CONTAMINANT MIGRATION THROUGH SOIL-CEMENT MATERIALS

by

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DEDICATION

This work is dedicated to the memory of my grandfather, Phil. His influence equipped me not only with the capacity and motivation to complete this work but the courage, curiosity, and confidence to attempt it.

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ABSTRACT

To assess the long-term performance of soil-cement materials used in source-control remediation methods (i.e. cement-based solidification/stabilization), procedures to measure or estimate contaminant migration parameters are essential. Previous research indicates that diffusion may be an important mechanism in contaminant transport through soil-cement materials. However, there is a paucity of information regarding the diffusion of contaminants through these materials.

The development of a single-reservoir diffusion apparatus and methodology to assess the effective diffusion coefficient (D_e) and effective porosity (n_e) of dissolved, conservative, inorganic chemicals for saturated, cured, monolithic soil-cement specimens is discussed. This is the only study known to investigate these parameters for these materials.

The results of tritiated water diffusion tests on 14 different soil-cement mixtures are presented and the influence of curing time and mixture properties such as water-to-cement ratio, cement content, and grain-size distribution are examined. Results suggest that, to determine reasonable assessments of the longer-term parameters, soil-cement samples should be cured for a minimum of 70 days before commencing diffusion testing. Values of n_e (0.21 to 0.41) and D_e (2.50×10^{-10} m^2/s to 7.0×10^{-10} m^2/s) determined are similar to those previously determined for a number other low-hydraulic conductivity materials (i.e. saturated inactive clays).

The water content of the initial mixture is shown to have a substantial effect on the diffusive properties as the results indicate that both the total porosity (n) and the effective porosity, n_e, generally increase with increasing initial water content. For the range of soils used in this investigation, grain-size distribution did not have a substantial effect on the values of n_e or D_e determined from diffusion testing.

The adaptation of a double-reservoir diffusion testing apparatus and methodology to evaluate the distribution coefficient (K_d) and D_e of organic contaminants is also presented. This apparatus is used to evaluate K_d and D_e of benzene, ethylbenzene, naphthalene, and trichloroethylene for three soil-cement mixtures. Values of K_d (0 to 2.5 cm^3/g depending on the compound and soil-cement mixture tested) determined from diffusion testing, batch testing, and theoretical estimates from the literature were in general agreement. Values of D_e for the organic compounds ranged from 1.50×10^{-10} to 3.0×10^{-10} m^2/s.

LIST OF ABBREVIATIONS AND SYMBOLS USED

c: concentration $[ML^{-3}]$

c_b: concentration in the receptor solution $[ML^{-3}]$

c_{bo}: initial concentration in the receptor solution $[ML^{-3}]$

CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act

c_o: initial concentration $[ML^{-3}]$

C-S-H: calcium-silicate-hydrate

c_t: concentration in the source reservoir $[ML^{-3}]$

c_{to}: initial concentration in the source reservoir $[ML^{-3}]$

C_w: initial concentration of in the specimen water $[ML^{-3}]$

D_e: effective diffusion coefficient through porous media $[L^2T^{-1}]$

DML: dynamic monolithic leaching test

D_o: free-solution diffusion coefficient $[L^2T^{-1}]$

D_p: porous media diffusion coefficient ($D_p = n_e \times D_e$) $[L^2T^{-1}]$

D_R: retarded diffusion coefficient $[L^2T^{-1}]$

$D_{RBenzene}$: retarded diffusion coefficient for benzene $[L^2T^{-1}]$

$D_{REthylbenzene}$: retarded diffusion coefficient for ethylbenzene $[L^2T^{-1}]$

$D_{RNaphthalene}$: retarded diffusion coefficient for naphthalene $[L^2T^{-1}]$

$D_{RTrichloroethylene}$: retarded diffusion coefficient for trichloroethylene $[L^2T^{-1}]$

e: void ratio [-]

f_a: advective mass flux $[ML^{-2}T^{-1}]$

f_b: mass flux of contaminant into the receptor reservoir $[ML^{-2}T^{-1}]$

f_d: diffusive mass flux $[ML^{-2}T^{-1}]$

FID: flame ionization detector

f_{oc}: fraction of organic carbon [-]

f_t: mass flux of contaminant from the source reservoir $[ML^{-2}T^{-1}]$

GCL: geosynthetic clay liner

G_S: specific gravity [-]

H_b: equivalent height of the receptor reservoir (volume per unit area) [L]

H_{bs}: depth of the base stratum [L]

H_r: equivalent height of source reservoir (volume per unit area) [L]

i: hydraulic gradient [-]

ITRC: Interstate Technology & Regulatory Council

k: hydraulic conductivity [LT^{-1}]

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

$K_{dBenzene}$: distribution coefficient of benzene [$M^{-1}L^3$]

$K_{dEthylbenzene}$: distribution coefficient of ethylbenzene [$M^{-1}L^3$]

$K_{dNaphthalene}$: distribution coefficient of naphthalene [$M^{-1}L^3$]

$K_{dTrichloroethylene}$: distribution coefficient of trichloroethylene [$M^{-1}L^3$]

K_{oc}: partition coefficient of a compound between organic carbon and water [$M^{-1}L^3$]

K_{ow}: octanol-water partition coefficient [-]

MCL: USEPA maximum contaminant level

n: total porosity [-]

n_e: effective porosity [-]

PAH: polycyclic aromatic hydrocarbon

PCB: polychlorinated biphenyl

PVC: polyvinyl chloride

q_c: volume of leachate collected per unit area per unit time [LT^{-1}]

RCRA: Resource Conservation and Recovery Act

RMSE: root-mean-square error

S: mass of solute removed form solution per unit mass of solid [-]

S/S: solidification/stabilization

SPLP: synthetic precipitation leaching procedure

SPME: solid-phase microextraction

TCLP: toxicity characteristic leaching procedure

UCS: unconfined compressive strength

v: darcy velocity [LT^{-1}]

VOC: volatile organic compound

V_R: retarded groundwater velocity [LT^{-1}]

w: water content (-)

W:C: water-to-cement ratio

ρ: bulk density [ML^{-3}]

ρ_d: dry density [ML^{-3}]

λ: first order decay constant [T^{-1}]

τ: tortuosity [-]

γ_w: unit weight of water [ML^{-3}]

Throughout this thesis, square brackets denote the fundamental dimensions mass [M], length [L], and time [T] for dimensionally consistent equations. Scale units such as kilogram (kg), metre (m), and second (s) are presented in round brackets for equations that are dimensionally inconsistent.

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CHAPTER 1: INTRODUCTION

Before environmental laws and regulations were common, a culture developed where wastes of all types were disposed of without proper consideration of the effects on human health and the environment. This resulted in the contamination of many locations with toxic chemicals and hazardous wastes. For instance, in 2004 the USEPA (2004a) estimated that there were over 300 000 sites in the United States where toxic chemicals posed unacceptable risk to public health and the environment. In this same report, the USEPA estimated that at existing levels of cleanup activity, remediation of these sites would take approximately 30 to 35 years and cost over 200 billion U.S. dollars.

The use of soil-cement mixing for source-control remediation (i.e. cement-based solidification/stabilization; S/S) is one technology that has seen increasing use for treatment of contaminated sites in recent years. There have recently been several high-profile cement-based S/S projects in Canada, most notably the remediation of the Sydney Tar Ponds and Coke Ovens site in Sydney, Nova Scotia (Earthtech 2006).

It is generally acknowledged that cement-based S/S treatment will not be able to entirely prevent all potential contaminants from entering the surrounding environment in perpetuity; some contaminants are expected to inevitably escape from the wasteform. Historically, cement-based S/S materials have been designed to meet prescriptive regulations based on a number of characteristics (e.g., hydraulic conductivity, unconfined compressive strength, and leaching performance). However, the ultimate objective of any source-control technology is to reduce contaminant migration to a rate where there are no substantial negative effects to human health and the environment. A typical method of quantifying this objective is to design the treatment so that off-site water quality is not impacted to the extent that the concentration exceeds allowable limits (ITRC 2011). Contaminant migration modeling allows for quantification of the potential impacts of proposed treatment options and may be used to improve decision making regarding technology selection and treatment level, to prioritize sites, and to predict performance

(ITRC 2011). The accuracy of this modeling will depend on the assumptions and parameters used to develop the model.

For soil-cement materials the vast majority of research on contaminant transport has focused on measuring, estimating, and limiting the advective flux. There is a paucity of information available regarding the diffusive migration of dissolved contaminants through soil-cement materials in spite of the fact that diffusion may be expected to be an important transport mechanism in many cement-based S/S systems (Stegemann and Côté 1991).

Established methods to measure or estimate the diffusive properties of cement-based S/S materials are required to develop input for contaminant migration models. Ideally, the diffusive parameters determined for cement-based S/S materials will be consistent with parameters commonly used for other materials so that the various technologies can be directly compared and the effects of combined treatment methods (e.g., treatment using both cement-based S/S and slurry walls) may be analyzed. Results of laboratory leaching tests that are currently performed on cement-based S/S materials are not indicative of how released contaminants travel through the subsurface and may be difficult to relate to diffusive parameters or groundwater concentrations in the field (ITRC 2011).

Tests to measure the diffusive properties of soil-cement materials must be developed to provide parameters required for contaminant migration models. There is also a need to understand the typical range of diffusive properties for these materials and to understand how the diffusive parameters are affected by various mixture and material properties. The work in this thesis aims to address these concerns by studying diffusion of relatively mobile contaminants such as tritium and volatile organic compounds (VOCs). The objective of this work is to develop and apply methods to estimate contaminant migration (i.e., diffusive) properties and to show how they may be used to develop strategies for cement-based S/S treatment. Contaminant migration modeling will allow estimates of contaminant impact at points of interest and may ultimately result in more successful, long-term designs of cement-based S/S treatment.

1.1. RESEARCH OBJECTIVES

The principal objective of this thesis is to develop and apply conventional single- and double-reservoir diffusion testing techniques to measure contaminant migration parameters of inorganic and organic contaminants for monolithic soil-cement specimens. It is also hypothesized that the material properties of the soil-cement specimens will influence the contaminant migration parameters. To achieve these goals, the following specific research objectives were devised:

1. To develop a diffusion testing apparatus, laboratory procedures, and modeling techniques to measure the diffusive parameters (i.e., effective diffusion coefficient, effective porosity) of a conservative, inorganic contaminant (i.e., tritiated water) for laboratory prepared soil-cement specimens.

2. To evaluate the influence of several mixture properties such as cement content, water-to-cement ratio, and grain-size distribution on the diffusive parameters of monolithic soil-cement materials.

3. To adapt the diffusion apparatus, laboratory procedures, and methodology to measure the diffusive and sorptive parameters (i.e. D_e and K_d) of dissolved organic compounds for soil-cement specimens.

4. To evaluate the diffusive and sorptive parameters of four organic compounds (i.e., benzene, ethylbenzene, naphthalene, and trichloroethylene) for soil-cement mixtures at three different water-to-cement ratios.

5. To compare the distribution coefficient (K_d) obtained from batch testing, diffusion testing, and theoretical estimates for the four organic compounds for three different soil-cement mixtures.

6. To investigate how the diffusive parameters determined above will affect the migration of contaminants through soil-cement materials.

1.2. THESIS ORGANIZATION

To address the objectives discussed above, this thesis is divided into seven chapters. As a "paper-based" thesis each chapter has been written to be largely independent of the others without significant interrelation between chapters.

Chapter 1, the current chapter, provides a brief introduction to the work and outlines why the work is required, the research objectives, thesis format, and summarizes the original contributions of the work discussed herein.

Chapter 2 presents the results of a literature review that discusses the remediation of contaminated sites with cement. History, current design and practice, treatment methods, mechanisms, and laboratory and field-testing of cement-based S/S materials are discussed. This chapter serves as an introduction to cement-treatment and aims to provide sufficient background to ensure the reader is prepared for the material presented in the subsequent chapters.

Chapter 3 focuses on the development of an apparatus and laboratory methodology to measure the diffusive parameters of monolithic, soil-cement materials using a conservative tracer (tritiated water). In particular, the effect of curing time and the influence of porosity on the interpretation of the diffusion test are investigated. This chapter has been published as a full paper in the Geotechnical Testing Journal (Goreham et al. 2012).

Chapter 4 discusses the results of a series of diffusion tests using tritiated water as a tracer. A single-reservoir diffusion test method (developed in Chapter 3) was used to measure the effective porosity and effective diffusion coefficient of forty-two laboratory prepared, saturated, monolithic, soil-cement specimens. The effects of cement content, water content, water-to-cement ratio, and grain-size distribution are investigated. This chapter has been published as a full paper in the Canadian Geotechnical Journal (Goreham and Lake 2013a).

In Chapter 5, the use of a double-reservoir diffusion test to measure the diffusive and sorptive properties of three volatile organic compounds (benzene, ethylbenzene, and trichloroethylene) for monolithic, soil-cement specimens is discussed. The results of diffusion and batch testing on three different soil-cement mixtures are presented. This chapter also presents modeling to show the relative effects of the contaminant migration parameters (n_e, D_e, and K_d) on contaminant transport using a theoretical site.

Chapter 6 discusses the use of a double-reservoir diffusion test to investigate the diffusive and sorptive properties of naphthalene for three different soil-cement mixtures. Batch testing is also performed on the three mixtures to provide an estimate the distribution coefficient, K_d independent of the diffusion tests. The effect of sorption on the long-term diffusion of contaminants is illustrated by example using a theoretical site. A modified and condensed version of this chapter has been presented at the 5th International Young Geotechnical Engineer's Conference, in Marne-la-Vallée, France and has been published in the corresponding proceedings (Goreham and Lake 2013b).

The seventh, and final chapter of this thesis, provides a brief summary and conclusions of the research project and presents recommendations for future work.

1.3. ORIGINAL CONTRIBUTIONS

The original contributions of this thesis include:

- The development of a testing apparatus and methodology to measure the diffusive properties of inorganic compounds for monolithic soil-cement materials.

- An investigation of the effects of cement content, water-to-cement ratio, curing time, and grain-size distribution on the diffusive properties of a conservative inorganic chemical (tritiated water) through monolithic soil-cement specimens.

- The modification and application of a testing apparatus and methodology for obtaining diffusion coefficients of volatile organic compounds (VOCs) for monolithic soil-cement specimens.

- The determination of diffusive and sorptive parameters of four organic chemicals for three different soil-cement mixtures.

CHAPTER 2: LITERATURE REVIEW

2.1. INTRODUCTION

This chapter provides an introduction to soil-cement mixing for source control remediation of contaminated sites (i.e. cement-based solidification/stabilization). An overview of the history and practices of cement-based solidification/stabilization (S/S) is presented. The treatment of inorganic and organic contaminants is discussed as well as the performance testing commonly used to evaluate the level of treatment provided. The role of diffusion in cement-based S/S treatment is explained in the context of the paucity of methods to assess the diffusive transport parameters of cement-based S/S materials.

Soil-cement mixing has been used as a source-control technology for the treatment of contaminated sites for several decades (USEPA 1989a). The objective of soil-cement mixing from a source-control remediation perspective is to reduce the release (or the rate of release) of contaminants from the wasteform to the surrounding environment. When cement is used as the primary additive and is mixed with contaminated media to reach this goal, this technology is often referred to as cement-based S/S. This process may result in a 'solidified' mass where physical changes occur to the pore structure of the wasteform which results in an increased strength, a lower hydraulic conductivity, and a larger average particle size (Batchelor 2006).

2.2. CEMENT-BASED S/S TREATMENT

Cement-based solidification/stabilization (S/S) is one of the most common source-control technologies involving cement. The more general term, solidification/ stabilization (S/S) refers to the mixing of contaminated materials (e.g., contaminated soil, sediment, sludge, and waste) with various binders and additives to chemically and physically "contain" the contaminants present in these materials. Typically, S/S processes consist of mixing inorganic cementitious or pozzolanic reagents with contaminated material to result in a more durable and more solid material with a low-hydraulic conductivity (ITRC 2011).

Cementitious and pozzolanic binders that have been used in S/S include Portland cement, fly ash, ground granulated blast furnace slag, silica fume, cement kiln dust, and various forms of lime (ITRC 2011). Other binders and additives that are sometimes used in S/S treatment include: soluble silicates, clay, gypsum, bitumen, urea formaldehyde, polyester, epoxy, and polyethylene as well as a number of proprietary products (Conner 1990). However, Portland cement is the most commonly used binder (Spence and Shi 2005; ITRC 2011).

In cement-based S/S treatment, contaminated media are generally thought to be subjected to two separate phenomena; solidification and stabilization. The term "stabilization" refers to the chemical reaction of the contaminated material with reagents to produce a more chemically stable wasteform (Bone et al. 2004; Batchelor 2006; Paria and Yuet 2006). The contaminants are stabilized by reducing their solubility, mobility, or toxicity (Batchelor 2006). For example, contaminants in the dissolved phase are free to move through the wasteform, however, when a reaction occurs to precipitate contaminants into a solid phase they become significantly less mobile (Conner 1990). Common examples of stabilization include heavy metals reacting with hydroxide ions to form insoluble metal hydroxides (Conner 1990) and metals reacting with the cement to form metal salts as a precipitate (Arafat et al. 1999). Other processes such as adsorption and reduction/oxidation reactions also may contribute to the stabilization aspect of treatment.

Contaminants that do not readily react chemically with the binder, and thus are not stabilized by cement-based S/S processes, may still be treated by the "solidification" aspect of treatment. The term "solidification" is generally considered to refer to changes in the physical properties of the wasteform. For instance, relatively mobile contaminated media such as dusts, sludges, and liquids which may be transported relatively easily may be converted into relatively immobile solid forms. Solidification may result in either a granular or monolithic wasteform where soluble contaminants may become physically encapsulated or otherwise restricted by the physical structure of the treated material (Shi and Spence 2005; Batchelor 2006; ITRC 2011). Other effects of solidification include an increase in compressive strength, a lower permeability, and a larger average particle size (Batchelor 2006). As a result of solidification, the hydraulic conductivity of the wasteform is often reduced to a value much lower than the surrounding soils which results in a large proportion of the groundwater flowing around the wasteform, rather than through it. This effect further slows the release of contaminants into the environment. In a system such as this, diffusion of contaminants through the material may often control the rate of release from the monolith (ITRC 2011).

Research of cement-based S/S materials has been principally focused on the stabilization aspect of treatment (i.e., chemical interactions between the binder and contaminant), particularly with respect to the stabilization of metals (Conner 1990; Bone et al. 2004; Paria and Yuet 2006). In many cases, consideration of the solidification aspect of treatment is restricted to assessment of the hydraulic conductivity (e.g., ASTM D5084) and unconfined compressive strength (e.g., ASTM D1633, ASTM D2166); there has generally been limited consideration of the diffusive properties of cement-based S/S materials. In other low-hydraulic conductivity materials (e.g., compacted clay liners) it has been shown that diffusion plays a significant role in contaminant migration (Rowe et al. 2004). Stegemann and Côté (1991) report that for cement-based S/S wasteforms, the infiltration of water is expected to be negligible, and the rate of a contaminant release is likely to be dominated by diffusion when hydraulic conductivities are less than approximately 10^{-9} m/s. Hydraulic conductivities near or below this value are achievable for many cement-based S/S projects. When treatment results in a monolith, an accurate assessment of the diffusive properties may provide support for both the pre-design (technology selection) phase and for detailed design of cement-based S/S systems.

2.2.1. History and Use

Cement-based S/S was initially used to treat radioactive wastes in the 1950s and has since been used as a remediation technology for many hazardous wastes and contaminated materials (Conner 1990). Cement-based S/S has been used in the United States since approximately 1980 for the immobilization of contaminants in hazardous wastes, industrial sludges, contaminated soils, and incinerator residues (USEPA 1989b).

When properly applied, cement-based S/S treatment has been shown to be a cost-efficient and effective technology, particularly with respect to the treatment of heavy metal contaminated soils (Conner 1990; Bone et al. 2004; Paria and Yuet 2006). However, there has been relatively little work assessing the long-term behavior of cement-based S/S systems. Recently, a multinational project, Performance Assessment of Stabilised/Solidified Waste Forms (PASSiFY) has been undertaken to investigate the effect of time on S/S materials obtained from full-scale remediation operations. As part of this project, Antemir et al. (2010) studied the performance of eight full scales sites, determining that all wasteforms were performing satisfactorily after up to 16 years of service. This is in agreement with a report by the ITRC (2011) which states that many cement-based S/S wasteforms are likely capable of maintaining their integrity for centuries.

In the United States, cement-based S/S treatment is often applied to materials regulated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, commonly referred to as Superfund), the Resource Conservation and Recovery Act (RCRA), and other state regulated cleanup operations (Means et al. 1996; Bone et al. 2004). In the fiscal years 2005 to 2008 S/S was the most common ex-situ treatment selected and the second most commonly used in-situ treatment for CERCLA sites (USEPA 2010).

Cement-based S/S technology has less extensive history in Canada, but it has seen increased high-profile use with projects being undertaken in British Columbia, Manitoba, and Nova Scotia (Cement Association of Canada 2007). The largest, and most notable, project is the remediation of the Sydney Tar Ponds and former Coke Ovens Site in Sydney, Nova Scotia. Approximately 700 000 tonnes of heavy metal, polycyclic aromatic hydrocarbon (PAH), and polychlorinated biphenyl (PCB) contaminated sediments were treated with in-situ cement-based S/S (Earthtech 2006).

2.2.2. Current Design and Practice

Cement-based S/S has found use for the treatment of a broad range of organic and inorganic contaminants. Table 2.1 outlines contaminant groups for which the cement-based S/S treatment is demonstrated effective or thought to be potentially effective. Cement-based S/S is commonly the technology of choice when treating sludges, wastes containing high-levels of metallic contaminants, wastes with poor handling characteristics, and for large volumes of contaminated soil (Means et al. 1996).

Table 2.1 — Effectiveness of S/S treatment for chemical groups (modified from ITRC 2011).

Chemical Groups	USEPA (1993, 2009)	Paria and Yuet (2007)	Wilk (2003, 2007)	PASSiFy (2010)	Bates et al. (2002)
Organic Chemicals					
Halogenated volatile (e.g., solvents, gases)	N/N	D[a]	-/-	-	-
Nonhalogenated volatile (e.g., ketones/furans, aromatics)	N/N	D[a]	-/-	-	-
Halogenated semi-volatiles (e.g., chlorinated benzenes/phenols)	D/D	-	-/-	-	-
Nonhalogenated semi-volatiles/non-volatile (e.g., PAHs, nonchlorinated phenols	D/D	-	-/-	-	-
PCBs	P/D	-	-/-	-	-
Pesticides	P/D	-	-/-	-	-
Dioxins/furans	P/P	-	-/-	D	D
Organic cyanides / organic corrosives	P/-	-	-/D	-	-
Pentachlorophenol	-/-	-	-/D	-	D
Creosotes, coal tar	-/-	-	-/D	-	D
Heavy oils	-/-	-	D/-	-	-
Inorganic Chemicals					
Volatile metals	D/-	-	-	-	-
Non-volatile metals	D/D	-	-	-	-
Asbestos	D/-	-	-	-	-
Radioactive materials	D/D	-	-	-	-
Inorganic corrosives (e.g., hydrochloride, sodium hydroxide)	D/-	-	-	-	-
Inorganic cyanides (e.g., salts of cyanide; CN^-)	D/-	-	-	-	-
Reactive Chemicals					
Oxidizers	D/-	-	-	-	-
Reducers	D/-	-	-	-	-

D: Demonstrated Effectiveness: successful treatability test at some scale completed.
P: Potential Effectiveness: expert opinion that technology will work.
N: No Expected Effectiveness: expert opinion that technology will not/does not work.
- : Not reported.
[a] With appropriate pre-treatment.

