching tests used in practice.
- Task 4: To use the quantitative numbers found in this study to demonstrate potential implications of the work in the context of contaminant migration from cement-based S/S treatments.

Below is a summary of the results obtained from this study, as part of the tasks identified above.

4.1.1 Laboratory Studies

Three laboratory studies were conducted in support of this research; 1) batch testing of typical S/S individual components and mixtures, 2) dynamic leach testing following the American Nuclear Society ANS 16.1 methodology, and 3) a single extraction batch test using the standard synthetic precipitation leaching procedure (SPLP).

4.1.1.1 *Batch Testing*

The batch testing experiments conducted in support of Task 1 and Task 2 demonstrated the effect various soil cement components and mixtures have on the sorption of naphthalene, as detailed below.

4.1.1.1.1 Soil Materials, Without Cement

- *Sand, Kaolinite, and Burnside Till:* The sorption of naphthalene to Burnside till was noticeably higher than that for that of the sand and kaolinite materials, as determined by Afshar (2008), which may be attributed to the smaller grain size and larger percentage of organic carbon.
- *Fly Ash and Organoclay:* The batch testing of organoclay and fly ash resulted in non-detect levels (<0.004 mg/L) of naphthalene, suggesting that sorptive uptake to both fly ash and organoclay is high for naphthalene (essentially 100% under batch test conditions). This was not unexpected as both materials are known to be excellent sorbents to higher molecular weight organic compounds.
- *Burnside Till Mixed with 2% Organoclay:* The addition of the small percentage of organoclay significantly improved the sorption capacity of the natural Burnside till soil, increasing the experimental sorption from 6.9 L/kg for Burnside till alone to 109.4 L/kg for Burnside till augmented with 2% organoclay.

4.1.1.1.2 Soil Materials, With Cement

- *Mixtures of Cement with Sand, Kaolinite, Humic Acid:* As expected, due to the absence of any organic matter, naphthalene sorption was shown to be significantly lower to SKC(10%) than to the SKC-1% HA and SKC-2% HA mixtures. Sorption to the SKC(10%) mixture was found to be essentially zero. The level of naphthalene sorption increased as 1% HA was added to the sand kaolinite mixture prior to

mixing and curing with cement. The addition of 2% humic acid for the SKC-2%HA samples only marginally increased the level of naphthalene sorption from 1% humic acid.

- *Mixture of Cement with Fly Ash:* Naphthalene sorption for cured mixtures of cement and fly ash (i.e. SKC-1/3 FA and SKC-2/3 FA) were reduced from the essentially 100% sorption obtained from the unaltered fly ash (FA) sample. Notably, naphthalene showed lower sorption to SKC-1/3 FA than to the SKC-2/3 FA mixture.
- *Mixtures of Cement with Burnside Till:* Naphthalene showed somewhat lower sorption to BTC(10%) relative to the Burnside till alone. This is most likely the cement making the sorption sites inaccessible for naphthalene partitioning onto the soil organic matter. The replacement of portions of the cement with fly ash significantly increased the sorption of naphthalene to the mixture but the amount of increase in fly ash from $1/3$ to $2/3$ in the mixture did not cause a sizeable increase in sorption.
- *Mixtures of Cement with Organoclay:* In soil cement mixtures amended with organoclay, naphthalene showed a high sorption to all mixtures. Naphthalene showed very similar sorption to both SKC-2%OC and BTC-2%OC soil cement mixtures. Similar to soil cement mixtures containing fly ash, sorption values for cured mixtures of cement and organoclay (i.e. SKC-2%OC and BTC-2%OC) were observed to be significantly reduced when compared to organoclay alone or the Burnside till amended with organoclay.

From the batch tests performed, it was generally observed that the level of organic carbon had a significant effect on the performance of the contaminant to the solids tested. Comparing all the batch test results, it is clear that organoclay and fly ash contribute significantly to the capacity of soil cement mixtures to sorb naphthalene.