2.2.2.1. Treatment of Inorganic Contaminants

A significant amount of research has been published regarding the effectiveness of cement-based S/S processes for inorganic contaminants, particularly with respect to heavy metals such as arsenic, cadmium, chromium, copper, nickel, lead, and zinc (Paria and Yuet 2006). The reason for this focus is due to the prevalence of heavy metal contamination, the potential toxicological risk heavy metals pose to humans and the environment, and the fact that there are relatively few other options for effective treatment of heavy metal contaminated materials. Sanchez et al. (2000), Li et al. (2001), Poon et al. (2001), Alpaslan and Yukselen (2002), Bone et. al. (2004), Malviya and Chaudhary (2006), and Moon and Dermatas (2006) are some of the many examples of literature discussing cement-based S/S treatment of inorganic contaminants. It is apparent from a review of this literature that cement-based S/S treatment has a relatively successful history in treating a wide range of inorganic contaminants

Many chemical factors influence the performance of cement-based S/S treatment. In the treatment of metals, pH is largely considered the most important chemical factor with regards to leaching performance (e.g., contaminant speciation; ITRC 2011). Porewater pH strongly affects several processes including mineral and precipitate dissolution, adsorption/desorption reactions, and the aqueous solubility of inorganic species (ITRC 2011). Many heavy metals of are precipitated as nearly insoluble hydroxides in alkaline environments (Shi and Spence 2005). Additives such as kiln dusts, coal fly ash, blast furnace slag, and silica fume are sometimes utilized during cement-based S/S treatment with the intended effect of optimizing the pH of the wasteform to encourage precipitation.

Some inorganic contaminants are known to interfere with cement hydration reactions. When present in sufficient quantities, copper, lead, and zinc have all been shown to have a deleterious effect on the physical properties of cement-based S/S wasteforms (Shi and Spence 2005). However, undesirable effects caused by inorganic contaminants can usually be addressed in the mix design process for a specific material (Shi and Spence 2005).

2.2.2.2. Treatment of Organic Contaminants

S/S treatment of organic contaminants is generally viewed as more challenging than the treatment of inorganic contaminants with a field history containing both successes and failures (Bone et al. 2004). Common organic contaminants present in materials treated by cement-based S/S include pesticides, herbicides, petroleum products, polycyclic aromatic hydrocarbons (PAHs), volatile organic compound (VOCs), polychlorinated biphenyls (PCBs), and dioxins/furans (ITRC 2011). Due to differences in hydrophobicity and polarity, many organic compounds do not readily bond with cementitious materials. Instead, these compounds must be treated by the 'solidification' aspect of treatment as they are physically entrapped within the treated material (Arafat et al. 1999; ITRC 2011). Alternatively, they may be treated by additives that encourage sorption.

In some respects, materials impacted by organic contaminants are generally easier to remediate than those impacted by inorganic contaminants as their molecular structure can be altered to make them less hazardous or innocuous (Glasser 1993). Due to this, hazardous organic compounds are often more effectively treated by destructive or degradative treatments (e.g., oxidation, combustion) than by cement-based S/S. However, due to the fact that many contaminated sites (e.g., manufactured gas plant sites, wood-treating sites, refineries, oil recycling facilities, and pesticide/herbicide manufacturing plants) contain both organic and inorganic contaminants, significant efforts have been made to adjust cement-based S/S processes to more effectively treat organic contaminants (ITRC 2011).

The potential for organic compounds to retard hydration of cementitious materials is well documented (e.g., Eaton et al. 1987; Sheffield et al. 1987; Montgomery et al. 1991; Trussell and Spence 1994; Tremblay et al. 2002; and Stegemann 2005). This retarding effect is a complex function of both concentration and the presence of other organic compounds (Bone et al. 2004) but is often able to be solved at the mix design stage.

Sorption of organic compounds is largely thought to occur by partitioning on organic matter (Rowe et al. 2004). Although cement-based S/S wasteforms have a relatively high specific surface, the surfaces are generally polar and inefficient at sorbing the principally non-polar organic contaminants (Batchelor 2006). Clays, activated carbon, peat moss, zeolites, fly ash, organic polymers, rubber particulate, rice hull ash, and other natural materials have been used as sorbent additives which serve to adsorb and immobilize organic compounds (Arafat et al. 1999; Stegemann 2005). Once the organic contaminants are sorbed onto the surface of the sorbent, together they may be encapsulated in the soil-cement matrix (Arafat et al. 1999).

2.2.2.3. Laboratory and Field Testing

Most cement-based S/S projects require treatability studies and performance testing to ensure adequate performance of the final product. Typically, the only performance tests required by regulation or policy in the United States are unconfined compressive strength and extraction-type leaching tests (Wilk 2003). Ideally, the compliance tests chosen should be justified based on site-specific conditions and the requirements for the proposed site. The majority of common tests performed on cement-based S/S materials have been adopted or adapted from test methods initially designed for other materials (e.g., soil and concrete; Perera et al. 2005; ITRC 2011).

Bone et al. (2004) define leaching as “the transfer of a substance or compound from a solid to a liquid phase when the two are in contact”. Leaching is a complex phenomenon that occurs in nature as a result of physical and chemical processes. Both chemical (e.g., reactions at the surface) and physical (e.g., mass transport through the pore structure) effects significantly influence the rate of leaching from a cement-based S/S material (ITRC 2011). Numerous leaching tests have been employed to evaluate cement-based S/S materials; many of these tests are similar and differ in only minor ways such as leachant-leachate contact time, liquid/solid ratio, and leachate pH and composition (ITRC 2011). The aim of a leaching test is typically to quantify or estimate the amount or the rate of contaminant release that will occur from a cement-based S/s material in the field.

The performance of cement-based S/S wasteforms may be monitored both within and outside of the treated area. Drinking water standards are often used as an indirect means of monitoring this performance. For many sites in the United States, the USEPA's maximum contaminant level (MCL) or drinking water is used as a benchmark for leaching performance (Antemir et al. 2006). Typically, the treatment goal is for the concentration in the groundwater at a point of compliance (e.g., a monitoring well near the property boundary) to remain below a prescribed value (e.g., the MCL) in perpetuity (Antemir et al. 2006). The results of leaching and diffusion testing may be used to develop contaminant migration models which may further be used to estimate how much contaminant is available for transport and how it is expected it move through the subsurface over time.

Two distinct types of leaching tests are performed to evaluate the leaching potential of solidified materials: equilibrium (extraction) leaching tests and mass transfer (dynamic) leaching tests. The term "leachability" has taken on two different meanings depending on the type of leaching test being discussed. It may be used to describe either the extent of leaching (e.g., the percent of total contaminant that has been leached) or the rate of release of contaminant.

Equilibrium leaching tests are commonly performed on size-reduced (crushed) samples and aim to measure contaminant release related to specific chemical conditions (e.g., pH). The most common extraction-type leaching tests are the Toxicity Characteristic Leaching Procedure (TCLP; USEPA 2004b) and the Synthetic Precipitation Leaching Procedure (SPLP; USEPA 2004c) which are often the leaching tests required by regulation. Single-batch extraction procedures such as the TCLP and SPLP are broadly used as they are easy to conduct and yield results that are simple to interpret (ITRC 2011). However, since the samples are crushed before testing, these tests only result in a single data point and provide no understanding of the release-causing mechanisms or on the kinetics of leaching (ITRC 2011).

Although not used as frequently in industry (beyond nuclear applications), mass transfer leaching tests (e.g., ANS 16.1, American Nuclear Society 2003; EA NEN 7375:2004; BS EN 15863, BSI 2008) may be used to determine some information on the kinetics of leaching of soil-cement materials. Dynamic leaching tests are performed on intact cement-based S/S mixes. Although many different dynamic leaching tests are available, the procedures are generally similar; an intact specimen is placed in contact with a leachant (e.g., demineralized water) and the leachant is replaced at specific and predetermined time intervals. Often, this procedure is used to determine a diffusion coefficient. However, this parameter often varies temporally during the length of the test, a trend that suggests diffusion is not actually the primary mechanism being measured (Andrés et al. 1995). The results of dynamic leaching tests may be influenced by mechanisms such as dissolution or surface wash off, in which case an accurate estimation of the diffusion coefficient may not be obtainable (Malviya and Chaudhary 2006). Diffusion coefficients obtained from these tests may be orders of magnitude higher than the free-solution diffusion coefficient, D_o, which indicates that diffusion is not the controlling release mechanism (e.g., Pariatamby et al. 2006).

In some cases, different leaching tests may be used at various stages of design and implementation. For example, longer duration tests (i.e., mass transfer tests) are more appropriate in the pre-design or design stage than they are as compliance tests (ITRC 2011) where shorter-term tests (i.e., equilibrium tests) are more practical as quality-assurance tests. A summary of a selection of the most common leaching tests is presented in Table 2.2 (Paria and Yuet 2006).

Table 2.2 — Summary of leaching conditions for some common leaching tests (Modified from Paria and Yuet 2006).

Test Method	Leaching medium	Liquid/solid ratio by weight	Maximum particle size	Number of extractions	Time of extraction
TCLP	Acetic acid (pH ≈ 5 and 3)	20:1	9.5 mm	1	18 h
SPLP	Sulfuric/nitric acid (pH ≈ 4.2 and 5)	20:1	9.5 mm	1	18h
ANS 16.1	Water	V_L/S^a = 10cm	Intact specimen	10	Fixed time intervals
Extraction Procedure Toxicity Characteristic (EP Tox)	0.4 mol/L acetic acid (pH 5)	16:1	9.5 mm	1	24 h
California Waste Extraction Test (Cal WET)	0.2 mol/L sodium citrate (pH 5)	10:1	2.0 mm	1	48 h
Multiple Extraction Procedure	Same as EP Tox then synthetic acid rain (sulfuric acid: nitric acid in 60:40 wt% mixture)	20:1	9.5 mm	9 or more	24 h per extraction
Monofilled waste extraction procedure (MWEP)	Distilled/deionized water	10:1 per extraction	9.5 mm or monolith	4	18 h per extraction
Equilibrium leach test	Distilled water	4:1	150 µm	1	7 days
Acid neutralization capacity	HNO_3 solution of increasing strength	3:1	150 µm	1	48 h
Sequential extraction tests	0.04 mol/L acetic acid	50:1	9.5 mm	15	24 h per extraction
Sequential chemical extraction	Five leaching solutions increasing in acidity	16:1 to 40:1	150 µm	5	2 to 24 hours
International Atomic Energy (IAEA) standard leach method	Distilled water	V_L/S^a = 10cm	Monolith	12	Fixed time intervals

[a] Ratio of leachant volume (V_L) to specimen surface area (S).

2.2.3. Physical Pore Structure of Cementitious Materials

Although there is a paucity of information on the pore structure of cement-based S/S materials, the physical pore structure of concretes and cement pastes are generally well understood. Consequently, the information known about the pore structure of concretes and cement pastes may be used provide insight into the pore structure of other cementitious materials (e.g., cement-based S/S materials).

Porosity characteristics of cementitious materials are complex and dynamic as they simultaneously undergo changes due to both continuing hydration reactions and deterioration caused environmental exposure (Hearn et al. 2006). The relative amounts, size, and shapes of pores are known to affect the engineering properties (e.g., strength, durability, shrinkage, creep, permeability, and diffusivity) of concretes (Hearn et al. 2006). As the pore structure is constantly changing, the engineering properties can also be expected to change with time.

In concretes, the initial porosity is composed of the sum of the volume of the voids in the aggregate, the mixing water (water in the mixture in excess of that required for hydration), intentionally entrained air, and accidental air voids due to incomplete compaction (Hearn et al. 2006). As cementitious reactions occur, cement hydrates are formed which reduce the porosity as they expand to nearly double their initial volume into the water-filled spaced between cement grains and around the aggregate (Conner 1993; Hearn et al. 1993). Generally, cement-based S/S materials will not include air-entrainment and often contain relatively few aggregates (which also typically have low porosity). Therefore, much of the porosity can be expected to occur from mixing water and accidental air voids. Due to the various sources of porosity, the range of pore size distribution that occurs in cementitious materials is relatively large. Table 2.3 summarizes the different types and sizes of pores typically found in concretes.

Table 2.3 — Size distribution of pores and cracks (Hearn et al. 2006).

Type of Pore/Crack	**Typical Dimension (μm)**
Interlayer hydration space (gel pores)	0.001 to 0.03
Capillary voids	0.01 to 50
Entrained air	1 to 50
Entrapped air	1000 to 3000
Microcracks	1 to 60

Interlayer hydration space (i.e., gel pores) comprise the water-filled space between layers of calcium-silicate-hydrate gel (the main product formed by the hydration of Portland cement). These pores are small and have little impact on the engineering properties

(Hearn et al. 2006). Larger pores (>1 μm) tend to be caused by formulation (water-to-cement ratio) and processing (e.g., air bubbles) and have more substantial effect on the engineering properties.

Hearn et al. (2006) suggests that, in concretes, unintentional (air) voids can be avoided by ensuring adequate workability and compaction energy. Workability is affected by the quantity, size, and surface characteristics of the aggregate, the water-to-cement ratio, and the use of admixtures. Although increasing the water-to-cement ratio improves the workability, the porosity of concretes and cement pastes generally increase with increasing water-to-cement ratio due to the associated increase in the volume of capillary voids.

The formation of capillary voids depends on the initial packing of the cement grains against one another and against other surfaces (e.g., container walls and waste particulate matter) and the initial water-to-cement ratio (Glasser 1993). As the water-to-cement ratio increases, so does the percentage of capillary pores which may substantially affect the engineering properties (e.g., permeability and strength) of the final product. For a pure cement paste, a water-to-cement ratio of 0.25 contains sufficient water to achieve complete hydration but will not flow or be sufficiently workable without the addition of plasticizers (Glasser 1993). A water-to-cement ratio of 0.30 is considered critical for sufficient flow and workability, but more water is present than is chemically required for hydration. Water-to-cement ratios above this value increase the fluidity of the mixture but results in the inclusion of progressively more trapped porewater, increasing the pore space of the hardened product (Glasser 1993). It is expected that the water-to-cement ratios required for soil-cement materials will be higher as the soil will have some affinity for water, but the general trends should remain the same.

In practice, the window of applicable water-to-cement ratios where the material has sufficient mixability and does not produce bleed water may be relatively small (Glasser 1993). Water-to-cement ratio is important, but due to the nature of the material being treated, cannot be optimized for all cement-based S/S treatments. Often, the material being treated by cement has a high antecedent water content which inevitably results in high in-situ water-to-cement ratios (Conner 1993).

Microcracks may be caused by externally applied loads as well as due to stresses induced from drying, carbonation, or thermal gradients. The cracks are generally larger than most capillary pores and they may have a substantial effect on contaminant transport properties as they may provide continuous flow paths through the cement matrix (Hearn et al. 2006).

2.2.4. Contaminant Transport through Porous Media

Many decisions regarding contaminated sites are driven by contaminant concentrations (ITRC 2010). However, these decisions may be improved by also considering how contaminants are moving and are expected to move throughout the environment (i.e., contaminant transport). Contaminant transport analyses allow for the prediction and evaluation of performance and the prioritization of sites, and may also reduce remediation costs by identifying high-priority treatment areas (ITRC 2010). The ITRC (2010) lists several key questions contaminant transport estimates may help answer:

- How stable is a contaminant plume?
- How will a proposed remedial action affect the future distribution, transport, and/or fate of the contaminants?
- What will be the risks and exposures at various points and times?
- How much source remediation is required before transitioning to other technologies, or allowing natural attenuation to complete remediation?
- What are the options for optimizing existing remedial actions to reduce costs?

Although leaching tests aim to provide an estimate of the performance of a treated wasteform, the results of these laboratory tests typically do not provide sufficient information on how contaminants travel through the subsurface for use in contaminant migration analysis. The ITRC (2011) states that "*A remaining significant concern is how to relate leaching performance with established criteria at a point of compliance*" and proposes a method for developing material performance specifications for leaching tests based on mass transport. Among the conclusions of this document were:

- Mass flux and discharge estimates have been proven valuable for contaminated site management and should be used more frequently.
- The use of mass flux and mass discharge estimates will increase rapidly as the benefits of mass flux and discharge information are more widely recognized.
- Useful mass discharge and mass flux estimates often can be developed from existing site data or limited sampling, often for little cost.

The method proposed by the ITRC (2011) uses dynamic leaching tests to estimate contaminant migration. The laboratory tests are extrapolated to the field condition considering the exposed surface area of, and the rate of flow through, a monolithic wasteform. A roughly estimated "dilution-attenuation factor" is applied to the concentration to account for the dilution and attenuation that occurs between the wasteform and the point of compliance. Although the relative simplicity of this calculation makes it worthwhile, the rate of leaching from a flux-based test often changes with time throughout dynamic leaching tests (which complicates the interpretation of the results) and the dilution-attenuation factor is crudely estimated. Furthermore, parameters determined from flux-based leaching tests combine the effect of many processes. Even when the results are determined to be diffusion-controlled, the resulting retarded diffusion coefficient (D_R, to be discussed in more detail below) is not appropriate for certain boundary conditions (e.g., when a finite mass of contaminant is being modeled; Rowe et al. 2004).

Diffusion tests similar to those developed by for Rowe et al. (1988) for clayey soils, and discussed for a number of materials in Rowe et al. (2004), applied to cement-based S/S materials may be valuable when used in place of, or in conjunction with, mass transport methods like the one presented by the ITRC (2011). These diffusion tests offer a number of benefits, including allowing a direct comparison to work performed on other engineering materials (e.g., compacted clay liners, bentonite slurry walls, and geosynthetics) and independent estimations of sorptive and diffusive parameters.

2.2.4.1. Advection and Dispersion

From a contaminant migration perspective, advection, or advective transport, is the movement of contaminant with flowing groundwater due to a hydraulic gradient (Sharma and Reddy 2004). The groundwater seepage velocity for one-dimensional steady-state flow may be described by Darcy's law (Rowe et al. 2004):

$$v = \frac{ki}{n_e} \tag{2-1}$$

Where: k is the hydraulic conductivity [LT^{-1}], n_e is the effective porosity [-], and i is the hydraulic gradient [-]. In this chapter, square brackets denote the fundamental dimensions mass [M], length [L], and time [T] for dimensionally consistent equations.

The effective porosity is defined as the ratio of the volume of void space that conducts flow, divided by the total volume. Due to the fact that not all void space conducts flow, the effective porosity is always equal to or less than the total porosity. The one-dimensional steady-state mass flux (contaminant per unit area per unit time) transported by advection may be expressed by Equation 2-2 (Rowe et al. 2004).

$$f_a = n_e v c \tag{2-2}$$

Where: f_a is the advective mass flux [$ML^{-2}T^{-1}$] and c is the concentration of contaminant [ML^{-3}].

Dispersion is a transport mechanism associated with high flows and relatively high permeabilities such as those found in aquifers (Rowe et al. 2004). Dispersion is caused by mixing and spreading due to variations in the velocity of the groundwater due to convoluted flow pathways. The amount of dispersion that occurs is typical directly proportional to the groundwater velocity (Rowe et al. 2004). In diffusion-controlled systems with low advective flux and low groundwater velocities, contaminant transport due to dispersion is generally negligible (Rowe et al. 2004; Malviya and Chaudhary 2006).

2.2.4.2. Diffusion

Diffusion is the process that describes the movement of solutes in a solution in response to a concentration gradient. Fick's first law (Equation 2-3) states that for free solutions; one-dimensional diffusive flux is proportional to the concentration gradient (Daniel and Shackelford 1988).

$$f_d = D_o \frac{dc}{dz} \tag{2-3}$$

Where: f_d is the diffusive mass flux, D_o is the free-solution diffusion coefficient, c is the concentration of the solute, and dc/dz is the concentration gradient. D_o, represents the maximum rate of diffusion a species can experience under ideal conditions (i.e., over a microscopic scale, in pure water at infinite dilution; Daniel and Shackelford 1988; Rowe et al. 2004). Under non-ideal conditions (e.g., macroscopic scale, concentrated solutions) a number of other effects influence diffusion (e.g., electroneutrality, solute-solute, and solute-solvent interactions; Daniel and Shackelford 1988).

When diffusion occurs through a porous media, the diffusing contaminant is unable to move in a straight line but is forced to diffuse through tortuous, irregular, paths (Rowe et al. 2004). As these pathways are too complex to measure directly, a measure of their effect on the diffusing particles, the tortuosity (τ), is often determined indirectly. Although not strictly true, tortuosity is often thought of as a sort of physical retardation that is a property of the solid matrix (be it monolithic or comprised of compacted granular materials). Tortuosity is often described as the ratio of the distance a species travels along a winding path between two points to the straight-line distance between those same points. However, measured values of tortuosity are actually complex factors that consider not just increased length of flow path but also: changes in fluidity, and electrostatic interactions due to the presence of solid particles (Rowe et al. 2004). The effective diffusion coefficient, D_e, is related to D_o by the tortuosity factor, τ, as shown in Equation 2-4 (Rowe et al. 2004).

$$D_e = \tau D_o \tag{2-4}$$

Fick's first law may be used to describe the diffusive mass flux (f_d) [$ML^{-2}T^{-1}$] through porous media (Equation 2-5; Rowe et al. 2004).

$$f_d = -n_e D_e \frac{dc}{dz} \tag{2-5}$$

Where: n_e is the effective porosity [-], D_e is the effective diffusion coefficient [L^2T^{-1}], and dc/dz is the concentration gradient. The negative sign in Equation 2-5 is required due to the fact that the dc/dx term is taken as negative by convention.

Fick's second law describes how diffusion causes concentrations to change with time (Equation 2-6):

$$\frac{dc}{dt} = -n_e D_e \frac{d^2c}{dz^2} \qquad (2\text{-}6)$$

Equation 2-6 may be integrated for appropriate initial and boundary conditions to obtain a description of the solute concentration changes with respect to time and space.

Many experimental approaches determine a retarded diffusion coefficient, D_R, which is a combined measure of diffusion, volumetric water content, and sorption by the convention used herein. Unfortunately, the literature is not consistent in its definition and naming of diffusion coefficients so this parameter may be referred to by number of terms (e.g., apparent diffusion coefficient, effective diffusion coefficient). In general, this thesis uses the terminology suggested by Rowe et al. (2004).

2.2.4.3. Sorption

Sorption is a term that refers to a number of processes including adsorption (the binding of molecules or particles to a surface), absorption (the incorporation of molecules or particles in a solid matrix), ion exchange, and any other process which removes chemicals from solution and associates them with solid phases (Schwarzenbach et al. 2003; Rowe et al. 2004). In the simplest case, sorption may be modeled as both linear and reversible (Equation 2-7; Rowe et al. 2004). This linear sorption model assumes that at any given time the concentration of solute sorbed to solids is directly proportional to the concentration of the solute in solution.

$$S = K_d c \qquad (2\text{-}7)$$

Where: S is the mass of solute removed from solution per unit mass of solid [-]; K_d is the distribution coefficient [$M^{-1}L^3$] and c is the equilibrium concentration of solute [ML^{-3}]. It is often appropriate to use this simple model when concentrations are low or there is high sorbent intake since the relationship between S and c is approximately linear under these conditions. Other models (e.g., Langmuir, Freundlich) are used to describe non-linear relationships that exist for higher concentrations and low sorbent intake.

For organic contaminants, K_d is often found to be a function of the hydrophobic character of the organic compound and the amount of organic matter present and may be expressed by Equation 2-8 (Mohamed and Antia 1998).

$$K_d = K_{oc} f_{oc} \tag{2-8}$$

Where: K_{oc} is the partition coefficient of a compound between organic carbon and water $[L^3M^{-1}]$, and f_{oc} is the fraction (by mass) of organic carbon in the medium. Relationships have been developed to relate the organic carbon partition coefficients from physiochemical properties such as the octanol-water partition coefficient (Karickhoff et al. 1979).

2.2.4.4. Decay

Losses due to biological and radioactive decay may typically be modeled as first order decay (Mohamed and Antia 1998). In this case, the rate of reduction of concentration is proportional to the current concentration and may be expressed by Equation 2-9:

$$\frac{dc}{dt} = -\lambda c \tag{2-9}$$

Where: c is concentration [-], t is time [-], and λ is the first order decay constant $[T^{-1}]$.

2.3. ONE-DIMENSIONAL CONTAMINANT TRANSPORT EQUATION

Combining the equations for advective flux, diffusive flux, dispersion, sorption, and decay results in the transient expression for one-dimensional contaminant transport through intact porous material (Equation 2-10; Rowe et al. 2004).

$$n_e \frac{\partial c}{\partial t} = n_e D_e \frac{\partial^2 c}{\partial z^2} - n_e v \frac{\partial c}{\partial z} - \rho_d K_d \frac{\partial c}{\partial t} - n_e \lambda c \tag{2-10}$$

When neglecting decay, this equation is sometimes rearranged to the form shown in Equation 2-11 (Rowe et al. 2004):

$$\frac{\partial c}{\partial t} = D_R \frac{\partial^2 c}{\partial z^2} - v_R \frac{\partial c}{\partial z} \tag{2-11}$$

Where: D_R and v_R are defined by Equations 2-12 and 2-13:

$$D_R = \frac{D_e}{1 + \frac{\rho K_d}{n_e}} \tag{2-12}$$

$$v_R = \frac{v}{1 + \frac{\rho K_d}{n_e}} \tag{2-13}$$

Although this procedure to simplify the one-dimensional contaminant transport equation is frequently used, and is mathematically correct, it is not generally appropriate for flux controlled (constant mass) boundary conditions and thus the universal use of Equation 2-12 and Equation 2-13 (and the use of v_R and D_R) is often discouraged (e.g., Rowe et al. 2004).

In porous media with low advective flux (less than approximately 0.03 m^2/s), as may be expected from landfill liners, slurry walls, and many cement-based S/S wasteforms, the rate of contaminant migration is expected to be largely controlled by diffusion (Rowe et al. 2004). Stegemann and Côté (1991) suggest that for cement-based S/S wasteforms, the rate of contaminant release is likely to be diffusion-controlled when the hydraulic conductivity of the wasteform is less than approximately 1×10^{-9} m/s.

In fractured media, as may be the case for weathered cement-based S/S wasteforms, contaminants are likely to move relatively quickly along the fracture openings. However, diffusion may play a role as diffusion from the soil-cement matrix into the fractures (i.e., matrix diffusion). Matrix diffusion has been shown to be an important mechanism in limiting the movement of contaminant as it moves through fractured bedrock (Freeze and Cherry 1979; Barone et al. 1992a). Intact rock generally has a low hydraulic conductivity and contaminant migration primarily occurs by advective-dispersive transport along the fractures. This process creates a concentration gradient between the porewater in the fracture, and the adjacent porewater in the intact material. Contaminant may be removed from the fractures as diffusion drives the contaminant from the fractures into the intact rock matrix (Rowe et al. 2004). A similar process may be expected to occur in some weathered cement-based S/S materials. At times, there may be a substantial concentration gradient between any fractures and the intact soil-cement matrix. As leaching progresses, due to the ingress of water, the concentration of contaminant in the fracture may become lower than that in the matrix and diffusion from the matrix into the fractures may become an important mechanism in contaminant migration.

2.4. DIFFUSION COEFFICIENTS FOR SOILS AND ROCKS

There is a significant amount of information available on the diffusive properties of fine-grained soils and rocks. This information is largely due to the influence of diffusion on the performance of landfills (for soil) and deep geological deposits for nuclear wastes (for rock). A summary of diffusion coefficients on various soils (primarily clays) for a variety of contaminants is presented by Rowe et al. (2004). Some typical values of diffusion coefficients for soils, rocks, and other geomaterials (i.e., soil-bentonite slurry walls, and geosynthetic clay liners) are presented in Table 2.4.

Table 2.4 — Typical effective diffusion coefficients for selected geomaterials.

Material	Contaminant	D_e (m^2/s)	Author
Saturated inactive clays	Various	1×10^{-10} to 7×10^{-10}	Rowe et al. (2004)
Geosynthetic clay liners (GCLs)	Sodium, Chloride	5×10^{-11} to 5×10^{-10}	Lake and Rowe (2000)
Soil and bentonite slurry walls	Trichloroethylene	3.4×10^{-10} to 4.2×10^{-10}	Krol and Rowe (2004)
Intact shale	Chloride	1.4×10^{-10} to 1.6×10^{-11}	Barone et al. (1990)

2.5. DIFFUSION COEFFICIENTS FOR CEMENT-BASED MATERIALS

Diffusion through structural concretes (e.g., Page and Treadaway 1982; Luping and Sørensen 1998), cement mortars and pastes (e.g., Spinks et al. 1952; Goto and Roy 1981), and composite concrete and cementitious chemical barriers (e.g., Ganjian et al. 2004; Claisse et al. 2006) is relatively well studied. Although there has been work investigating the leaching behavior of soil-cement materials for a specific mix design (e.g., Malviya and Chaudhary 2006) there is a paucity of literature investigating the effects of varying mixture characteristics on the diffusion and porosity properties of soil-cement materials.

Soil-cement materials and their pore structure are appreciably different from concretes, cement mortars, cement pastes, and other cementitious materials. Although it can be expected that these materials all have different pore structures and contaminant migration properties due to their different composition, there is value in discussing these similar materials due to the paucity of literature of diffusive properties of soil-cement products.

Due to the potential for chloride to cause corrosion of reinforcing steel there has been a significant amount of research regarding chloride diffusion through structural concretes (e.g., Kayali and Zhu 2005; Vedalakshmi et al. 2008). This is often measured using tests such as ASTM C1556-04 which results in a retarded diffusion coefficient, $D_{R,}$ (although it is referred to as an apparent diffusion coefficient, by the test procedure). The results of several studies on cementitious materials are presented in Table 2.5. When considering the data presented in Table 2.5, one should keep in mind that the value of D_R is typically less than the value of D_e due to the reducing effects sorption and volumetric water content which are incorporated in the latter.

Table 2.5 — Diffusion coefficients for various cementitious materials.

Contaminant	**D_e (m^2/s)**	**Binder/Material**	**Author**	**Test Method**
Tritiated water	4.4×10^{-10}	Hardened cement paste	Tits et al. 2003	Through/Out Diffusion
$^{22}Na^+$	1.8×10^{-10}	Hardened cement paste	Tits et al. 2003	Through/Out Diffusion
Contaminant	**D_R (m^2/s)**	**Binder/Material**	**Author**	**Test Method**
Phenol	3.2×10^{-13}	OPC-Sand	Hebatpuria et al. 1999	ANS 16.1
Naphthalene	1.3×10^{-13} to 2.0×10^{-114}	OPC-Sand	Hebatpuria et al. 1999	ANS 16.1
Cesium 137	3.1×10^{-13}	OPC Paste	Rahman et al. 2007	IAEA
Cesium 137	2.6×10^{-15}	OPC-Red Clay	Rahman et al. 2007	IAEA
Cesium 137	1.8×10^{-16}	OPC-Bentonite	Rahman et al. 2007	IAEA
Cobalt 60	1.4×10^{-13}	OPC Paste	Rahman et al. 2007	IAEA
Cobalt 60	1.0×10^{-15}	OPC-Red Clay	Rahman et al. 2007	IAEA
Cobalt 60	6.6×10^{-12}	OPC-Bentonite	Rahman et al. 2007	IAEA
Europium 152,154	1.4×10^{-15}	OPC Paste	Rahman et al. 2007	IAEA
Europium 152,154	8.6×10^{-18}	OPC-Red Clay	Rahman et al. 2007	IAEA
Europium 152,154	8.6×10^{-18}	OPC-Bentonite	Rahman et al. 2007	IAEA
Na^+	3.0×10^{-12}	Soil-Cement	Tiruta-Barna et al. 2006	DML[c]
K^+	4.5×10^{-11}	Soil-Cement	Tiruta-Barna et al. 2006	DML[c]
Ca^{2+}	5.0×10^{-12}	Soil-Cement	Tiruta-Barna et al. 2006	DML[c]
Naphthalene	2×10^{-11} to $4\times10^{-12(a)}$	Soil-Cement	Tiruta-Barna et al. 2006	DML[c]
Phenanthrene	3.0×10^{-12}	Soil-Cement	Tiruta-Barna et al. 2006	DML[c]
Na^+	9.7×10^{-12}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
K^+	2.4×10^{-11}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Cl^-	4.7×10^{-11}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
SO_4^{2-}	3.3×10^{-12}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Ca^{2+}	1.3×10^{-13}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Pb^{2+}	1.1×10^{-12}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Zn^{2+}	8.2×10^{-15}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Fe^{2+}	4.3×10^{-12}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Mn^{2+}	2.9×10^{-12}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Cu^{2+}	9.7×10^{-13}	Soil-Cement	Malviya and Chaudhary 2006	NEN 7345
Contaminant	**$D_p = n_e \times D_e$ (m^2/s)**	**Binder/Material**	**Author**	**Test Method**
Tritiated water	1.4×10^{-11} to 8.7×10^{-11}	Cement Paste	Yamaguchi et al. 2009	Through diffusion
Tritiated water	1.1×10^{-13} to 9.8×10^{-12}	Mortar	Delagrave et al. 1998	Through diffusion

[a] Tests were performed with varying concentrations of methanol and water as co-solvents.
[b] This value represents the average of ten tests over a range of waste/binder and water/solid ratios.
[c] Dynamic monolithic leaching test (Tiruta-Barna et al. 2003).

2.6. SUMMARY AND CONCLUSIONS

Cement-based S/S treatment is a source-controlled remediation technology that is used to treat materials impacted by both organic and inorganic contaminants by reducing the risk to humans and the environment. Cement-based S/S treatment generally aims to reduce contaminant migration by altering the physical and chemical properties of the treated materials. Additives (e.g., fly ash) are sometimes used to improve performance (e.g., increase sorption).

Cement-based S/S does not typically destroy contaminants and will not prevent them from entering the surrounding environment in perpetuity; the objective is to reduce the effects on human health and the environment to an acceptable level by slowing their release into the environment. This is accomplished by physically and chemically immobilizing the contaminants within the wasteform. Cement-based S/S treatment generally results in a material with an increased compressive strength and a decreased permeability. In many cases, the hydraulic gradient and hydraulic conductivity may be reduced to values that make diffusion the dominant transport mechanism. Theoretical modeling allows the potential impact of the proposed treatment to be quantified. The 1D contaminant migration equation, which includes terms to represent advection, diffusion, sorption, and decay, may be used in contaminant migration analyses.

Although there is a paucity of literature on the physical pore structure of soil-cement materials, the pore structure of a number of other cementitious materials is relatively well understood. The size and shape of the pores are known to have an effect on the engineering properties of porous media (Mitchell 1993; Hearn et al. 2006) and it is anticipated that this is also true for soil-cement materials.

Historically, there has been limited study and consideration of the diffusive properties of cement-based S/S wasteforms as research and development has largely focused on the stabilization (i.e., chemical treatment) of contaminants. Diffusion has been shown to play a significant role in contaminant migration for other low-hydraulic conductivity materials, and is expected to be an important mechanism for contaminant migration for some cement-based S/S materials. Thus, it is important to have methods to measure or estimate the diffusive properties of soil-cement materials.

Although numerous leaching tests have been used to assess the performance of cement-based S/S materials, these tests typically do not provide sufficient information to extrapolate the results of the tests to field-scale contaminant migration. Diffusion tests similar to the tests presented by Rowe et al. (1988), which yield separate parameters for diffusion and sorption may be valuable to develop parameters that can be used in contaminant migration assessments. Additionally, parameters determined from these tests may easily be compared with those determined for other materials.

CHAPTER 3: CHARACTERIZING POROSITY AND DIFFUSIVE PROPERTIES OF MONOLITHIC CEMENT-BASED SOLIDIFIED/STABILIZED MATERIALS[1]

3.1. INTRODUCTION

Solidification/stabilization (S/S) is a contaminant source-control technology which aims to protect human health and the environment by reducing the migration of hazardous constituents from a contaminated material. Ideally, in S/S treatment, a binder is mixed with waste or contaminated environmental media to create a less hazardous wasteform. This may be achieved by reducing the solubility or mobility of harmful contaminants (Bone et al. 2004; Shi and Spence 2005).

Cement-based S/S involves the immobilization of potentially harmful components of a material through chemical and physical interactions using a cementitious binder. The term “solidification” refers to changes in the physical properties of the contaminated material (Bone et al. 2004; Batchelor 2006). Effects of solidification include an increase in compressive strength, a lower permeability, and physical encapsulation of contaminated material in the solidified matrix (Batchelor 2006). The term “stabilization” refers to the adsorption and chemical reaction of contaminants and reagents to produce a less soluble wasteform (Paria and Yuet 2006). There is a significant body of literature discussing the stabilization aspect of S/S treatment (i.e., chemical interactions between the binder and constituents of interest), particularly with respect to the stabilization of metals (Conner 1990; Bone et al. 2004; Paria and Yuet 2006). Conversely, there has been relatively little examination of the solidification aspect of S/S treatment. In many cases, consideration of the solidification aspect of treatment is restricted to assessment of the

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[1] A version of this chapter has been published:
Goreham, V., Lake, C.B., and Yuet, P.K., 2012, “Characterizing Porosity and Diffusive Properties of Monolithic Cement-Based Solidified/Stabilized Materials,” *Geotechnical Testing Journal*, Vol. 35, No. 4, pp. 529–538.

hydraulic conductivity and unconfined compressive strength; there has generally been limited consideration of the diffusive properties of cement-based S/S wasteforms.

For porous media with low hydraulic conductivities (e.g., landfill liners, slurry walls, and many cement-based S/S wasteforms) contaminant migration may be largely controlled by diffusion (Conner 1990; Rowe et al. 2004). Specifically, Stegemann and Côté (1991) suggest that for cement based S/S wasteforms, the infiltration of water is expected to be negligible and the rate of a contaminant release is likely to be governed by diffusion when the hydraulic conductivity of the cement S/S material is less than approximately 10^{-9} m/s. Hydraulic conductivities near or below this value are technically achievable for many cement-based S/S projects, although these values may not always be achieved in practice. In fractured media, as may be the case for weathered cement-based S/S wasteforms, contaminants are likely to move by advective dispersive transport along the fractures. In this case, the diffusive flux from the cement-based S/S matrix into the fractures (i.e., matrix diffusion) may be an important contributor to contaminant migration. In either case, an accurate assessment of the diffusive properties may provide support for both the predesign (technology selection) phase and for long-term contaminant migration modeling.

If long-term contaminant migration assessments of these materials are to be performed, it is important to have proper methods for testing the diffusive properties of cement-based S/S wasteforms. Ideally, parameters obtained from these testing methods should be consistent with conventional design parameters used for other materials so that different treatment options may be directly compared and the effects of combined treatment methods (e.g., combined cement-based S/S wasteforms with slurry walls) may be analyzed.

The purpose of this chapter is to show that a relatively simple, single-reservoir, diffusion test based on previous work for clayey soils by Rowe et al. (1988) may be used to evaluate the diffusive properties of cured, monolithic, cement-based S/S specimens. The method presented is for tritiated water, a conservative tracer, but may be modified for other inorganic or organic contaminants. The purpose of using a conservative tracer in this study is to allow for a determination of the physical properties of the cement-based S/S wasteform independent of significant chemical interaction. One advantage of using such a test is that it can be performed in a matter of weeks yet obtain porosity and diffusion parameters that may be used to model long-term contaminant transport through cement-based S/S materials for hundreds of years, provided the physical integrity of the treated material does not change.

3.2. BACKGROUND

Since the diffusion test presented herein is performed with no hydraulic gradient and a conservative tracer, the transient expression for one-dimensional diffusive transport through an intact, porous specimen may be described by Equation 3-1 (Rowe et al. 2004):

$$n_e \frac{\partial c}{\partial t} = n_e D_e \frac{\partial^2 c}{\partial z^2} - n_e \lambda c \tag{3-1}$$

Where: n_e is the effective porosity [-], c is the concentration in the specimen at depth z and time t [ML^{-3}], D_e is the effective diffusion coefficient [L^2T^{-1}], and λ is the first order decay constant of the contaminant species [-]. In this chapter, square brackets denote the fundamental dimensions mass [M], length [L], and time [T] for dimensionally consistent equations.

This equation is often written without the final term which is only necessary if the contaminant undergoes decay (e.g., the radioactive decay occurring in tritiated water). The term n_e used in Equation 3-1 represents the effective porosity available for transport during the duration of the laboratory test. Implicit with the use of the effective porosity n_e on the left-hand side of Equation 3-1 is the assumption that a portion of the porosity is entirely inaccessible to the diffusing substance. It is possible that for longer-term tests, the calculated effective porosity may increase slightly as diffusive transport occurs into and through some of the pores which are inaccessible for the duration of the tests discussed herein.

There has been a significant amount of work investigating diffusion through soils (e.g., Dutt and Low 1962; Kemper and Van Schaik 1966; Lai and Mortland 1961; Gillham et al. 1984). Similar methods have also been used in the study of diffusion through geosynthetic clay liners (GCLs; Lake and Rowe 2000), soil-bentonite slurry walls (Krol and Rowe 2004), and rock (Barone et al. 1989; Gurumoorthy and Singh 2004). Due to the potential for chloride to cause corrosion of reinforcing steel, there has been substantial research concerning the diffusion of chloride through concretes and cement pastes (e.g., Spinks et al. 1952; Page et al. 1981; Page and Treadaway 1982; Luping and Sørensen 1998). Contaminant movement through cementitious materials has been quantified using tests such as ASTM C1556-04 (2004), which results in a single parameter that represents diffusion, sorption, and porosity. This is referred to as an apparent diffusion coefficient D_a by the test procedure but is often referred to as a retarded diffusion coefficient D_R by other researchers (e.g., Rowe et al. 2004).

To shorten the testing time required, rapid chloride permeability tests have been developed (e.g., AASHTO T277-07 2007; ASTM C1202-10 2010). These standards specify the rating of chloride permeability (from negligible to high) based on the electrical charge passed through a specimen subject to a dc voltage (60 V) over a relatively short amount of time (6 hours). Although the results from these types of tests have been used to infer diffusion coefficients for cementitious materials, this has generally been discouraged in the literature (e.g., Andrade 1993; Feldman et al. 1994; Snyder et al. 2000; Shi 2005). Essentially, these test methods result in a measurement of the electrical conductivity of concrete, which depends largely on the pore solution chemistry (Andrade 1993; Shi 2005). The results of the test may be greatly influenced by factors that have little effect on chloride transport which may lead to misleading or invalid conclusions (Snyder et al. 2000; Shi 2005). Furthermore, changes to the pore fluid and microstructure imposed by the test itself, influences the results (Feldman et al. 1994).

Dynamic leaching tests are often performed on intact cement-based S/S specimens. When performing a dynamic leaching test, the specimen is placed in contact with a leachant that is replaced at specific, predetermined time intervals and the concentration of the contaminant in each removed sample of leachant is measured (Garrabrants and Kosson 2005). This process allows for an approximate determination of a retarded diffusion coefficient D_R which often varies temporally during the test, a trend that indicates diffusion is not always the primary mechanism being measured (Andrés et al. 1995). Often the results are governed by mechanisms such as dissolution or surface wash off (Malviya and Chaudhary 2006). Some common dynamic leaching tests include ANSI/ANS 16.1 (American Nuclear Society 2003), EA NEN 7375 (2004), and BS EN 15863 (British Standards Institution 2008). The fact that D_R is a single parameter representing both diffusive and sorptive properties is not ideal when trying to extend results to other contaminants and also is not appropriate for the finite mass boundary conditions used in the test method described below (Rowe et al. 2004).

3.3. LABORATORY PROCEDURE

The basis of design for the diffusion test method presented below is from similar testing that has been developed for clays (Rowe et al. 1988) and rock (Barone et al. 1989). In these tests, a reservoir of the fluid of interest is placed above a saturated porous medium. In the tests performed herein, the fluid is a 10 megabecquerel (MBq) per litre (L) solution of tritiated water. One Bq is defined as the activity of a quantity of radioactive material in which one nucleus decays per second. As the tritiated water is allowed to migrate into the specimen (in the absence of a hydraulic gradient), a concentration profile is developed through the specimen. Measurements of the concentration profile and the change in source concentration with time allow determination of an effective diffusion coefficient (D_e) and effective porosity (n_e).

3.3.1. Development of Diffusion Apparatus

Tritiated water was chosen as the tracer for this study as it has no charge, is readily soluble, and has shown negligible interaction with soil particles (Rowe et al. 2004) and cement hydrates (Delagrave et al. 1998). As will be discussed in more detail below, various test parameters were input into a 1D finite layer contaminant migration program, POLLUTE v6 (Rowe et al. 1998), to determine an appropriate size for the diffusion apparatus. Properties assumed for this initial modeling included a tritium half-life of 12.32 years (Lucas and Unterweger 2000), a D_e of 2.0×10^{-10} m^2/s, and an n_e of 0.20.

A specimen length of 150 mm was chosen for testing so the specimen could be divided into eight adequately sized sections at the conclusion of the test. From a feasibility perspective, a test time of less than one month was desirable. To investigate the influence of testing time and specimen length on tritiated water concentration profiles in the prepared materials, modeling was performed using the assumed diffusion parameters ($D_e = 2.0\times10^{-10}$ m^2/s, and $n_e = 0.20$). Figure 3.1(a) presents the theoretical final diffusion profile through the specimen (normalized to the initial concentration c_o) for the assumed diffusion parameters after test durations of 7, 14, 28, 56, and 84 days, considering a source reservoir volume of 100 mL with twice-weekly 50-µl sampling. As can be seen in Figure 3.1, modeled test times of more than one month (56 and 84 days) resulted in tritiated water approaching the base of the specimen. At modeled test times less than one month (7 and 14 days), the tritiated water had migrated less than 50 % of the depth of the specimen. Additional modeling indicated that the proposed cell geometry and a 28-day test duration were suitable for testing materials within the range of reasonably expected values of n_e and D_e.

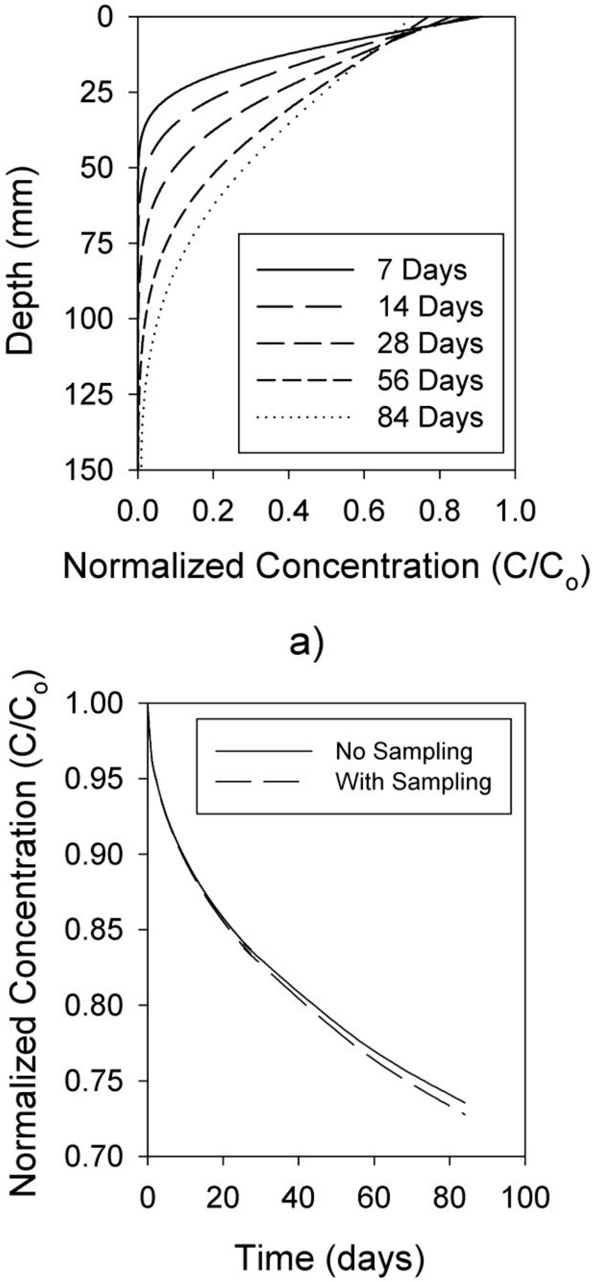

Figure 3.1 — Theoretical normalized concentration distribution based on $D_e = 2.0\times10^{-10}$ m^2/s and $n_e = 0.20$. a) Concentration profile changing with time b) reservoir concentration with and without sampling (modified from Goreham et al. 2010).