The results of the batch testing show that sorption of naphthalene increased with the addition of organic matter, i.e., humic acid, fly ash, organoclay. Generally, increased

amounts of organic matter resulted in increased sorption. Specifically, sorption of 2% humic acid mixtures was marginally greater than 1% humic acid mixtures, and sorption of $\frac{2}{3}$ fly ash mixtures was greater than $\frac{1}{3}$ fly ash mixtures. Of note, sorption decreased when cement was added compared to the sorption of individual components (i.e. sorption of BT-2%OC was greater than the sorption of BTC-2%OC). This is consistent with the findings of Afshar (2008) who found that the addition of cement reduced the sorption capacity for a variety of volatile organic contaminants. This is most likely due to the coating of sorption surfaces by the cement and changes in the fly ash structure from pozzolanic activity. Improved sorption would be expected when additives such as fly ash and organoclay are added as pre-treatment or stabilization process prior to solidification.

The normalized K_d value with respect to the fraction of organic matter in the soil, or the organic carbon-water partition coefficient, K_{oc} , allows comparison of each sorbent used in terms of its relative “efficiency” of naphthalene sorption. The K_d values obtained from each of the batch tests were normalized with respect to the fraction of organic carbon to yield K_{oc} values. The log K_{oc} values for naphthalene obtained from the batch test data were generally similar to the calculated log K_{oc} . The experimental log K_{oc} values were higher than the calculated log K_{oc} of 3.2 for both of the individual soil-cement additives, i.e. fly ash and organoclay. The experimental log K_{oc} values were generally lower than the log K_{oc} of 3.2 for all of the soil cement mixtures with the exception of the SKC-2/3FA and those containing organoclay. Organoclay mixtures, with and without cement, showed higher sorption efficiency relative to the natural soil as calculated using the relationship developed by Karickhoff et. al. (1979). Again, the presence of cured cement appears to reduce sorption efficiency in soil-cement mixtures.

Since the organic contaminant, in this case, naphthalene, was introduced to soil-cement mixtures after the cement curing process, the results of the batch testing can be considered a conservative estimate of sorption capacity.

4.1.1.2 Leach Test Results

The results of the dynamic leach testing (ANS 16.1) conducted in support of Task 3 indicated that after 19 days, there was no appreciable leaching of naphthalene

from any of the five (5) different natural soil (Burnside till) based cement mixtures using intact S/S samples and water as the leachant. The results of the more aggressive single extraction batch test (SPLP), also conducted in support of Task 3, showed that detectable amount of naphthalene leached from each of the five different natural soil (Burnside till) based cement mixtures using crushed S/S samples and acidic leachant. The lowest concentration of naphthalene in the leachate was generated from the BTC-2/3FA soil-cement mixture (0.06 µg/L), while the BTC+2%OC soil-cement mixture (0.73 µg/L) showed the highest concentration of naphthalene in the leachate. These results are contrary to the batch test results which found that the organoclay demonstrated the greatest sorption capacity. This may be explained by the comparatively aggressive sulphuric/nitric acid extraction procedure which may leach naphthalene more readily from the organoclay or consume a portion of the organoclay, releasing the sorbed naphthalene.

4.1.2 Modelling

The results of the contaminated site scenario modeling conducted in support of Task 4 using the 1-D model POLLUTE demonstrated the following:

- S/S treated soil attenuated the migration of naphthalene from a modelled contaminated site significantly more than untreated soil.
- The sorption capacity of soil-cement mixtures has an impact on the attenuation of the migration of naphthalene. The higher the sorption capacity of the soil-cement mixture, the longer naphthalene is attenuated.

4.2 Conclusions

The results of the laboratory analysis and predicative modelling conducted in support of this thesis have demonstrated that the sorption of naphthalene in cement-based S/S treatment can be improved with the addition of additives. The extent of sorption was quantified conservatively in soil-cement mixtures through the batch testing experiments

and the leaching tests conducted showed that in the short term the additives tested improve the sorption of naphthalene.

4.3 Recommendations for Future Work

Based on the findings of this research, the following recommendations are presented:

- A full term ANS16.1 testing program would better ascertain the long term effectiveness of S/S treatment of naphthalene-contaminated soils. Additionally, a modified testing program extending longer than the 90 days prescribed in the test would be beneficial.
- The use of activated carbon has been discussed in the literature as an effective additive for the treatment of naphthalene-impacted soils with S/S. A testing program incorporating activated carbon would qualify the effectiveness of fly ash and organoclay and provide the basis for a cost-benefit analysis for these additives.
- Other commercially viable amendments could also be assessed for their effectiveness in naphthalene sorption within various S/S treatment scenarios.
- The desorption of organic contaminants, specifically naphthalene, from additives over time (i.e. diffusion test) would be beneficial for practitioners of S/S in the selection of appropriate soil-cement mixtures.
- In order to better simulate in-situ S/S conditions, factors such as increased ionic strength of contaminated groundwater, temperature variation during cement curing and co-mingled contaminants should be evaluated with respect to their effect on sorption of organic contaminants.