The source reservoir volume of 100 mL was chosen so that the diffusion of tritiated water into the specimen would decrease the concentration in the source reservoir by at least 15 %. This 15 % reduction was judged to be outside the range of any analytical reproducibility issues (estimated as 5 % based on an assessment of the analytical method). Modeling revealed that larger source reservoir volumes resulted in source concentration reductions of less than 15 %. A source reservoir volume significantly smaller than 100 mL would have created some practical sampling issues (i.e., small fluid heights on the specimen). The sampling rate from the source reservoir (50 µl twice weekly) was chosen to balance the ability to obtain frequent tritium concentration measurements and to minimize mass removal from the system (although this mass removal was accounted for by the model). Figure 3.1(b) presents theoretical modeling of the normalized source reservoir concentration with, and without, sampling. Inspection of Figure 3.1(b) shows that the source concentration would be reduced to less than 82.5 % of c_o after 28 days for the assumed parameters. Figure 3.1(b) also shows the almost unobservable effect of sampling on the source reservoir concentration over the first 28 days of testing.

Finally, it was determined that a tritium concentration of approximately 10 MBq/l was sufficient to provide acceptable accuracy in liquid scintillation counting while otherwise minimizing the use of, and thus worker exposure to, tritiated water.

Based on these design parameters, a diffusion cell was constructed out of polyvinyl chloride. The cell design is shown in Figure 3.2. The 70-mm inside diameter of the diffusion cell was designed to tightly fit around the prepared specimens. There is a sampling port in the centre of the cover such that routine sampling (using an automatic pipette) of the source reservoir may be easily performed. A similar opening in the bottom of the cell was sealed with a hex screw (with polytetrafluoroethylene tape on the threads to prevent leakage) that was left in during the duration of the test. The hex screw was removed at the beginning and end of the test to facilitate specimen insertion and removal.

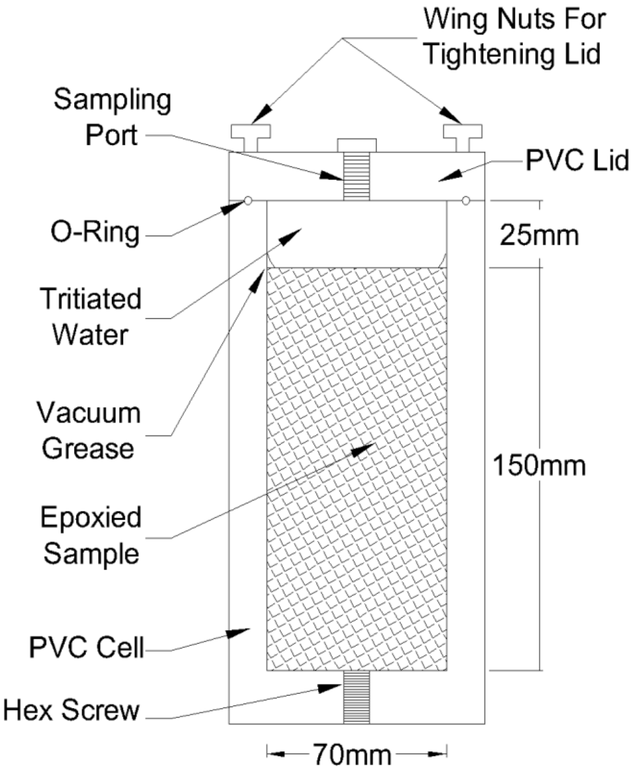

Figure 3.2 — Schematic of the diffusion test apparatus used in this study.

3.3.2. Specimen Preparation

Specimens were prepared by mixing 80 % silica sand with 20 % kaolinite (by dry mass) in a 20 L plastic bucket. Water was added to result in a 13 % water content, corresponding with the standard-proctor optimum water content of the sand-kaolinite blend. The sand-kaolinite blend, classified as SC by the Unified Soil Classification System (ASTM D2487 2010), was mixed using a combination of a large scoop, a tamping rod, and drill with paint mixer attachment. A cement paste at a 1:1 water-to cement ratio was mixed until homogeneous using the drill and paint mixer attachment. CSA type 10, general use, Portland cement provided by Holcim Cement was used to formulate the grout. Immediately upon completion of mixing, the cement paste was added to the sand-kaolinite blend to result in a cement content of 15 % (by dry mass of sand-kaolinite blend). The grout and sand-kaolinite blend were thoroughly mixed together using the same tools described above. The overall percentages (on both a total mass and total dry mass basis) of each material used in the mixture are shown in Table 3.1. It is acknowledged that there exists a wide variety of potential combinations of soil mineralogy, soil grain-size distributions, cement contents, and water contents that make up cement-based S/S products in practice. The combination of soil, cement, and water used in this research were chosen to ensure consistent mineralogy and grain size distribution for experimental purposes and to ensure that the materials could be thoroughly mixed with the laboratory equipment.

Table 3.1 — Proportions of materials used in mix design.

Material	Percent of Total Wet Mass	Percent of Total Dry Mass
Cement	10.5	13.0
Sand	56.0	69.6
Clay	14.0	17.4
Water	19.5	24.3

After mixing, six replicate specimens were promptly cast in 150-mm-long molds cut from 70-mm diameter Shelby tubes. A base for these molds was created using a sheet of plastic, taped firmly in place. Three replicate specimens (labeled a, b, and c) were used for diffusion testing and three additional specimens were used as “dummy” specimens to determine physical properties of the solidified material (e.g., specific gravity, density, water content).

To prevent the specimens from adhering to the molds, a 0.5-mm-thick insert made of cellulose acetate was placed around the inside surface of each mold prior to casting. Each specimen was placed in three layers of equal thickness with each layer corresponding to approximately one third of the total volume. As suggested by Stegemann and Côté (1991), evenly distributed tamping over the cross section of the molds was performed after placement of each layer. Each layer was tamped 21 times with pressure just sufficient to ensure uniform filling of the mold (to remove any pockets of air). The molds were filled until the mixture extended slightly above the top, and the specimens were cut flush with a wet trowel using a gentle sawing motion. Immediately after casting all specimens were placed in separate, tightly sealed plastic bags and stored at 21(±2) °C. After 7–14 days, specimens were gently extruded from their molds and promptly returned to the plastic bags where they were allowed to cure for a minimum of 12 weeks at the same temperature prior to testing.

3.3.3. Water Content, Porosity, Bulk Density, and Specific Gravity Measurements

As will be discussed in detail below, at the completion of each diffusion test, the specimen was cut into sections and crushed. Tritiated water in the crushed sample was then extracted using a "wash" of distilled water. To properly account for the diluting effect of the wash it is important to know the initial amount of water in the sample. However, due to radiation safety concerns, samples containing tritium could not be oven dried to determine the water content. For water content determination, three dummy specimens were made at the same time as diffusion test specimens, from the same materials, subject to the same curing times and conditions, and saturated using the same procedure as the specimens outlined for diffusion testing (discussed below). To measure water content (w) after saturation, the outside of the specimens were patted dry and weighed. The specimens were then allowed to dry in an oven at 115 °C to a constant mass (1 day) and weighed again. The average w for the three dummy specimens was 0.22. The authors acknowledge that drying cementitious materials at this temperature may evaporate some water of hydration, but for the purposes of determining the mass of water in the specimen which contributes to the wash, it is appropriate to include this water in the concentration calculations.

The specific gravity ($G_s = 2.61$) of the oven-dried and crushed (to grain-size < 2 mm) dummy specimens were tested by the Minerals Engineering Centre, Dalhousie Univ., using helium pycnometry with a (Quantachrome) stereopycnometer. Knowing the total volume of the specimens (geometrically) also allowed for estimation of the average total porosity n (0.37), void ratio e (0.58), average saturated bulk density ρ (2003 kg/m^3), and average dry density, ρ_d (1636 kg/m^3), of the three dummy specimens.

3.3.4. Saturation

Just prior to testing, specimens were saturated in the flexible-wall permeameter in general accordance with ASTM D-5084-10 (2010). Initially, a confining stress of 76 kPa (11 psi) and a back-pressure of 41 kPa (6 psi) were applied to the specimen. The stress and pressure were increased at 69 kPa (10 psi) increments until the final confining and saturation pressures of 558 kPa (81 psi) and 524 kPa (76 psi) were obtained. β values of greater than 0.95 inferred saturation which was confirmed to be 101 % when calculated with the following relationship:

$$S = w\frac{G_S}{e} \tag{3-2}$$

Where: w [-] is the average water content, G_s [-] is the specific gravity, and e [-] is the average void ratio (for the three dummy specimens).

3.3.5. Diffusion Testing

Extruded specimens were approximately 150 mm in length and had a diameter of 69 mm. Once saturated and removed from the permeameter cell, the outside cylindrical and bottom surfaces were patted dry and two coats of two-part bisphenol-A-based epoxy resin (West System Epoxy 105/205, Bay City, MI) were applied to seal the sides of the cylinder. To ensure proper curing, each coat of epoxy was allowed to set for a period of 8 to 12 h, as per the manufacturer's recommendations. After application of the epoxy, the final outer diameter of each specimen was approximately 70 mm. When mounting the specimen in the diffusion cell, vacuum grease was used to fill any void space between the edge of the specimen and the diffusion cell and was also applied to where the top perimeter of the specimen meets the diffusion cell (as shown in Figure 3.2). The reservoir of the diffusion cell was then filled with distilled water and spiked with tritiated water to result in a final volume of 100 mL and an initial nominal concentration of 10 MBq/l (samples were taken to measure the actual initial concentration). On a weekly basis the diffusion cell was gently rotated by hand to ensure adequate mixing of tritiated water in the source solution.

For the 28-day duration of the tests, 50-μl samples were taken from the source reservoir and replaced with an equal volume of distilled water twice weekly. Samples were mixed with scintillation fluid in 6-mL scintillation vials and stored (typically ≤ 5 days) until liquid scintillation counting was performed at the Department of Pharmacology, Dalhousie University. All samples sent for liquid scintillation counting were acidified by adding 8 mL of a 50 % weight/volume solution of trichloroacetic acid to each litre of stock scintillation fluid to prevent chemiluminescence.

Upon completion of the test, the tritiated water in the source reservoir was extracted using a syringe. The hex screw was removed from the bottom of the cell and the specimen was pushed out of the cell gently through the opening, wiped clean of vacuum grease with a paper towel, and cut into eight sections using a hacksaw. The top 50 mm of the specimen was cut into four 12.5-mm sections and the bottom 100 mm into four 25 mm sections. The top third of the specimen (50 mm) was sectioned into smaller segments as this portion contains the largest tritium concentration and largest concentration gradient. Each section was crushed (to a grain-size less than approximately 2 mm) using a mortar and pestle and a representative 20 g sample was placed in a 50-mL polypropylene tube with 20 mL of distilled water. Specimens were cut and crushed in a glovebox to meet radiation safety requirements. Each tube was shaken by hand four times over a period of 24 h. After allowing the crushed material to settle for 24 to 48 h, a 0.5 mL sample of the supernatant from each tube was filtered through a 45-μm syringe filter and placed in scintillation vials with 4.5 mL of acidified scintillation fluid. The vials were stored in a dark cupboard until liquid scintillation counting (≤ 2 days).

3.4. MODELING AND ANALYSIS

The model used to interpret the results of this testing (Rowe et al. 1998) has historically compared well to long-term values determined in the field for a number low hydraulic conductivity materials (e.g., rocks, natural and compacted clays, and geomembranes; Rowe et al. 2004). A summary of the theory used by Rowe et al. (1998) and Rowe et al. (2004) to back-calculate diffusion and porosity parameters for porous media is presented below for completeness.

In the proposed test, the leachate source solution represents a finite mass boundary condition and the bottom base of the specimen is a zero flux boundary condition. A finite mass boundary condition is one where the concentration or mass of contaminant decreases with time (i.e., there is no renewal) during the duration of the test (or field condition) to be modeled (Rowe et al. 2004). As the test proceeds, contaminant is transported from the source reservoir and into the specimen. The concentration c_t [ML^{-3}] in the reservoir at any time may be described by the following equation (Rowe and Booker 1994):

$$c_t(t) = c_o - \frac{1}{H_r}\int_0^t f_t(t)dt - (\frac{q_c}{H_r} + \lambda)\int_0^t c_t(t)dt \qquad (3\text{-}3)$$

Where: c_o is the initial concentration in the source solution [ML^{-3}], H_r is the equivalent height of source fluid (volume of source fluid per unit area) [L], $f_t(t)$ is the mass flux of contaminant into the porous medium at any time t [$ML^{-2}T^{-1}$], and q_c is the fluid collected for sampling per unit area, per unit time [LT^{-1}]. A zero flux boundary condition represents an impermeable base stratum which is assumed to allow no transmission of contaminant. This may be represented mathematically by Rowe and Booker (1994):

$$f(z = H_{bs}) = 0 \qquad (3\text{-}4)$$

Where H_{bs} [L] is the height of the base stratum.

The laboratory diffusion test may be modeled by solving Equations 3-1, 3-3 and 3-4 and the contaminant migration parameters (D_e, n_e) may be inferred by the values that give the best fit to the measured source and profile concentrations. Since concentrations of tritiated water initially in the specimen were not measured directly, an interpretation of the porosity is required to determine the initial water volume, and hence concentration, in each 20 g sample of crushed material. Given the potential for the calculated n_e of the specimens to be larger than the laboratory porosity when it is assumed that all water in the specimen was accessible to tritium, it was necessary to investigate two different interpretations of the experimental diffusion profile. Hereafter, these are referred to as the "total porosity method" and "effective porosity method" and are discussed in detail below.

3.4.1. Total Porosity Method for Interpreting Laboratory Diffusion

The laboratory results of the diffusion test were interpreted by assuming all water in the specimen (i.e., the "total porosity") was accessible to the tritium for contaminant migration. For each of the eight sections used to determine the concentration profile, the initial mass of water in each 20 g sample of crushed material M_W was determined by the following equation:

$$M_W = \frac{wM_T}{1+w} \tag{3-5}$$

Where: w (-)is the average water content determined from the three dummy specimens (0.22), and M_T [M] is the total mass of the sample (20 g).

Using an assumed density of water (0.998 g/mL) at the laboratory temperature of 22 °C, the volume of water initially present in each 20-g sample, V_W [L^3], was estimated using the result from Equation 3-5. Knowing the volume of distilled water added to the crushed sample V_{DW} [L^3] (equal to 20 mL for this work), and the concentration measured in the wash extracts C_{Wash} [ML^{-3}] the initial concentration of tritium in the specimen water C_W [ML^{-3}] was calculated for each layer with the following equation:

$$C_W = (\frac{V_W + V_{DW}}{V_W})C_{Wash} \tag{3-6}$$

A best-fit analysis was then performed comparing the aforementioned model with the measured changes in source concentration with time and the concentration profile through the specimen. A least squares analysis (with equal weighting for all points) was used to compare the experimental data to each set of theoretical results. A matrix of values of n_e ranging from 0.35 to 0.47 (in increments of 0.01) and D_e ranging from 0.5×10^{-10} to 2.5×10^{-10} m^2/s (in increments of 0.5×10^{-10} m^2/s) were analyzed. The theoretical plots corresponding to the combination of n_e and D_e which yielded the lowest root-mean-square error (RMSE) for each of the three replicates is plotted in Figure 3.3 with the laboratory diffusion profiles.

In Figure 3.3 the solid circles represent the measured values determined from laboratory testing and the dashed lines show the theoretical best-fit values as determined by the least squares analysis. All concentrations are normalized to the initial concentration in the source reservoir c_o. The results of the analysis are fairly consistent with n_e of 0.46, 0.45, and 0.43 for the three replicate specimens and D_e of 1.5×10^{-10} m^2/s for each. The fit to the source concentration versus time plots have RMSE of 0.031, 0.020, and 0.026, for specimens a, b, and c, respectively. The plots of concentration versus depth profiles do not match the observed data as well with RMSE of 0.050, 0.052, and 0.044 for the three replicates. Inspection of Figure 3.3 reveals that the best-fit diffusion profile systematically overestimates concentrations at shallow depths (from just below the surface to about 30 mm depth) and underestimates concentrations at deeper locations (from approximately 40 mm depth to the bottom of the specimen). The overall RMSE for the three tests are 0.042, 0.039, and 0.036 for specimens a, b, and c, respectively. All

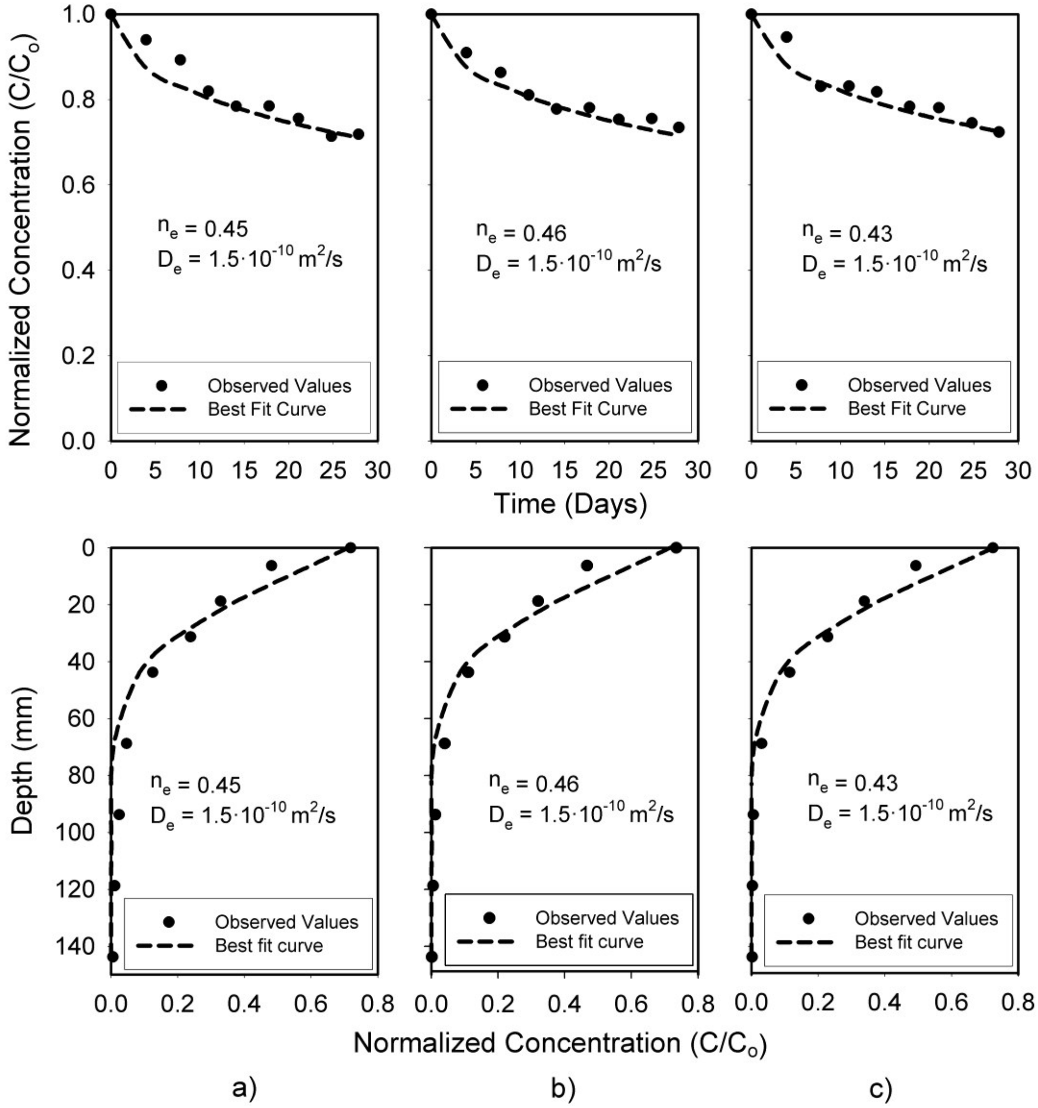

Figure 3.3 — Diffusion test results (normalized concentration vs. time in the source reservoir on the top and normalized concentration profiles at the end of the test on bottom) using the “total porosity method” to interpret the laboratory results (solid circles) and best-fit curves determined from modeling (dashed lines) for three replicate specimens.

three values of n_e, determined from diffusion testing, are larger than the total porosity determined from the saturated specimens (0.37). This result suggests that this “total porosity” method of establishing n_e and D_e is not appropriate since n_e should generally be less than, or equal to, the total porosity.

3.4.2. Effective Porosity Method for Interpreting Laboratory Diffusion

The laboratory results of the diffusion test were also interpreted assuming that part of the water in the specimen (e.g., hydration water, water in isolated pores) was inaccessible to tritium. This method is similar to the "total porosity method" presented above, with the exception of how the observed concentration profile is interpreted. In this case it was required to first assume a value of n_e to define the experimental diffusion profile.

M_W was calculated using Equation 3-5, but in this case it was assumed that only a portion of the water in the specimen was accessible to the tritiated water. The rest of the water in the specimen was assumed to act only to dilute the concentration when the water was extracted with the wash procedure at the end of the experiment. The ratio of the water accessible to the tritium in each specimen, M_{AW} [M], to the total mass of water in the 20 g sample, M_W, was assumed to be proportional to the ratio of n_e to n (Equation 3-7):

$$M_{AW} = M_W(\frac{n_e}{n}) \tag{3-7}$$

The mass of the inaccessible water in each sample, M_{IW} [M], is consequently represented by Equation 3-8.

$$M_{IW} = M_W(\frac{n - n_e}{n}) \tag{3-8}$$

The initial concentration of tritium in the "accessible" portion of the specimen, C_{AW} [ML^{-3}], may be determined from the measured concentrations of the supernatant, by Equation 3-9.

$$C_{AW} = (\frac{V_{AW} + V_{IW} + V_{DW}}{V_{AW}})C_{Wash} \tag{3-9}$$

Where V_{AW} [L^3] and V_{IW} [L^3] are the volumes of the accessible and inaccessible water in the sample, respectively (derived from M_{AW} and M_{IW} and knowing the density of water) and all other terms are as previously defined.

The observed concentration profiles, calculated from Equation 3-9, were compared to theoretical values based on an assumed value of D_e. A least squares analysis was performed and this process was repeated for D_e ranging from 1.5×10^{-10} to 4.0×10^{-10} m^2/s (in increments of 0.5×10^{-10} m^2/s). This whole process (including reapplication of Equations 3-7 to 3-9) was repeated for a number of different assumptions of n_e (0.25 to 0.31), each increasing by 0.01 and resulting in a unique observed diffusion profile. The theoretical plots corresponding to the combination of n_e and D_e which resulted in the best fit (by RMSE) for the three replicate specimens are shown with the corresponding observed data in Figure 3.4. Appendix B shows, by example, the process described above used to interpret the best-fit n_e and D_e.

In Figure 3.4 the solid circles represent the (normalized) observed data and the dashed lines show the curves corresponding to the theoretical best-fit values as determined by modeling. This method of analysis results in a better fit to the experimental data compared to the "total porosity method." The RMSE values for the three tests 0.028, 0.023, and 0.023 are (on average) 37 % lower than the values obtained using the total porosity method. Almost all of this improvement is due to the better fits of the concentration versus depth profiles, which have RMSE of 0.026, 0.024, and 0.020 (less than 50 % of the values determined from the total porosity method). The results of the three diffusion tests were fairly consistent with a best-fit n_e of 0.27, 0.26, and 0.28 and D_e of 3.0×10^{-10}, 3.0×10^{-10}, and 2.5×10^{-10} m^2/s for specimens a, b, and c, respectively. Based on the consistency of the results and the better fit, the authors believe that the "effective porosity method" for determining the laboratory diffusion profile is a superior approach. Subsequent discussion in this chapter refers to results obtained using this method.

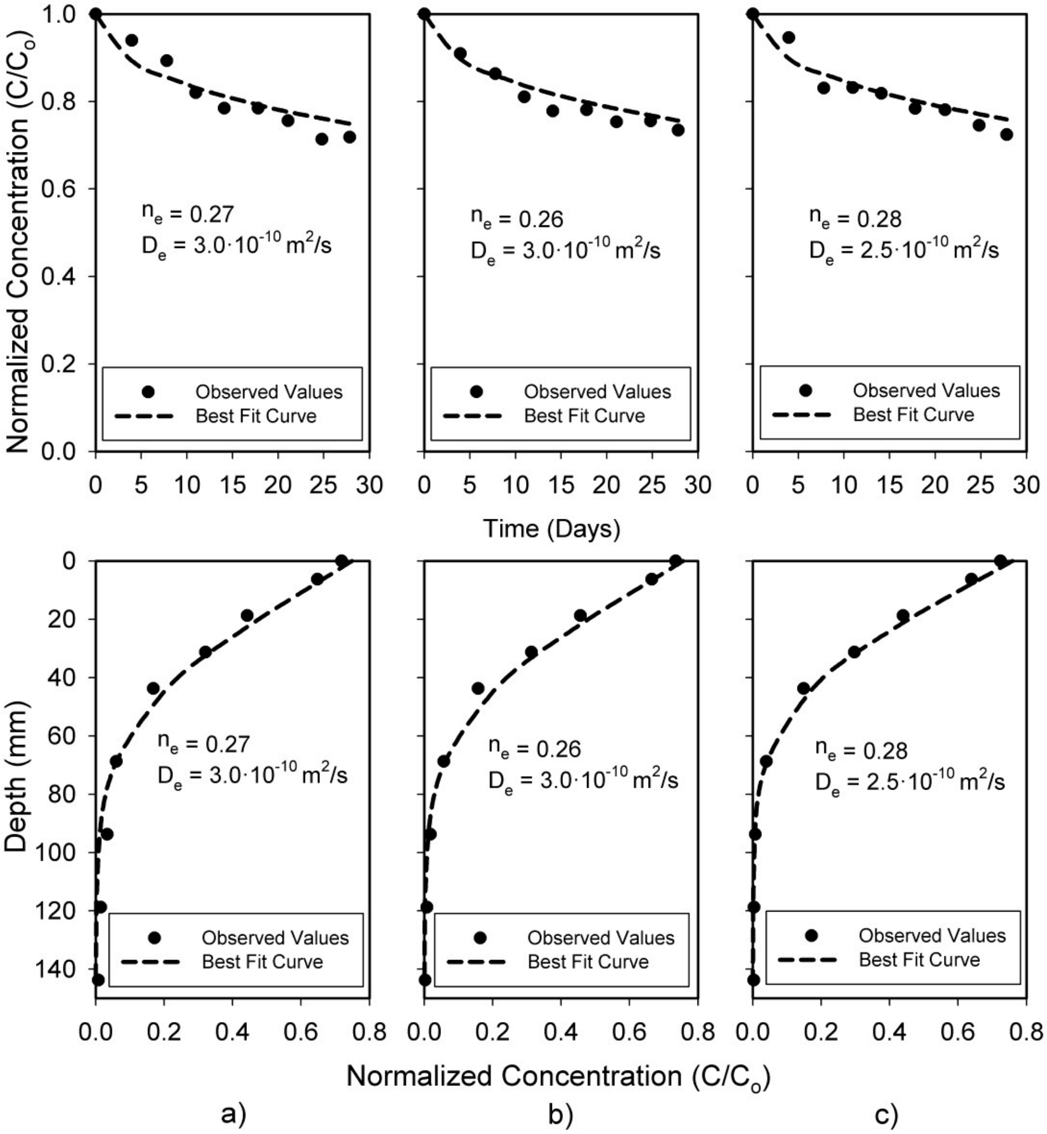

Figure 3.4 — Diffusion test results (normalized concentration vs. time in the source reservoir on the top and normalized concentration profiles at the end of the test on bottom) using the "effective porosity method" to interpret the laboratory results (solid circles) and best-fit curves determined from modeling (dashed lines) for three replicate specimens.

3.4.3. Sensitivity of Analysis

To illustrate the effect of varying D_e in the analysis, and in order to show the sensitivity of the selection of D_e on the theoretical results, a brief example is presented. Figure 3.5 repeats the results of the diffusion test on specimen c. Included with the experimental and best fit ($D_e = 2.5\times10^{-10}$ m^2/s) plots is an additional theoretical plot corresponding to a D_e of 3.5×10^{-10} m^2/s.

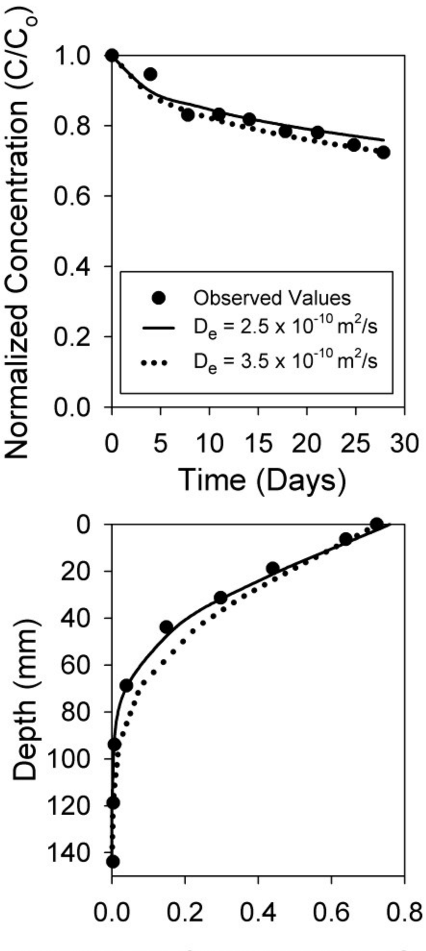

Figure 3.5 — Figure illustrating the effect of varying diffusion coefficient in the model. Shown are the normalized observed data (solid circles), concentration profile from the best fit parameters (solid line), and concentration profile from a diffusion coefficient incremented by 1.0 x10^{-10} m^2/s from the best fit parameter (dotted line) for specimen c.

Figure 3.5shows that although the source reservoir concentrations for the case where $D_e = 3.5\times10^{-10}$ m^2/s fit to the data fairly well (RMSE of 0.026 compared to only 0.025 for the best-fit D_e), the concentration profile with depth does not fit the data as well (RMSE of 0.041 compared to 0.020 for the best-fit D_e). Overall, the RMSE was increased to 0.034 compared to 0.023 for the best-fit parameters.

3.4.4. Effect of Curing/Hydration Time

A study was undertaken to determine the effect of curing time on the product of n_e and D_e (which is proportional to diffusive flux for a constant concentration gradient). In this study, triplicate specimens were cast and allowed to cure for periods of 14, 28, 70, and 126 days prior to the start of diffusion testing. The results of diffusion testing on these specimens are summarized in Figure 3.6.

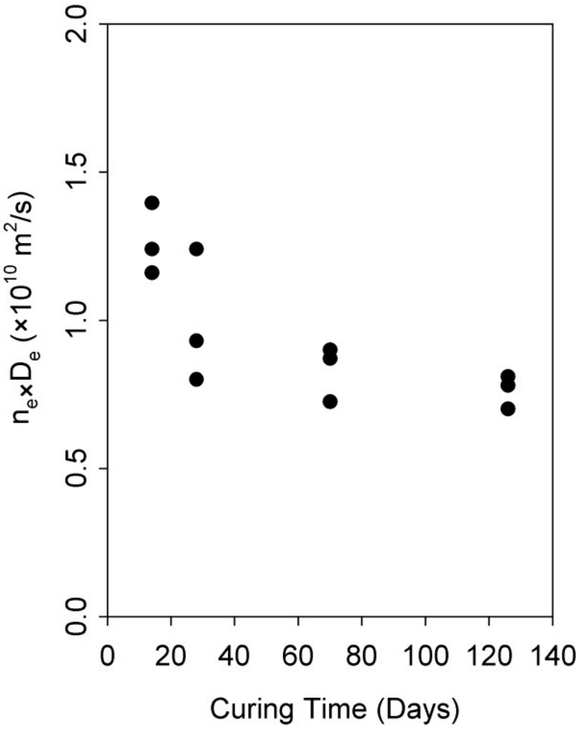

Figure 3.6 — The product of n_e and D_e as a function of curing time.

Inspection of Figure 3.6 indicates that the value of $n_e \times D_e$ changes considerably over the first 28 days of curing (the average value of $n_e \times D_e$ decreases by 22 % from the specimens cured for 14 day to the specimens cured for 28 days). However, after this initial period, it appears that the diffusive parameters do not change as quickly (the average value of $n_e \times D_e$ changes by 8 % from the 70 day to the 126-day specimens). Thus, diffusion testing occurring after 70 days curing should yield values approaching the values that can be expected over the long-term for intact specimens. This observation is consistent with the 56 to 84 day recommendation by Stegemann and Côté (1991) for curing specimens prior to the start of dynamic leaching testing.

3.5. CONCLUSIONS

The main objective of this chapter was to apply a single-reservoir type diffusion test to saturated, cured, monolithic, cement-based S/S specimens with the intent of determining the effective porosity n_e and the effective diffusion coefficient D_e using tritiated water diffusing through a soil-cement specimen. The apparatus and methods employed to perform the porosity and diffusion parameter assessment have been explained in detail with specific measures for the soil-cement specimens.

Two separate methods of interpreting the laboratory diffusion profile were presented and analyzed. It was shown that, when the porosity is required for determination of the experimental diffusion profile through the specimen, the best assumption was that only a portion of the water in the specimen was accessible to the tritium (i.e., the "effective porosity method"). Using this method, excellent fits to the experimental data were obtained. Values of RMSE for this method were approximately 37 % less than those obtained assuming all water was available for transport (i.e., the "total porosity method"). Consistent results were obtained between triplicate specimens. Laboratory determined n_e and D_e for tritiated water through the specimens ranged from 0.26 to 0.28 and 2.5×10^{-10} m^2/s to 3.0×10^{-10} m^2/s, respectively.

To assess the influence of curing time on the parameters obtained from diffusion testing, different curing times of 14, 28, 70, and 126 days were adopted. Curing times of greater than 70 days were found to be sufficient to assess the longer-term diffusion coefficients of the material tested. From a practical testing perspective, this would mean a total testing time of approximately 100 days for the methods discussed in this chapter.

The method provided in this chapter for evaluating n_e and D_e for cement-based S/S wasteforms allows for the parameters obtained from such a test to be implemented in the predesign or design portion of a project such that the parameters obtained are consistent with conventional design parameters used for contaminant migration assessment of source-controlled remediation sites (i.e., combined cement-based S/S wasteforms with slurry walls, compacted clay, geomembranes, etc.).

3.6. ACKNOWLEDGEMENTS

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CHAPTER 4: THE INFLUENCE OF WATER ON DIFFUSION AND POROSITY PARAMETERS OF SOIL-CEMENT MATERIALS[2]

4.1. INTRODUCTION

Early field studies have demonstrated the importance of diffusive properties in predicting the long-term contaminant migration performance of source-controlled containment systems such as clayey landfill liners (Goodall and Quigley 1977). Hence, there is a significant amount of information available on the diffusive properties of soil and rock materials, largely due to the influence of diffusion on the performance of landfills and deep geological disposal for nuclear wastes. Diffusion coefficients for clayey barriers for a wide variety of contaminants are presented in a number of references including Shackelford et al. (1989) and Rowe et al. (2004); similar diffusion coefficients can be found for engineered barrier systems, such as geosynthetic clay liners (Lake and Rowe 2000), compacted bentonites (Madsen and Kahr 1993), soil-bentonite slurry walls (Gullick 1998; Krol and Rowe 2004), and intact and fractured rock (Barone et al. 1990).

The use of soil–cement mixing as a remediation source-control technology for contaminated sites has been around for several decades (USEPA 1989a). From a source-control remediation perspective, the objective of mixing cement (or other additives) with contaminated media is to minimize the release of contaminants (both organic and inorganic) to the surrounding environment. When cement is used as the primary additive, this technology is generally referred to as cement-based solidification–stabilization (S/S). By mixing cement with contaminated soil, a "solidified" structure can be obtained, resulting in physical changes to the pore structure of the treated soil, such as increased

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[2] A version of this chapter has been published:
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strength, a lower hydraulic conductivity, and a larger average particle size (Batchelor 2006). When treatment results in a monolith, the hydraulic conductivity may be reduced to a value (i.e., 1×10^{-10} m/s or less) where diffusion becomes an important mechanism for contaminant release (Stegemann and Côté 1991).

Most of the previous work related to diffusion through soil-cement materials has been focused on examining the leaching behavior of contaminants for a specific mix design (Malviya and Chaudhary 2006) as opposed to studying the effects of varying mixture characteristics on the diffusion and porosity properties of the material. Results of diffusion testing performed for structural concretes (Page and Treadaway 1982; Luping and Sørensen 1998), cement mortars and pastes (Spinks et al. 1952; Goto and Roy 1981), and composite concrete and cementitious chemical barriers (Ganjian et al. 2004; Claisse et al. 2006) can be found. However, the literature contains few studies examining the role of the physical characteristics on the diffusive properties of monolithic soil-cement materials.

Conventionally, dynamic or semi-dynamic leaching tests have been performed on intact cementitious materials. In these tests, a specimen is placed in contact with a leachant that is measured (and often replaced) at specific time intervals (Garrabrants and Kosson 2005). A diffusion coefficient may be calculated from this data. However, this parameter, which is referred to as a retarded diffusion coefficient (D_R) by some researchers (e.g., Rowe et al. 2004), often varies temporally during the test. This may indicate that diffusion is not the primary mechanism being measured and that transport may be limited by other parameters such as dissolution or surface wash-off (Andrés et al. 1995; Malviya and Chaudhary 2006). Additionally, D_R, is a single parameter representing both diffusive and sorptive properties. Use of D_R is not appropriate when trying to extend results to other contaminants or for finite mass boundary conditions as used in the test methods employed in this study.

This chapter aims to examine diffusion of a conservative tracer (i.e., tritiated water) through laboratory-prepared, monolithic, soil-cement specimens. Specifically, the influence and importance of cement and water content on the relevant diffusive parameters (i.e., effective diffusion coefficient, D_e, and effective porosity, n_e) are investigated.

4.2. MATERIALS AND METHODS

The laboratory procedure for establishing D_e and n_e for monolithic soil-cement mixtures used for this study is discussed in detail in the previous chapter. A reservoir of tritiated water was placed above a monolithic soil-cement specimen and the tritiated water was allowed to diffuse into the specimen under conditions of zero hydraulic gradient. The diffusion test setup was similar to the single reservoir, transient diffusion tests discussed by Shackelford (1991) and Rowe et al. (2004). By measuring the change in source concentration with time, and the concentration profile with depth at the end of the test, D_e and n_e for the solute and mixture were inferred. Shackelford (1991), Rowe et al. (2004), and Goreham et al. (2012) discuss details of diffusion and diffusion testing. For the sake of completeness, a summary of the laboratory procedures employed is presented below.

4.2.1. Specimen Preparation

Eight of the 14 mixtures utilized a soil that consisted of a mixture of 80% silica sand and 20% kaolinite (soil A). Before mixing with cement grout, water was added to the soil resulting in a 13% water content (corresponding to the standard Proctor optimum water content).

Mixtures utilizing three other soils were tested to investigate the effect of grain-size distribution and to confirm trends observed for soil A. Soil B consisted of silica sand and soil C consisted of the same components as soil A, but with different proportions of silica sand and kaolinite (see Table 4.1). The fourth soil (soil D) was a silty sand native to the province of Nova Scotia, Canada. To maintain consistent mixture proportions, all soils had a water content of 13% before mixing with cement grout.

Table 4.1 — Properties of soils used in this study.

Soil	% Fines	% Sand	USCS Classification	Components/Origin
A	20	80	SC	Blend of silica sand and kaolinite
B	0	100	SP	Silica sand
C	40	60	SC	Blend of silica sand and kaolinite
D	35	65	SM	Falmouth, Nova Scotia, Canada

Soil-cement mixtures were prepared by adding various proportions of Portland cement paste to the soils. Mixing of both the cement paste and soil-cement mixture were performed using a large scoop, a tamping rod, and drill with paint-mixer attachment. Canadian Standards Association (CSA 2008) Type 10, general use, Portland cement used in this study was supplied by Holcim Canada Inc. (formerly St. Lawrence Cement). Table 4.2 summarizes the different mixtures used to create the specimens tested in this study.

For each mixture, triplicate cylindrical specimens were cast in 150 mm long molds cut from 70 mm diameter Shelby tubes for each diffusion and hydraulic conductivity test. These molds were lined with a 0.5 mm thick insert of cellulose acetate to prevent the specimens from adhering to the inside surface of the mold. Each specimen was placed in three layers of equal thickness with each layer corresponding to approximately one-third of the total volume of the mold. Twenty-one evenly distributed tamps over the cross-section of the mold were performed after placement of each layer. Triplicate specimens used for unconfined compressive strength (UCS) testing were cast in 50 mm cubic molds. Immediately upon casting, all specimens were placed in separate, airtight, plastic bags and stored at 21 ± 2 °C. After 7 to 14 days, specimens were extruded from their molds and promptly returned to the plastic bags.

Table 4.2 — Soil-cement mixtures tested.

Mixture	Soil	Cement[a] (%)	Grout W:C[b]	Total Fraction Cement	Total Fraction Soil	Total Fraction Water	Total W:C[c]
a	A	5	2	0.04	0.78	0.18	4.60
b	A	10	2	0.07	0.70	0.23	3.30
c	A	15	2	0.10	0.63	0.27	2.87
d	A	20	2	0.12	0.58	0.31	2.65
e	A	10	1	0.08	0.75	0.17	2.30
f	A	10	1.5	0.07	0.73	0.20	2.80
g	A	15	1	0.10	0.70	0.20	1.87
h	A	15	1.5	0.10	0.66	0.24	2.37
i	B	5	2	0.04	0.78	0.18	4.60
j	B	10	2	0.07	0.70	0.23	3.30
k	C	15	2	0.10	0.63	0.27	2.87
l	C	25	2	0.13	0.53	0.34	2.52
m	D	5	2	0.04	0.78	0.18	4.60
n	D	10	2	0.07	0.70	0.23	3.30

[a] Cement content as a percentage of dry soil mass.

[b] Water-to-cement ratio of cement grout.

[c] Total water-to-cement ratio including water content of soil at mixing (13%).

4.2.2. Unconfined Compressive Strength and Hydraulic Conductivity Testing

UCS and hydraulic conductivity testing were performed predominately as index testing and to provide commonly measured physical properties. Both tests were performed on triplicate specimens after 56 days curing. UCS testing was performed with a constant loading rate of 0.1 mm/min and hydraulic conductivity testing was performed in general accordance with ASTM (2010) D5084 “Method A – Constant Head”. An effective confining pressure of 103 kPa (15 psi) and a nominal hydraulic gradient of 14 were used during permeation with de-aired, distilled water.

4.2.2.1. Specific Gravity and Porosity Measurements

Due to radiation safety concerns, specimens containing tritium could not be oven-dried to determine the water content. Therefore, triplicate specimens for porosity measurement were made at the same time, from the same materials, and subjected to the same curing times and conditions as specimens for diffusion and hydraulic conductivity testing. Total porosity was determined by measuring the total volume of the specimens (geometrically) and measuring the mass of water lost upon drying at 115 °C. For each mixture, the specific gravity of a sample of oven-dried and crushed (to grain-size < 2 mm) specimen was tested by the Minerals Engineering Centre, Dalhousie University, using helium pycnometry.

4.2.3. Diffusion Testing

To allow time for the majority of cement hydration and pozzolanic reactions to occur, specimens used for diffusion testing were allowed to cure for a minimum of 84 days before being saturated in flexible wall permeameter cells. Specimens were saturated in general accordance with ASTM (2010) D5084-10 (details are presented in Chapter 3). After saturation, specimens were removed from the permeameter cells, prepared for diffusion testing, and placed in diffusion apparatuses. The specimens were laterally sealed in the cell with two coats of two-part bisphenol-A-based epoxy resin (West System Epoxy 105/205, Bay City, Mich.) and silicon vacuum grease.

For each test, the 100 mL source reservoir of the diffusion cell was filled with distilled water and spiked with concentrated tritiated water. Initial concentrations ranged from 10.0 to 28.1 MBq/L and are presented with the results of diffusion testing in Appendix A. Throughout the 28 (±4) day duration of each diffusion test, tritiated water migrated (under conditions of zero hydraulic gradient) from the source reservoir into the soil-cement specimen. Samples (50 μL) of the fluid in the source reservoir were taken twice weekly and replaced with an equal amount of distilled water. At the conclusion of each test, the fluid in the source reservoir was removed, the specimen was sectioned into eight segments using a hacksaw, and each segment was crushed with a mortar and pestle. A 20 g sample of the crushed material from each segment was mixed with a 20 mL "wash" of distilled water in a 50 mL polypropylene tube that was shaken by hand four times over a period of 24 h. A 0.5 mL sample of this wash was filtered through a 45-μm syringe filter. All samples were mixed with 4.5 mL of acidified scintillation fluid in 6 mL scintillation vials and sent to the Department of Pharmacology at Dalhousie University for liquid scintillation counting.

Both D_e and n_e were obtained by fitting theoretical values to the measured changes in the source concentration versus time and to the concentration profile through the specimen at the end of the test. Modeling was performed with a one-dimensional finite layer computer program (POLLUTE v6; Rowe et al. 1998). Input values of D_e and n_e were varied by 0.5×10^{-10} m^2/s and 0.01, respectively. The best-fit parameters (i.e., D_e and n_e) were determined from the parameters that had the lowest root-mean-square error (RMSE) when comparing the theoretical and experimental results.

4.3. RESULTS AND ANALYSIS

The results of a typical diffusion test (on mixture a) are presented in Figure 4.1. Figure 4.1a shows the normalized concentration in the source reservoir over the duration of the test, and Figure 4.1b shows the normalized concentration profile through the specimen at the completion of testing. In Figure 4.1, the solid circles represent the measured values, from laboratory testing, and the dashed lines show the best-fit values.

The results of laboratory diffusion tests on all 42 specimens (triplicate testing of 14 mixtures) are presented in Appendix A and summarized in Table 4.3. The average results of triplicate tests of hydraulic conductivity and UCS for each mixture are also presented. Overall, D_e was found to vary from 2.5×10^{-10} to 7.0×10^{-10} m^2/s and n_e from 0.21 to 0.41. For comparison, Table 4.4 presents typical values of D_e for various materials (i.e., saturated inactive clays, geosynthetic clay liners, soil–bentonite slurry walls, intact shales, and cement pastes). The product of n_e and D_e, which is an overall representation of the diffusive flux through a specimen (Rowe et al. 2004), was determined to vary from a minimum of 0.7×10^{-10} to a maximum of 2.3×10^{-10} m^2/s. To give some perspective on the magnitude of these values, they are similar to values reported for compacted clay liners, which typically have D_e of approximately 1×10^{-10} to 7×10^{-10} m^2/s and n_e values that range from approximately 0.20 to 0.50 (Rowe et al. 2004). The results presented in Table 4.3, although limited to only a few different soils, show relatively little variability in D_e (it varies by a factor of less than three). Of note, the value of D_e determined for mixtures using soil B (mixtures i and j), which consisted entirely of sand, are comparable to those of other mixtures that contain kaolinite.