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Appendix A – Experimental Batch Test Data

Soil Cement Component or Mixture	Co	0.05		0.1		0.25		0.5		1.0	
		Ci	Sorb	Ci	Sorb	Ci	Sorb	Ci	Sorb	Ci	Sorb
SKC 10%C	Ci	0.042	0.037	0.074	0.066	0.286	0.250	0.398	0.411	1.017	0.989
	Sorb	0.194	0.246	0.320	0.435	-0.447	0.052	1.598	1.201	-0.375	0.203
SKC-1% HA	Ci	0.040	0.037	0.060	0.081	0.188	0.211	0.429	0.454	0.815	0.788
	Sorb	0.152	0.214	0.589	0.257	0.769	0.452	1.126	0.717	2.745	3.124
SKC-2%HA	Ci	0.032	0.035	0.065	0.071	0.190	0.206	0.395	0.392	0.828	0.816
	Sorb	0.266	0.229	0.503	0.403	0.921	0.735	1.548	1.682	2.576	2.829
SKC-1/3 FA	Ci	0.017	0.024	0.056	0.059	0.178	0.173	0.315	0.435	0.881	1.020
	Sorb	0.501	0.397	0.657	0.640	1.124	1.195	2.729	0.923	1.686	-0.299
SKC-2/3 FA	Ci	0.004	0.009	0.014	0.016	0.074	0.080	0.188	0.263	0.516	0.732
	Sorb	0.662	0.595	1.227	1.213	2.653	2.595	4.491	3.378	6.742	3.926
FA	Ci	0.004	0.002	0.003	0.037	0.014	0.004	0.029	0.074	0.077	0.006
	Sorb	0.705	0.733	1.495	0.974	3.822	3.586	7.035	6.369	13.305	14.508
BT	Ci	0.017	0.028	0.049	0.056	0.103	0.082	0.307	0.320	0.694	0.712
	Sorb	0.378	0.431	0.742	0.680	2.248	2.345	2.694	2.520	4.627	4.277
BTC(10%)	Ci	0.037	0.041	0.070	0.078	0.240	0.238	0.405	0.421	0.903	0.958
	Sorb	0.239	0.187	0.358	0.416	0.247	0.154	1.489	1.153	1.408	0.691
BTC- 1/3FA	Ci	0.028	0.027	0.051	0.047	0.162	0.149	0.346	0.350	0.785	0.794
	Sorb	0.387	0.396	0.655	0.691	1.236	1.567	2.289	2.220	3.266	3.011
BTC- 2/3FA	Ci	0.016	0.016	0.037	0.033	0.133	0.132	0.328	0.339	---	0.768
	Sorb	0.572	0.570	0.884	0.918	1.665	1.637	2.425	2.375	---	3.205
Organoclay	Ci	0.039	0.043	0.083	0.016	0.072	0.092	0.002	0.002	0.004	0.004
	Sorb	0.074	0.004	0.300	1.259	2.762	2.256	7.034	7.463	14.285	14.475
BT + 2%OC	Ci	0.005	0.005	0.012	0.012	0.028	0.026	0.059	0.059	0.131	0.102
	Sorb	0.693	0.686	1.358	1.346	3.208	3.241	6.563	6.386	12.622	13.196
SKC+2%OC	Ci	0.005	0.007	0.015	0.015	0.038	0.038	0.076	0.091	0.197	0.201
	Sorb	0.690	0.661	1.304	1.309	3.060	3.060	6.307	6.107	11.657	11.905
BTC+2%OC	Ci	0.007	0.007	0.015	0.016	0.050	0.043	0.098	0.097	0.201	0.207
	Sorb	0.600	0.608	1.199	1.191	3.038	3.168	6.135	6.367	11.804	11.672

Co = Initial Concentration in mg/L

Ci = Equilibrium Concentration in mg/L

Sorb = Amount of naphthalene sorbed in mg/kg