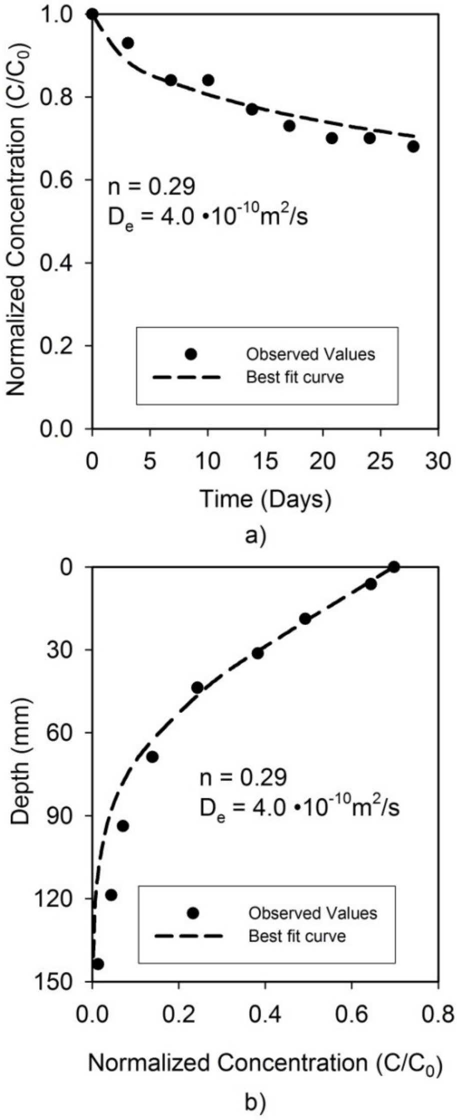


Figure 4.1 — Concentration profiles for specimen a1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

Table 4.3 — Results of laboratory testing on all specimens in this study.

Specimen	Soil	Mean k	Mean UCS	Mean n	Specific Gravity	D_e ($\times10^{10}$)	n_e	$n_e \times D_e$ ($\times10^{10}$)	RMSE[a]
		(m/s)	(kPa)	(-)	(-)	(m^2/s)	(-)	(m^2/s)	(-)
a1	A	5.3×10^{-9}	943	0.39	2.7	4.0	0.29	1.2	0.027
a2						5.0	0.31	1.6	0.028
a3						5.0	0.31	1.6	0.020
b1	A	3.8×10^{-9}	1563	0.40	2.6	4.5	0.28	1.3	0.021
b2						5.5	0.27	1.5	0.021
b3						4.0	0.27	1.1	0.020
c1	A	3.3×10^{-9}	2036	0.47	2.6	6.0	0.33	2.0	0.010
c2						5.0	0.34	1.7	0.025
c3						5.0	0.35	1.8	0.026
d1	A	2.7×10^{-9}	2181	0.50	2.6	6.5	0.35	2.3	0.029
d2						6.0	0.38	2.3	0.030
d3						5.5	0.38	2.1	0.033
e1	A	4.3×10^{-10}	1829	0.37	2.6	4.5	0.24	1.1	0.020
e2						4.0	0.22	0.9	0.014
e3						4.0	0.21	0.8	0.028
f1	A	4.2×10^{-10}	1603	0.41	2.6	4.5	0.24	1.1	0.031
f2						6.0	0.23	1.4	0.027
f3						5.5	0.28	1.5	0.026
g1	A	4.6×10^{-10}	3884	0.37	2.6	3.0	0.27	0.8	0.028
g2						3.0	0.26	0.8	0.023
g3						2.5	0.28	0.7	0.023
h1	A	4.2×10^{-10}	2500	0.43	2.6	4.0	0.30	1.2	0.020
h2						3.5	0.30	1.1	0.025
h3						3.0	0.29	0.9	0.036
i1	B	1.1×10^{-6}	280	0.36	2.6	5.0	0.30	1.5	0.039
i2						5.5	0.31	1.7	0.041
i3						6.0	0.28	1.7	0.040
j1	B	9.9×10^{-8}	1589	0.36	2.6	3.0	0.25	0.8	0.028
j2						3.0	0.24	0.7	0.027
j3						3.5	0.24	0.8	0.037
k1	C	7.3×10^{-10}	1440	0.48	2.6	5.0	0.31	1.6	0.033
k2						5.5	0.26	1.4	0.035
k3						5.0	0.27	1.4	0.027
l1	C	2.0×10^{-9}	2114	0.54	2.6	5.0	0.41	2.1	0.034
l2						5.5	0.37	2.0	0.035
l3						5.0	0.35	1.8	0.025
m1	D	5.4×10^{-9}	702	0.35	2.7	6.5	0.28	1.8	0.044
m2						6.0	0.29	1.7	0.035
m3						7.0	0.25	1.8	0.052
n1	D	3.2×10^{-9}	1194	0.37	2.7	6.0	0.26	1.6	0.037
n2						5.0	0.29	1.5	0.039
n3						5.5	0.27	1.5	0.032

[a] Root-mean-square error from best-fit parameters to diffusion test results.

Table 4.4 — Typical effective diffusion coefficients for various materials.

Material	D_e (m^2/s)	Author
Saturated Inactive Clays	1×10^{-10} to 7×10^{-10}	Rowe et al. 2004
Geosynthetic Clay Liners	5×10^{-11} to 5×10^{-10}	Lake and Rowe 2000
Soil-Bentonite Slurry Walls	3×10^{-10} to 4.5×10^{-10}	Krol and Rowe 2004
Intact Shales	1.4×10^{-10} to 1.6×10^{-10}	Barone et al. 1990
Cement Pastes	1.8×10^{-10} to 4.4×10^{-10}	Tits et al. 2003

4.3.1. Unconfined Compressive Strength, Hydraulic Conductivity, and Total Porosity

The interrelationship between water and cement content has been shown to play an important role in the engineering characteristics of cementitious materials such as concrete (Abrams 1918; Kosmatka et al. 2002; Hearn et al. 2006) and soil-cement materials (Bone et al. 2004; Shi and Spence 2004). Hence, it is useful to examine the importance of water and cement proportions on the UCS and hydraulic conductivity for the samples tested in this study.

As illustrated in Figure 4.2, the UCS for mixtures using soil A tends to decrease with increasing water-to-cement ratio. In the figures throughout this chapter, the symbols in the plot (e.g., the circles) represent the average of testing on triplicate specimens and the error bars represent the maximum and minimum values observed. When examining multiple specimens mixed at different water-to-cement ratios, for one particular cement content (10% or 15%; see shaded areas on Figure 4.2), the relationship of decreasing UCS with increasing water-to-cement ratio remains. This is consistent with well-established knowledge for cementitious materials (Kosmatka et al. 2002).

Similar results are observed when considering hydraulic conductivity testing. For any cement content (i.e., 10% or 15%; see shaded areas on Figure 4.3), the hydraulic conductivity tends to increase as the water-to-cement ratio increases. Again, this is consistent with the literature (e.g., Kosmatka et al. 2002). For comparable water-to-cement ratios, the hydraulic conductivity increases with increasing cement content. This is likely caused by the fact cement was added as grout and the increased cement content had a corresponding increase of excess water (leading to an increased porosity).

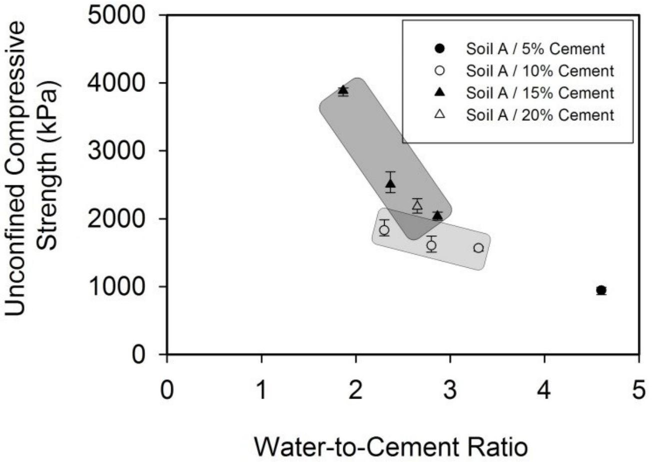


Figure 4.2 — Influence of total water-to-cement ratio and cement content on the unconfined compressive strength (UCS) for all mixtures using soil A.

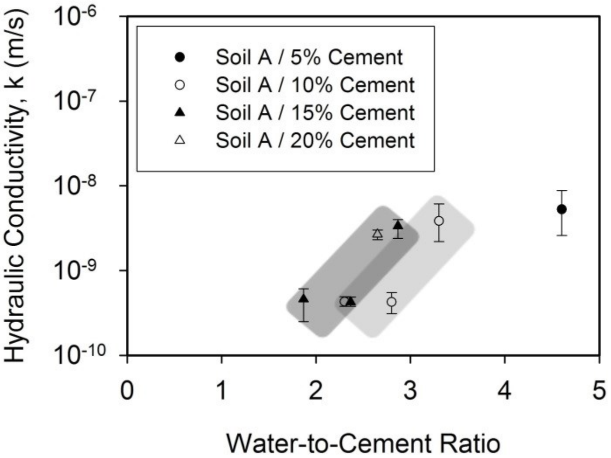
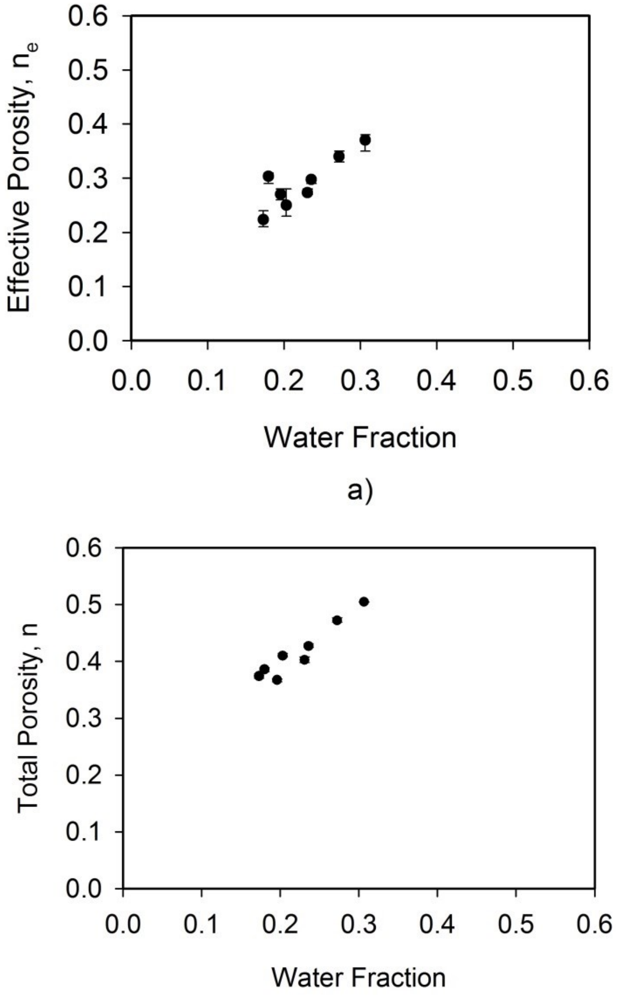


Figure 4.3 — Influence of total water-to-cement ratio and cement content on hydraulic conductivity (k) for all mixtures using soil A.

Figures 4.4a and 4.4b indicate that for soil A, increasing the fraction of water of the initial mixture generally increases both n and n_e. This observation is in agreement with the literature for other cementitious materials (Hearn et al. 2006). For mixtures with high water-to-cement ratios, the water in excess of the amount required to hydrate the cement (i.e., the mixing water) remains unreacted with cement and ultimately contributes to the pore volume (Hearn et al. 2006).



a)

b)

Figure 4.4 — Influence of the mass fraction of water on a) average total porosity (n) and b) effective porosity for all mixtures using soil A.

4.3.2. Effective Porosity, n_e, and Effective Diffusion Coefficient, D_e

From a performance criteria standpoint, it is useful to examine the diffusive transport of a contaminant (e.g., tritiated water) through a solidified mass. When performance criteria such as hydraulic conductivity and UCS are met by a given mixture, D_e and n_e may become the most important criteria with respect to contaminant migration through source-controlled cement-based S/S remediation systems. Diffusive transport is investigated in this chapter by examining the influence of mix design on the parameters controlling diffusion (i.e., n_e and D_e).

Figure 4.5 shows the values of n_e obtained from diffusion testing plotted against average total porosity for all mixtures using soil A. The value of n_e for all the specimens is less than n (i.e., plots below the 1:1 line in Figure 4.5), which indicates that some of the porosity is excluded from the diffusive transport of tritium over the duration of the laboratory testing (as discussed in Chapter 2). Testing by Kim et al. (1997, 2001) has shown that for compacted clays, the effective porosity, n_e, is often similar to the total porosity, n. However, as explained by Rowe et al. (2004), depending on the properties of the diffusing compound and the medium, this may not always be the case.

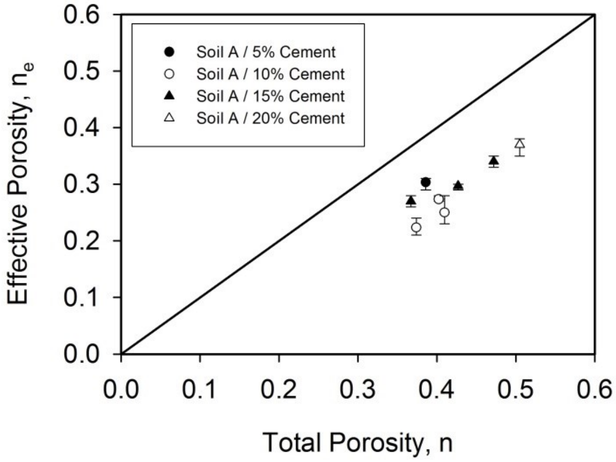


Figure 4.5 — Effective porosity (n_e) determined from diffusion testing vs. average total porosity (n) for all mixtures using soil A.

Figure 4.6 shows that, for soil A, when the cement content in the mixture is held constant at either 10% cement or 15% cement (refer to shaded areas on the figure), the mass transport by diffusion (represented by $n_e \times D_e$) also generally increases with increasing water content (i.e., increasing water-to-cement ratio).

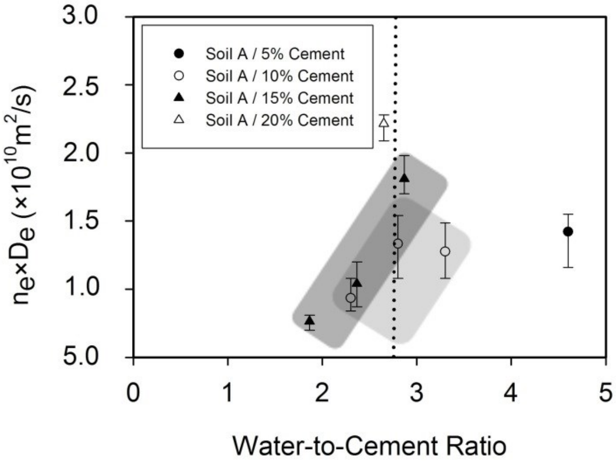


Figure 4.6 — $n_e \times D_e$ determined from diffusion testing vs. total water-to-cement ratio for all mixtures using soil A.

Furthermore, Figure 4.6 shows that when the water-to-cement ratio is held relatively constant (e.g., water-to-cement approximately 2.7 to 2.9 as denoted by the dotted line), $n_e \times D_e$ increases with increasing cement content. These results are very similar to what was observed in Figure 4.3 for hydraulic conductivity and may similarly be explained by the increase in water content (which results in an increased porosity) of mixtures with higher water-to-cement ratios for a given cement content. As shown in Table 4.3, similar trends and observations to those discussed above for $n_e \times D_e$ are apparent for each of n_e and D_e individually. However, the effects of water-to-cement ratio and cement content on n_e are clearer (Figure 4.7) than they are for either $n_e \times D_e$ or D_e. This relationship with water in the mixture can be clearly seen when examining Figure 4.4a, which shows the effect of the fraction of water (by mass) in the mixture on n_e for all mixtures using soil A. Figure 4.4a shows that n_e generally increases (approximately linearly) with increasing initial water fraction. As indicated by the data presented in Figure 4.4b, similar trends were observed for n. As diffusion occurs through the pore space, one would expect that n, a measure of the pore space, is related to D_e and $n_e \times D_e$. Figure 4.8 shows that, for soil A, $n_e \times D_e$ generally increases with increasing n. It also appears that cement content has some effect on the results; for a similar total porosity, $n_e \times D_e$ tends to be higher for lower cement contents than for higher ones.

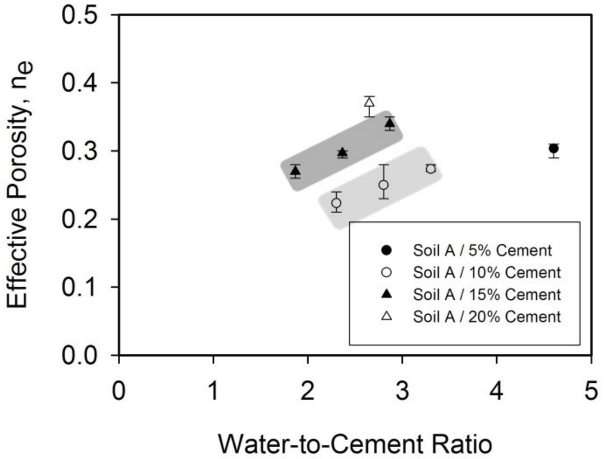


Figure 4.7 — Effective porosity (n_e) determined from diffusion testing vs. total water-to-cement ratio for all mixtures using soil A.

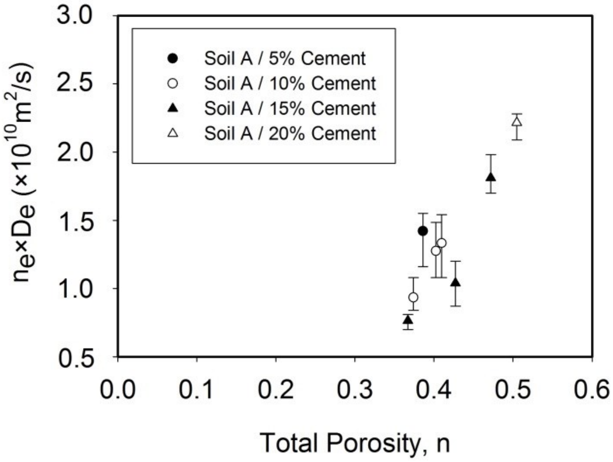


Figure 4.8 — $n_e \times D_e$ determined from diffusion testing vs. average total porosity (n) for all mixtures using soil A.

4.4. PRACTICAL APPLICATIONS

4.4.1. Adding Cement in Field Applications to Improve Transport Properties

When mixing soil–cement materials (e.g., cement-based S/S for remediation purposes), cement is often added in grout form. If the treatment is deemed inadequate (i.e., fails to meet performance specifications), one solution may be to introduce more cement to the mixture. This may be accomplished by either increasing the ratio of volume of grout to the volume of treated soil or by decreasing the water-to-cement ratio of the grout being added. The approach taken is influenced by the properties of the soil being mixed as well as the equipment being used for mixing. An increase in grout volume, for a grout at a given water-to-cement ratio, will result in an increase in the proportion of water in the mixture. This may increase the ease of mixing, but does not necessarily improve the performance of the final product (as shown by the results of diffusion testing presented in the previous sections). Furthermore, a reduction in the water-to-cement ratio while adding the same total amount of grout may improve the final performance, but hinder the “mixability” of the material. To illustrate the influence this decision-making process could have on the diffusion and porosity properties of the mixtures in this study, the influence of increased cement content (as a percent of dry mass) due to the use of additional grout on $n_e \times D_e$ for soil A is shown in Figure 4.9 for three different grout water-to-cement ratios (i.e., 1:1, 3:2, 2:1).

Figure 4.9 indicates differing trends with respect to $n_e \times D_e$ as the amount of grout (i.e., the cement content at a given water-to-cement ratio) in the mixture is increased for the three different grout water-to-cement ratios. For the grout with the highest water-to-cement ratio (2:1), $n_e \times D_e$ increases with increasing cement addition; however, for the two lower water-to-cement ratios (3:2 and 1:1), $n_e \times D_e$ decreases with increasing grout addition. This may be partially explained by the increased volume of water added for the higher water-to-cement ratio grout to obtain similar cement contents.

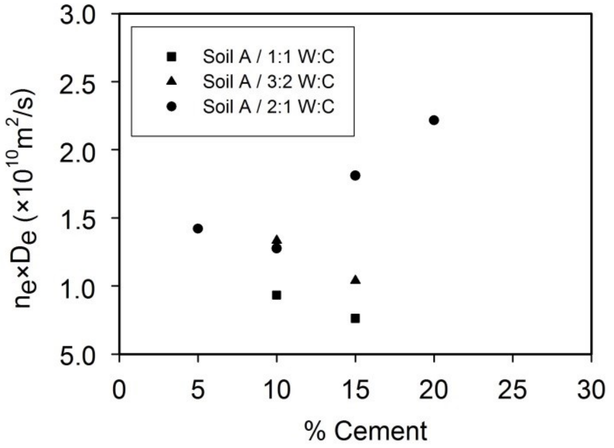


Figure 4.9 — $n_e \times D_e$ determined from diffusion testing vs. cement content (as a percentage of dry mass of soil) for soil A mixed with grouts of various water-to-cement ratios.

When examining the role of grout addition on the hydraulic conductivity, it is revealed that simply increasing the cement content by adding additional grout does not necessarily reduce the hydraulic conductivity of the hardened specimens. For specimens with a grout containing a 2:1 water-to-cement ratio (mixtures a–d), Table 4.3 shows a gradual increase in hydraulic conductivity as additional cement is added to the mixture in grout form. However, when mixing with grouts of lower water-to-cement ratios of 3:2 (mixtures f and h) and 1:1 (mixtures e and g), there is little, if any, change in hydraulic conductivity of the samples as the cement content is increased.

4.4.2. Pre-Design of Source-Controlled Cement-Based S/S Monoliths

Typically, source-control remediation options, such as cement-based S/S treatment, that reduce the advective flux to a value where contaminant transport is largely due to the diffusive flux, are considered ideal (Daniel and Shackelford 1988; Rowe et al. 2004). Thus, a design goal of cement-based S/S monoliths used for source-controlled remediation purposes is often to reduce the advective flux to a value where diffusion is the principle source of contaminant flux. In this case, contaminant transport from the monolith will be due to the relatively slow process of diffusion.

For the purposes of a pre-design or technology selection phase, where cement treatment of soil is being considered against other source-remediation technologies, it may often be sufficient to conservatively estimate the diffusive properties of the material. If a more accurate assessment is warranted, one could perform diffusion tests following the methods and principles discussed in Chapter 3 and by Shackelford et al. (1989) and Rowe et al. (2004). However, diffusion testing for each mix design considered may not be feasible from either a temporal or economic perspective for most projects. Conservative values of D_e and n_e may be obtained by performing diffusion testing on the mixtures with the highest expected porosity of all mixtures considered in design that meet the other performance criteria, such as UCS and hydraulic conductivity.

The results of diffusion testing presented in this chapter show that, for the specimens tested, the rate of diffusive transport generally increases with increasing water-to-cement ratio for given cement content (Figure 4.6), with increasing porosity (Figure 4.8), and with increasing cement content for a given water-to-cement ratio (Figure 4.6). Given that porosity is largely influenced by the amount of water in the initial mixture (Figure 4.4), any design aiming to minimize the diffusive transport of contaminants should aim to reduce the porosity to the minimum allowed by other constraints (e.g., mixability). From a pre-design standpoint, variability in soil gradation may not hinder the estimate of diffusion and porosity adopted. Figure 4.10 presents a plot showing average $n_e \times D_e$ for all mixtures by soil (symbol shape), cement content (symbol shade), and water-to-cement ratio (abscissa). Mixtures where essentially only the soil is changed (same cement content, same or similar water-to-cement ratio) tend to plot relatively close to one another. This is useful when considering that minor grain-size variations on most contaminated sites will likely have a relatively minor influence on the diffusive transport for a given soil–cement mix design.

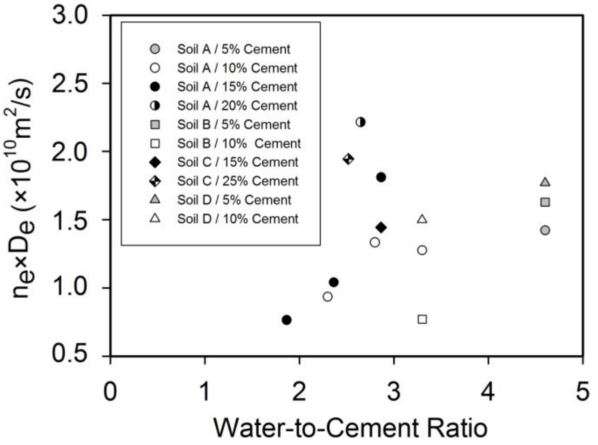


Figure 4.10 — Average n_e×D_e vs. total water-to-cement ratio for all mixtures.

4.5. SUMMARY AND CONCLUSIONS

In this chapter, the porous media properties of 14 soil-cement mixtures were quantified by evaluating D_e and n_e for a conservative inorganic solute (tritiated water) using a diffusion cell and methodology presented in Chapter 3. Values of D_e and n_e obtained from laboratory testing (2.5×10^{-10} to 7.0×10^{-10} m^2/s and 0.21 to 0.41, respectively) are of similar magnitude to those previously determined for compacted clay materials, which are frequently used as geoenvironmental liners.

Results show that the effective porosity, n_e, was never greater than the total porosity, n, and generally increased with increasing water content of the initial soil–cement mixture. For any given cement content, overall diffusive transport (represented by n_e×D_e) increased with increasing water-to-cement ratio. Likewise, for any given water-to-cement ratio, overall diffusive transport increased with increasing cement content. These results imply that when trying to improve performance of soil–cement materials, increasing the ratio of the volume of grout to the volume of treated soil may not be as effective as maintaining that ratio while reducing the water-to-cement ratio of the grout. For the three soil mixtures tested, soil gradation was not found to have a substantial effect on the diffusive parameters investigated. The testing methodology applied in this chapter and the results provided may serve as conservative estimates in the pre-design or technology selection phase when weighing cement treatment against other source-remediation options

4.6. ACKNOWLEDGEMENTS

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CHAPTER 5: DIFFUSION AND SORPTION OF VOLATILE ORGANIC COMPOUNDS THROUGH SOIL-CEMENT MATERIALS

5.1. INTRODUCTION

Cement-based solidification/stabilization (S/S) has been used to treat a wide variety of organic and inorganic chemical substances. Although organic compounds may be treated efficiently by a number destructive or degradative treatments (e.g., combustion), these methods are often ineffective or inefficient at treating inorganic substances. Furthermore, many impacted locations such as manufactured gas plant sites, wood-treating sites, refineries, oil recycling facilities, and pesticide/herbicide manufacturing plants contain both organic and inorganic contaminants at levels that compel treatment (ITRC 2011). As there are relatively few processes that effectively treat both organic and inorganic contaminants, it may often be economical to treat these sites using cement-based S/S. To determine how cement-based S/S treatment will perform in the long-term, it is essential to have the resources to estimate contaminant migration from soil-cement materials.

Volatile organic compounds (VOCs) are contaminants of interest as a result of their ubiquitous nature and due to the fact they pose a threat to human health and the environment at relatively low concentrations. Hence, there has been significant research investigating the diffusion of VOCs through a number of materials including compacted clay liners (Barone et al. 1992b; Kim et al. 2001), geomembranes (Rowe and Hrapovic 1995), and geosynthetic clay liners (Lake and Rowe 2004). However, there is a paucity of experimental investigation on the diffusion of VOCs through soil-cement (e.g., cement-based S/S) materials.

The objective of the work presented in this chapter is to develop a modified diffusion test method to examine the diffusion and sorption of three volatile organic compounds (i.e., benzene, ethylbenzene, and trichloroethylene) through cured, monolithic, laboratory-prepared soil-cement specimens at three different water-to-cement ratios. The purpose of this diffusion test is to examine the effective diffusion coefficients (D_e) and distribution coefficients (K_d) of soil-cement materials and to investigate the variation in these parameters between the three mixtures investigated. The interaction of these VOCs during testing is examined by testing trichloroethylene with three other organic compounds together in one test versus testing it in isolation. The effect of the value of n_e used in the interpretation of the diffusion tests is also investigated. To demonstrate the relative effects of the values of D_e, K_d, and n_e obtained from these laboratory tests, contaminant transport modeling is performed for a hypothetical site. To the authors' knowledge, there is no such published information on VOC diffusion through cement-based S/S materials.

5.2. BACKGROUND

5.2.1. Volatile Organic Compounds

This chapter examines VOC (benzene, ethylbenzene, and trichloroethylene) diffusion and sorption testing for three different soil-cement mixtures. Although all three compounds may be classified as VOCs, their physical properties vary considerably due to their different chemical structures (Figure 5.1).

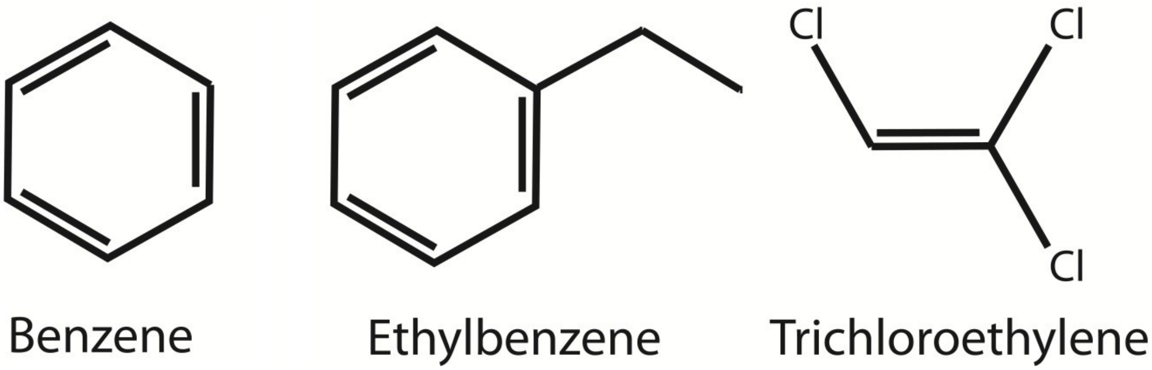

Figure 5.1 — Chemical structure of VOCs utilized in this study (Brown and Poon 2005).

Benzene and ethylbenzene are examples of aromatic hydrocarbons which are compounds characterized by the presence of a specific configuration of six carbon atoms forming a benzene ring (Manahan 2009). Aromatic hydrocarbons are known to be hazardous environmental pollutants (Brown and Poon 2005). Due to the nature of their chemical bonds and their lack of polar groups, aromatic hydrocarbons tend to have relatively low aqueous solubility (Brown and Poon 2005). Consisting of a single benzene ring, benzene is the simplest aromatic hydrocarbon, while ethylbenzene consists of a benzene ring with an attached ethyl group (Brown and Poon 2005).

Trichloroethylene is a chlorinated hydrocarbon, which is a class of hydrocarbons that contain at least one chlorine atom (Sharma and Reddy 2004). Chlorinated hydrocarbons are frequently used as coolants and in pesticides (Brown and Poon 2005). Due to their widespread use, subsurface contamination due to inadvertent leaks, spills, and improper disposal practices of chlorinated hydrocarbons has been prevalent since the mid-1900s (Castelbaum and Shackelford 2009).

The three VOCs utilized in this study have historically been used in a number of industrial and commercial applications. A summary of some of their common applications and their potential health effects is presented in Table 5.1.

Table 5.1 — VOC usage and toxicity information (USEPA 2000).

Chemical	Common Uses	Possible Health Effects
Benzene (C_6H_6)	Production of plastics, resins, and synthetic fabrics; solvent.	Anemia; decrease in blood platelets; increased risk of cancer.
Ethylbenzene (C_8H_{10})	Production of styrene (to make plastics); solvent; production of rubber and plastic wraps.	Problems with liver and kidney; increased risk of cancer.
Trichloroethylene (C_2HCl_3)	Grease removal from fabricated metal parts; production of textiles.	Problems with liver; increased risk of cancer.

Even at relatively low concentrations, many VOCs are often above drinking water or aquatic water guidelines set by regulatory agencies, as shown in Table 5.2. The particular compounds used in this study were selected as they have been listed as contaminants of concern in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (Agency for Toxic Substances &

Disease Registry 2007). VOCs have also been the subject of diffusive transport studies for barrier materials such as geomembranes (Rowe and Hrapovic 1995), compacted clays (Barone et al. 1992b), and geosynthetic clay liners (Lake and Rowe 2004) and therefore the results of this study will be able to be directly compared to these other materials.

Table 5.2 — USEPA Maximum Contaminant Level (MCL) and Canadian Council of Ministers of the Environment (CCME) Water Quality Guidelines for the Protection of Aquatic Life (Freshwater).

Compound	**USEPA MCL[a] (mg/L)**	**CCME[b] (mg/L)**
Benzene	0.005	0.021
Ethylbenzene	0.7	0.370
Trichloroethylene	0.005	0.0011

[a] United States Environmental Protection Agency (2010).
[b] Canadian Council of Ministers of the Environment (1999a-c).

Table 5.3 presents a selection of physical and chemical properties for benzene, ethylbenzene, and trichloroethylene. Although all three VOCs are considered to have relatively low solubility in water, solubility varies by an order of magnitude between the least soluble (ethylbenzene) and most soluble (benzene) of the three VOCs. Relative solubility and the hydrophilicity of a compound influence the potential for that contaminant to be sorbed to soil materials (Rowe et al. 2004).

Table 5.3 — Select physical and chemical properties of benzene, ethylbenzene, and trichloroethylene.

Properties	**Molecular Weight[a] (g/mol)**	**Boiling Temperature[a] (°C)**	**Solubility in Water @ 20°C[a] (g/L)**	**Log K_{ow}[a] @25°C**	**Dielectric Constant[a] @20°C**	**D_o @25°C[b] (m^2/s)**	**Specific Density @20°C[a] (g/cm^3)**
Benzene	78.1	80	1.79	2.13	2.3	1.16×10^{-9}	0.88
Ethylbenzene	106.2	136	0.17	3.15	2.5	9.16×10^{-10}	0.87
TCE	131.4	87	1.20	2.42	3.4	9.93×10^{-10}	1.46

[a] Schwarzenbach et al. (2003).
[b] Yaws (2010).

There have been relatively few studies investigating the diffusion of VOCs through soil-cement materials. Some researchers (e.g., Hebatpuria et al. 1999) have used dynamic leaching tests (e.g., ANS 16.1; American Nuclear Society 2003) to determine the diffusive parameters of organic contaminants through these materials. Although the diffusion coefficient resulting from these tests is often referred to as an "effective diffusion coefficient", it is referred to as a retarded diffusion coefficient, D_R, throughout this thesis. As discussed in Chapter 2, D_R includes effects of sorption and may be defined by Equation 5-1.

$$D_R = \frac{D_e}{1 + \frac{\rho K_d}{n_e}} \tag{5-1}$$

Where: D_R is the retarded diffusion coefficient $[L^2T^{-1}]$, D_e is the effective diffusion coefficient $[L^2T^{-1}]$, ρ_d is the dry density of the soil-cement $[ML^{-3}]$, K_d is the distribution coefficient $[M^{-1}L^3]$, and n_e is the effective porosity [-]. In this chapter, square brackets denote the fundamental dimensions mass [M], length [L], and time [T] for dimensionally consistent equations. Scale units such as kilogram (kg), metre (m), and second (s) are presented in round brackets for equations that are dimensionally inconsistent.

Leaching mechanisms other than diffusion (e.g., surface wash-off or dissolution) may significantly influence the results of these dynamic leaching tests (e.g., Hebatpuria et al. 1999; Malviya and Chaudhary 2006).

5.3. EXPERIMENTAL METHOD

5.3.1. Specimen Preparation and Testing Program

The soil-cement specimens used in this study were prepared using a procedure similar to the one discussed in Chapters 3 and 4 for the tritiated water diffusion testing program. A soil ("soil A" as it was referred to in Chapter 4) was prepared in the laboratory by mixing silica sand (80% by dry mass) with kaolinite (20% by dry mass) in a 20 L plastic bucket. Water was added to provide a water content of 13 % (corresponding to the proctor optimum water content). The soil and water were mixed using a large scoop, tamping rod, and drill with paint mixer attachment. Next, a cement grout at a known water-to-cement ratio (2:1, 3:2, or 1:1 for mixtures c, h, and g, respectively) was mixed until homogeneous using the drill and paint mixer attachment. The cement grout was immediately added to the soil mixture and they were mixed together until homogeneous. Sufficient grout was added to result in a 15% cement content (by dry mass). CSA Type 10, general use, normal Portland cement provided by Holcim (Canada) Inc. was used in all mixtures. To allow for comparison, the mixtures are the same as three mixtures used in the tritiated water diffusion testing program discussed in Chapter 4 and hence the sample naming and numbering system used in that chapter is continued. A summary of the proportions of water, cement, kaolinite, and sand for each of the three mixtures is provided in Table 5.4.

Table 5.4 — Summary of diffusion test conditions and mixture properties.

Mixture	**Soil**	**No. of Replicates**	**Source Solution**	**Cement[a] (%)**	**Total W:C[b]**	**Grout W:C[c]**	**Total Fraction**		
							Cement	**Soil**	**Water**
c	A	3	GROUP	15	2.87	2	0.10	0.63	0.27
c	A	2	Trichloroethylene	15	2.87	2	0.10	0.63	0.27
h	A	2	GROUP	15	2.37	1.5	0.10	0.66	0.24
h	A	2	Trichloroethylene	15	2.37	1.5	0.10	0.66	0.24
g	A	2	GROUP	15	1.87	1	0.10	0.70	0.20
g	A	2	Trichloroethylene	15	1.87	1	0.10	0.70	0.20

Note: GROUP refers to benzene, ethylbenzene, trichloroethylene, and naphthalene being tested simultaneously.

[a] Cement content as a percentage of dry soil mass.

[b] Total water-to-cement ratio including water content of soil at mixing (13%).

[c] Water-to-cement ratio of cement grout.

Immediately after mixing, the specimens were cast in 69-mm diameter by 30-mm long cylindrical polyvinylchloride molds. Evenly distributed tamping over the cross-section was performed using pressure just sufficient to ensure uniform filling of the molds. Specimens were placed in separate, tightly sealed, plastic bags and stored at 21 ± 2 °C.

After 56 days, specimens were extruded from their molds and promptly returned to the plastic bags. All specimens were allowed to hydrate for a minimum of 28 additional days (84 days total) before testing.

Diffusion testing and batch testing were performed on the three soil-cement mixtures using a solution containing benzene, ethylbenzene, trichloroethylene, and naphthalene. To investigate the effect of contaminant interaction between the VOCs, testing was also performed using trichloroethylene in isolation. A summary of the six different testing conditions is presented above in Table 5.4.

5.3.2. Diffusion Testing

There have been a number of studies investigating the diffusion of organic compounds through clay barriers (e.g., Barone et al. 1992b; Sawatsky et al. 1997; Donahue et al. 1999; and Krol and Rowe 2004) derived from a method proposed by Rowe et al. (1988). A similar method (adapted for soil-cement materials) was used in the work discussed herein and is summarized in the following paragraphs.

The diffusion testing apparatus and methodology used in this study were developed based on experience from previous work on inorganic diffusion testing through soil-cement materials (e.g., Chapters 3 and 4) as well as previous diffusion testing through geomaterials and geosynthetics reported in the literature (Barone et al. 1991; Rowe and Hrapovic 1995; Lake and Rowe 2004). Due to the fact that it is difficult (if not impossible) to accurately determine a concentration-depth profile for a volatile substance through a soil-cement material, a double-reservoir diffusion test (as described by Shackelford 1991) was used instead of the single-reservoir diffusion test used in the tritiated water diffusion testing program (Chapters 3 and 4). In the double-reservoir diffusion test, a source reservoir with a known initial concentration is placed on one side of a specimen and water is placed on the other (the receptor reservoir). The concentration in each reservoir is measured intermittently as time progresses. The experimental data may be compared with results of theoretical modeling to determine the best-fit contaminant migration parameters (i.e., n_e, D_e, and K_d).

Glass is a common material choice when working with VOCs due to the potential for organic compounds to sorb to or react with many synthetic polymers. Rowe and Hrapovic (1995), Lake and Rowe (2004), and Carignan et al. (2007) have successfully used double-reservoir glass diffusion cells to evaluate the diffusive properties of VOCs migrating through geomembranes, geosynthetic clay liners, and thermally treated drilling muds, respectively.

The diffusion cells used in this study were manufactured at glass blowing shops at the University of Guelph, Guelph, Ontario, Canada and Dalhousie University, Halifax, Nova Scotia, Canada. Two cells were repurposed from a previous study by Carignan et al. (2007) and six additional cells with similar dimensions were constructed specifically for this investigation. A sketch of a typical diffusion cell is presented in Figure 5.2. The diffusion cells were constructed of 70-mm internal diameter glass cylinders with thick flanges at both the top and bottom designed to support glass plates.

The soil-cement specimens were trimmed to fit snugly into the apparatus and a thin coating of bentonite (at a water content of approximately 100 %) was placed around the exterior perimeter of the specimens to ensure an adequate hydraulic seal between the specimen and the cell. A glass support was then placed in the bottom reservoir to prevent the specimen from moving within the cell. Using a two-part epoxy-resin (3M Scotch-DP 100) the top and bottom glass plates were attached to the top and bottom flanges, respectively. Care was taken to minimize the amount of epoxy that came in contact with the inside of the apparatus. To hydrate the bentonite, approximately 50 mL of water was immediately placed in the source reservoir which was above the specimen. After two days, the apparatus was inverted and 50 mL of water was added to the receptor reservoir. After two additional days, the water was drained from the apparatus before the reservoirs were filled to start diffusion testing. No leakage around the perimeter of the specimen was observed throughout this procedure.

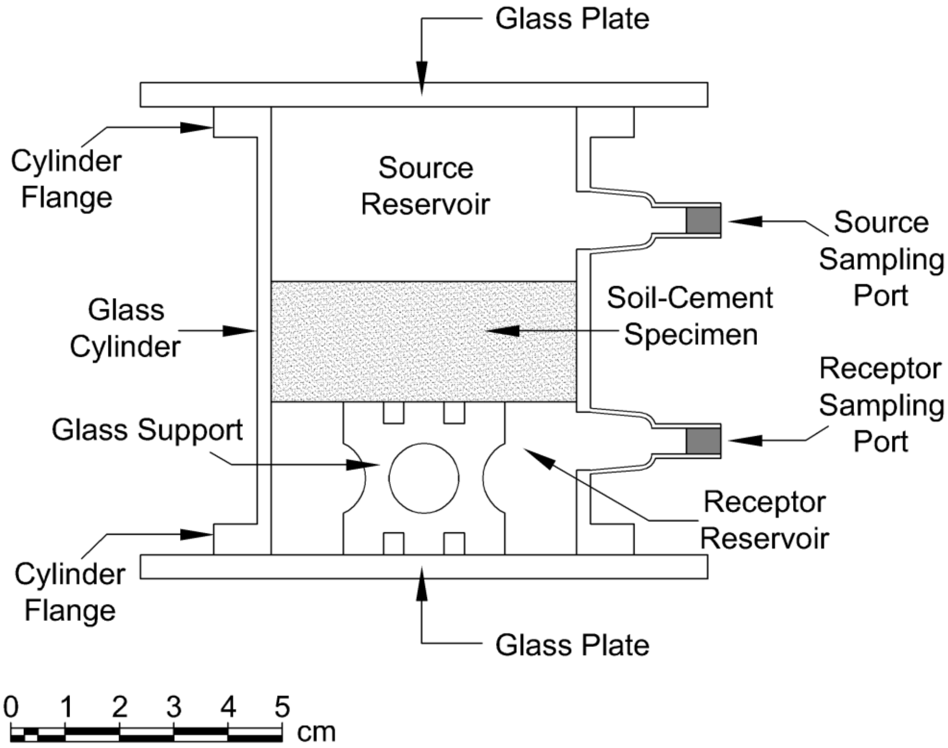

Figure 5.2 — Typical diffusion testing apparatus used in this study.

Source solutions were prepared in 1000 mL glass bottles one day prior to the start of diffusion testing. These bottles were filled with Type 1 ultrapure (i.e., Milli-Q® water), injected with the compounds being tested using a Hamilton gastight syringe, and sealed with polytetrafluoroethylene septa and crimp tops. The initial concentrations used in each test are listed in Table 5.5 and ranged from 26.0 to 50.9 mg/L for benzene, 10.4 to 49.4 mg/L for ethylbenzene, and 11.7 to 47.9 mg/L for trichloroethylene. Naphthalene concentrations ranged from 3.8 to 5.3 mg/L. The receptor reservoirs were filled with ultrapure water. The source and receptor solutions both contained a 1.0 g/L concentration of sodium azide to act as a biocide. All chemicals used in testing were supplied by Aldrich Chemical Company and had a minimum 99% purity.

Table 5.5 — Initial concentrations and reservoir volumes for all VOC diffusion tests.

Specimen	Volume		Initial Concentration, C_o			
	Source (mL)	Receptor (mL)	Benzene (mg/L)	TCE (mg/L)	Ethylbenzene (mg/L)	Naphthalene (mg/L)
c4	132.0	175.0	28.2	11.7	11.3	5.3
c5	131.0	170.0	26.5	13.7	10.4	5.0
c6	145.4	166.5	26.0	21.1	12.0	5.1
c7	135.1	170.4	-	34.9	-	-
c8	120.8	172.3	-	33.4	-	-
h4	128.9	168.3	50.0	47.0	46.7	4.2
h5	120.9	173.3	46.8	43.2	41.7	3.8
h6	132.0	175.9	-	37.7	-	-
h7	124.1	195.5	-	40.0	-	-
g4	138.9	165.1	50.1	47.8	49.0	3.9
g5	134.7	173.6	50.9	47.9	49.4	3.8
g6	148.9	165.8	-	32.5	-	-
g7	136.4	172.4	-	46.5	-	-

The diffusion cell was weighed before and after each reservoir was filled to determine the mass of each solution added. Volumes, which were calculated from the measured masses, are reported in Table 5.5. Concentrations of the source and receptor reservoirs were typically measured twice-weekly by removing 100 μL samples from each reservoir and testing them using gas chromatography. Immediately upon removal, the volume of solution removed from each reservoir was replaced with ultrapure water.

5.3.3. Batch Testing Procedure

Batch tests were performed to examine the capacity of the VOCs to sorb to the soil-cement materials used in diffusion testing. Procedures similar to those described by Lake et al. (2013) were employed. Batch tests provide estimates of K_d that are independent of diffusion testing. Prior to batch testing, specimens were cured for a minimum of 84 days, pulverized using a ceramic mortar and pestle, sieved through a 2 mm (U.S. No. 10) sieve, and oven-dried to a constant mass at 60°C. The testing was performed in 50-mL pyrex centrifuge tubes with open-top caps lined with polytetrafluoroethylene septa. Prior to batch testing, all glass centrifuge tubes and caps were thoroughly cleaned with hot soapy water, rinsed with tap water, and further rinsed with, and soaked in, ultrapure water. The centrifuge tubes were then placed in an oven at 150°C for a minimum of 4 hours.

As with diffusion testing, batch testing was also performed using a solution containing trichloroethylene in isolation and a solution containing trichloroethylene, benzene, ethylbenzene, and naphthalene together. To develop sorption isotherms, the VOCs were tested in triplicate at eight different concentration levels (i.e., 0.5, 1.0, 2.0, 4.0, 6.0, 10.0, 25.0, and 50.0 mg/L). Due to a vial breaking during testing, only duplicate results are available for mixture g at the 10.0 mg/L concentration level for the solution containing the group of chemicals. Due to its lower solubility in water, batch tests on the group of contaminants had naphthalene concentrations at 10% of those of the concentration of each VOC (i.e., 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 2.5, and 5.0 mg/L). A group of vials containing solutions at the same concentrations and subject to the same procedures presented above, but without any soil-cement material, were used as a control.

Three grams of crushed soil-cement were placed in each centrifuge tube which was filled with ultrapure water until the headspace was minimized. To achieve the desired initial concentrations, methanol stock solutions containing trichloroethylene (0.8 g/L); and benzene, ethylbenzene, trichloroethylene, (each 0.8 g/L) and naphthalene (0.08 g/L) were prepared in separate 125-mL Boston bottles. As with diffusion testing, all solutions used in the batch tests included 1.0 g/L of sodium azide to act as a biocide. A Hamilton gastight syringe was used to inject varying amounts of stock solution (to yield the desired concentrations) into each centrifuge tube. The centrifuge tubes were promptly capped and then mechanically agitated, end-over-end, for 24 ±2 hours at (21 ±2 °C). After agitation, solids and solution were separated using a Thermo IEC Centra GP8R centrifuge at 2500 rpm for 30 minutes. Three aliquots were taken from each tube and separately placed in 2-mL gas chromatograph auto sampler vials for gas chromatography analysis. These aliquots were 0.8 mL for tubes with initial concentrations of 10.0 mg/L or less and 0.3 and 0.15 mL for tubes with initial concentrations of 25 and 50 mg/L, respectively. Ultrapure water was added to the auto sampler vials, as required, to yield a total volume of 0.8 mL.

5.3.4. Gas Chromatography Procedures

In general, methods similar to those used by Afshar (2008) were employed for gas chromatography analysis. Concentrations of the VOCs were measured using a Varian 3800 gas chromatograph with a DB-5 column (30m x 0.25mm x 1.0 µm). Injections were performed with a Varian 8400 auto sampler outfitted with a 100 µm solid-phase microextraction (SPME) polydimethylsiloxane fibre. Headspace analyses were performed with a fiber adsorption time of five minutes followed by desorption time of one minute with an injector temperature of 280°C. Helium was used as the carrier gas and a split ration of 10:1 was used in all analysis. An initial column temperature of 45°C was held for 0.50 minutes, followed by a temperature ramp to 100°C at a rate of 8°C/min, the temperature was subsequently increased to 200°C at a rate of 50°C/min. A final temperature ramp brought the temperature to 250 °C at a rate of 10°C/min, this temperature was held for six minutes. All compounds were detected using a flame ionization detector (FID) at 325°C. Analysis of results and peak integration analyses was performed using Varian Star (v 6.20) software. The approximate retention time for benzene, ethylbenzene, and trichloroethylene were 2.7, 3.0, and 5.2 minutes, respectively.

External standards using concentrations of 0.5, 1, 2, 5, and 10 mg/L were used to quantify the concentrations of the VOCs. The R^2 values for the linear calibrations were typically greater than or equal to 0.995.

5.3.5. Soil-Cement VOC Diffusion and Distribution Coefficient Estimation

When modeling the diffusion tests, finite mass boundary conditions were used to represent the source and receptor reservoirs. These boundary conditions are used when there is a finite amount of mass in the system and the concentration at each boundary is constantly changing with time due to mass transfer through the specimen. The concentration at any time in the source reservoir, $c_t(t)$, may be described mathematically by Equation 5-2 (Rowe et al. 2004).

$$c_t(t) = c_o - \frac{1}{H_r}\int_0^t f_t(t)dt - \frac{q_c}{H_r}\int_0^t c_t(t)dt \tag{5-2}$$

Where: c_o is the initial concentration in the source solution [ML^{-3}], H_r is the equivalent height of source fluid (volume of source fluid per unit area) [L]; $f_t(t)$ is the mass flux of contaminant into the soil-cement at any time t [$ML^{-2}T^{-1}$]; q_c is the fluid collected for sampling per unit area, per unit time [LT^{-1}]. The concentration in the receptor compartment (ultrapure water at the beginning of the test), $c_b(t)$, may similarly be expressed mathematically by Equation 5-3.

$$c_b(t) = c_{bo} + \frac{1}{H_b}\int_0^t f_b(t)dt - \frac{q_c}{H_b}\int_0^t c_b(t)dt \tag{5-3}$$

Where: c_{bo} is the initial concentration in the receptor solution [ML^{-3}], H_b is the equivalent height of the receptor reservoir (volume of receptor reservoir per unit area) [L], and $f_b(t)$ is the mass flux of contaminant into the receptor reservoir at any time t [$ML^{-2}T^{-1}$].

As discussed by Rowe et al. (2004), the theoretical equation for transient one-dimensional contaminant transport (without decay) through a porous medium such as soil-cement, may be expressed by Equation 5-4.

$$n_e\frac{\partial c}{\partial t} = n_e D_e\frac{\partial^2 c}{\partial z^2} - n_e v\frac{\partial c}{\partial z} - \rho_d K_d\frac{\partial c}{\partial t} \tag{5-4}$$

Where: c is the concentration in the pore space of the soil-cement at depth z and time t [ML^{-3}], n_e is the effective porosity of the soil-cement [-], D_e is the effective diffusion coefficient [L^2T^{-1}], v is the Darcy velocity [LT^{-1}], ρ_d is the dry density of the soil-cement [ML^{-3}], and K_d is the distribution coefficient [$M^{-1}L^3$].

The purpose of any laboratory diffusion test is to obtain parameters describing diffusion (e.g., n_e, D_e, and K_d). Therefore, at the time of testing, these parameters are unknown. Any theoretical concentrations generated by solving Equations 5-2 to 5-4 require an assumption for these values. POLLUTE v.6 (Rowe et al. 1998), a finite layer computer program, was used to solve Equations 5-2 to 5-4 and a trial-and-error approach was used to match theoretical source and receptor reservoir curves with observed experimental data. Trial values of D_e were varied by increments of 0.25×10^{-10} m^2/s and trial values of K_d by increments of 0.1 cm^3/g. The best-fit to the experimental data, as determined by the least root-mean-square error (RMSE), allowed for the interpretation of D_e and K_d for the specimen and contaminant examined. To reduce the number of unknown parameters, the data was analyzed using two assumptions for the value of n_e.

- Firstly, the experimental data was analyzed assuming that n_e was equal to the average value of n_e determined from tritium diffusion testing (Chapters 3 and 4) for each mixture (0.34, 0.30, and 0.27 for mixtures c, h, and g, respectively).
- Secondly, the data was analyzed assuming that the value of n_e is equal to the average total porosity determined from water content upon oven-drying of all specimens of that mixture (0.48, 0.42, and 0.37 for mixtures c, h, and g, respectively).

The best-fit D_e and K_d were determined for each assumption of n_e.

5.4. RESULTS AND DISCUSSION

5.4.1. Water Content, Porosity, and Dry Density

Water content determinations were performed on all specimens used for diffusion testing. The different proportions of water added to the mixtures allowed for a range of porosities to be examined in this study. Table 5.6 compares the average water content and porosities (assuming saturation) of each mixture used in this testing program to the average for the same mixture used in the tritiated water diffusion testing program (Chapters 3 and 4).

Table 5.6 — Comparison of average water content, porosity, and dry density for specimens made for this study and similar specimens for the tritiated water diffusion testing program (discussed in Chapter 4).

Mixture	Grout W:C	Specimens from VOC Diffusion Testing Program			Specimens from Tritium Diffusion Testing Program		
		Water Content	Porosity	Dry Density (g/cm^3)	Water Content	Porosity	Dry Density (g/cm^3)
c	2:1	34%	0.47	1.36	35%	0.48	1.35
h	3:2	29%	0.43	1.47	30%	0.42	1.47
g	1:1	22%	0.37	1.63	23%	0.37	1.63

Although the degree of saturation was not directly measured on the specimens used for VOC diffusion testing, the water contents are very similar to those measured for specimens in the tritiated water diffusion testing program (which were calculated to range from 99% to 108% saturated). The average dry density (ρ_d, ML^{-3}) of each of these mixtures was calculated using Equation 5-5.

$$\rho_d = \frac{G_S \gamma_w}{1 + w G_S} \tag{5-5}$$

Where: G_s, is the specific gravity [-], w is the average water content [-], and γ_w is the unit weight of water [ML^{-3}].

5.4.2. Diffusion and Batch Testing

The results of diffusion testing were first interpreted assuming that n_e was equal to the average value of n_e determined from diffusion testing of tritiated water on the same mixture (Chapters 3 and 4). The result of a typical diffusion test analyzed using this assumption is presented in Figure 5.3. In this figure, the upper data points (starting at c/c_o=1) show the decrease in contaminant concentration with time in the source reservoir due to contaminant migration into the soil-cement specimen. The lower data points (starting at c/c_o=0) represent the increase in contaminant concentration in the receptor reservoir with time. Both the experimental data (solid circles) and theoretical best-fit (dashed lines) are presented. Figure 5.4 shows the same experimental data with the best-fit D_e and K_d determined by assuming that n_e was equal to the average total porosity determined based on the water-content of all specimens of that mixture. Plots showing the experimental data and theoretical best fits for all VOC diffusion tests performed in this study are included in Appendix C.

Table 5.7 summarizes the results of all 13 diffusion tests performed and presents the 27 values of D_e and K_d derived from them for each assumption of n_e. Also included in Table 5.7 are the 95 % confidence intervals of K_d determined from batch testing. Figures showing the linear sorption isotherms for all batch testing are included in Appendix D.

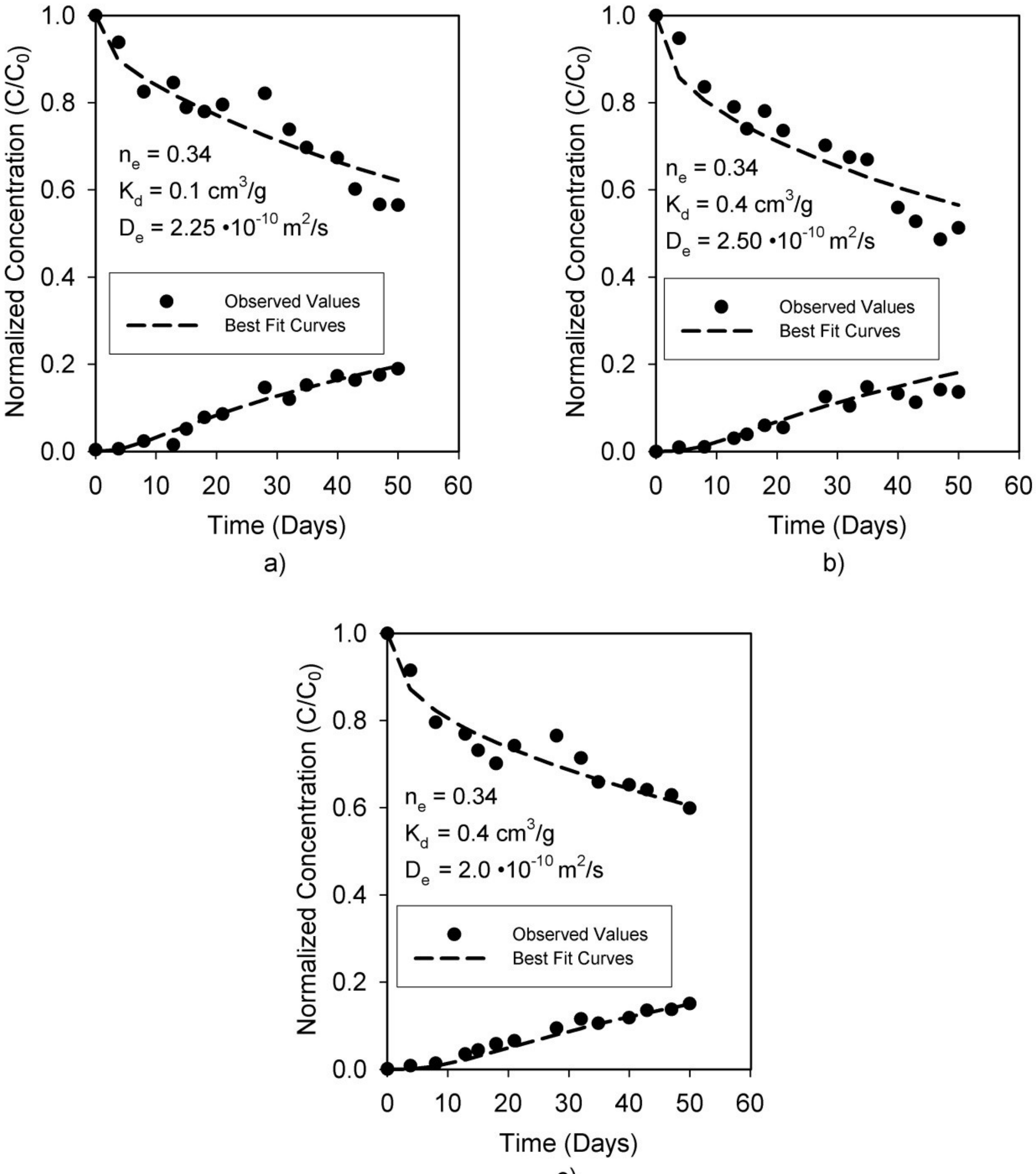

Figure 5.3 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen c4: a)benzene, b)trichloroethylene, c)ethylbenzene.

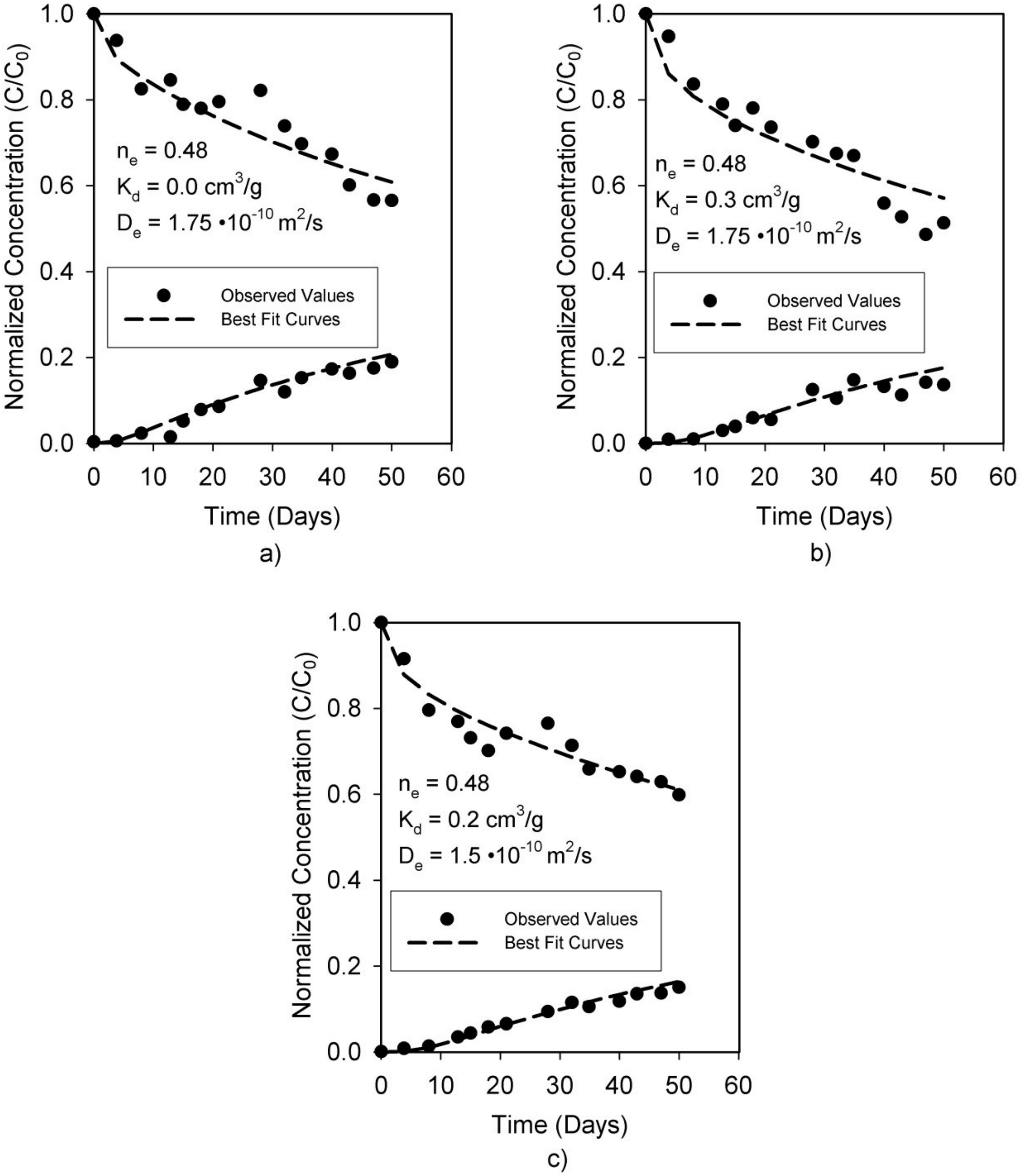

Figure 5.4 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c4: a)benzene, b)trichloroethylene, c)ethylbenzene.

Table 5.7 — Summary of batch and diffusion test results.

		Batch Testin	n_e from Tritium Diffusion Testing					n_e Oven-Drying				
Specimen	Tracer	K_d (95% CI) (cm^3/g)	n_e (-)	K_d (cm^3/g)	D_e ×10^{10} (m^2/s)	D_R ×10^{10} (m^2/s)	RMSE^b (-)	n_e (-)	K_d (cm^3/g)	D_e ×10^{10} (m^2/s)	D_R ×10^{10} (m^2/s)	RMSE^b (-)
c4	B	0.1 – 0.2	0.34	0.1	2.25	1.61	0.032	0.48	0.0	1.75	1.75	0.033
c5	B	0.1 – 0.2	0.34	0.1	2.50	1.79	0.107	0.48	0.0	1.75	1.75	0.107
c6	B	0.1 – 0.2	0.34	0.2	2.25	1.25	0.027	0.48	0.0	1.75	1.75	0.027
c4	TCE	0.4 – 0.8	0.34	0.4	2.50	0.97	0.039	0.48	0.3	1.75	0.95	0.039
c5	TCE	0.4 – 0.8	0.34	0.4	2.50	0.97	0.038	0.48	0.4	1.75	0.82	0.038
c6	TCE	0.4 – 0.8	0.34	0.5	2.50	0.84	0.038	0.48	0.4	1.75	0.82	0.037
c4	EB	0.4 – 0.7	0.34	0.4	2.00	0.77	0.023	0.48	0.2	1.50	0.96	0.023
c5	EB	0.4 – 0.7	0.34	0.4	2.25	0.87	0.045	0.48	0.3	1.50	0.81	0.045
c6	EB	0.4 – 0.7	0.34	0.7	2.25	0.60	0.025	0.48	0.5	1.75	0.73	0.026
c7	TCE[a]	0.3 – 0.5	0.34	0.5	2.50	0.84	0.026	0.48	0.4	1.75	0.82	0.026
c8	TCE[a]	0.3 – 0.5	0.34	0.3	2.50	1.14	0.022	0.48	0.2	1.75	1.12	0.022
h4	B	0.7 – 0.8	0.30	0.6	3.00	0.76	0.031	0.42	0.5	2.25	0.81	0.031
h5	B	0.7 – 0.8	0.30	0.5	2.25	0.65	0.034	0.42	0.4	1.50	0.63	0.034
h4	TCE	0.5 – 0.6	0.30	0.8	2.50	0.51	0.035	0.42	0.7	1.75	0.51	0.035
h5	TCE	0.5 – 0.6	0.30	0.7	2.00	0.45	0.045	0.42	0.6	1.50	0.48	0.044
h4	EB	1.0 – 1.3	0.30	1.0	2.75	0.47	0.027	0.42	0.9	2.00	0.48	0.027
h5	EB	1.0 – 1.3	0.30	1.0	2.25	0.38	0.031	0.42	0.9	1.50	0.36	0.031
h6	TCE[a]	0.2 – 0.4	0.30	0.5	3.00	0.87	0.032	0.42	0.4	2.25	0.94	0.032
h7	TCE[a]	0.2 – 0.4	0.30	0.4	3.00	1.01	0.026	0.42	0.3	2.00	0.98	0.027
g4	B	0.3 – 0.6	0.27	0.6	3.00	0.65	0.029	0.37	0.5	2.25	0.70	0.029
g5	B	0.3 – 0.6	0.27	0.5	2.75	0.68	0.025	0.37	0.4	2.00	0.72	0.025
g4	TCE	0.6 – 1.0	0.27	0.9	2.50	0.39	0.044	0.37	0.8	2.00	0.44	0.044
g5	TCE	0.6 – 1.0	0.27	0.6	2.25	0.49	0.049	0.37	0.5	1.75	0.55	0.049
g4	EB	1.1 – 1.2	0.27	1.3	3.00	0.34	0.033	0.37	1.3	2.25	0.33	0.033
g5	EB	1.1 – 1.2	0.27	0.9	2.75	0.43	0.030	0.37	0.8	2.00	0.44	0.030
g6	TCE[a]	0.3 – 0.5	0.27	0.6	3.00	0.65	0.037	0.37	0.7	2.25	0.55	0.037
g7	TCE[a]	0.3 – 0.5	0.27	0.8	2.75	0.47	0.025	0.37	0.7	2.00	0.49	0.025

[a] Tested alone (without other VOCs) B = Benzene, TCE= Trichloroethylene, EB = Ethylbenzene

[b] Root-mean-square error for best-fit parameters and laboratory diffusion test results.

When using n_e determined from tritium diffusion testing in the interpretation of the diffusion tests, D_e was found to range from 2.00×10^{-10} to 3.00×10^{-10} m^2/s for all three VOCs. When assuming n_e was equal to the total porosity derived from oven-drying, D_e was found to range from 1.50×10^{-10} to 2.25×10^{-10} m^2/s. As shown on Table 5.8, these values are comparable to published values of VOC diffusion coefficients for a number of materials such as geosynthetic clay liners, saturated inactive clays, and soil-bentonite slurry walls.

Table 5.8 — Effective diffusion coefficients for various materials.

Compound	**Material**	**D_e ($x10^{10}$ m^2/s)**	**Reference**
Benzene	Geosynthetic Clay Liner	2.2 to 2.5	Lake and Rowe (2004)
TCE	Geosynthetic Clay Liner	1.1	Lake and Rowe (2004)
Benzene	Saturated Inactive Clay	1.5 to 5.0	Hrapovic (2001), Myrand et al. (1987), Donahue et al., (1999)
EB	Saturated Inactive Clay	1.5 to 2.5	Hrapovic (2001)
TCE	Saturated Inactive Clay	2.0 to 2.5	Hrapovic (2001), Myrand et al. (1987)
TCE	Soil-Bentonite Slurry Wall	3.4 to 4.2	Krol and Rowe (2004)

EB= Ethylbenzene, TCE= Trichloroethylene

The values of D_e determined when assuming that n_e was equal the values obtained from tritium diffusion testing were always larger than those determined when assuming n_e was equal to the porosity determined from oven-drying. This is as expected as a slightly larger assumed value of n_e requires that the value of D_e be smaller to result in in the same diffusive flux (Equation 5-4). The value of $n_e\times D_e$, which is directly related to the diffusive flux, was found to range from 6.0×10^{-11} to 9.0×10^{-11} m^2/s when using the values of n_e obtained from tritium diffusion testing and 6.3×10^{-11} to 9.5×10^{-11} m^2/s when using values of n_e based on oven-drying. Additionally, there was no substantial difference in the values of D_e or $n_e\times D_e$ for trichloroethylene obtained from the tests where trichloroethylene was tested in isolation and those where it was tested with the other organic compounds as co-solutes. Consequently, under the specific test conditions, there was no indication that the diffusion of trichloroethylene was influenced by the other organic compounds.

The values of D_e and $n_e \times D_e$ obtained for the three different VOCs were similar. This is expected as the free-solution diffusion coefficients (D_o) of the three VOCs vary over a relatively narrow range (9.16×10^{-10} to 1.16×10^{-9} m^2/s). As discussed in Chapter 2, having similar D_o indicates that the three VOCs diffuse at similar maximum rates under ideal conditions (i.e., on a microscopic scale in pure water at infinite dilution). Therefore, if the three VOCs experience similar tortuosities (τ) when diffusing through soil-cement specimens, it can be expected that the measured values of D_e are similar. Unlike the results of diffusion testing on tritiated water (Chapter 3) no trend in $n_e \times D_e$ was observed with water-to-cement ratio. This may be due, in part, to the difficulty of VOC diffusion testing and analytic measuring relative to testing with and measuring a conservative, non-volatile, compound such as tritiated water.

Using Equation 5-1, D_R was calculated for each of the diffusion tests. D_R was found to range from 0.34×10^{-10} to 1.79×10^{-10} m^2/s when assuming n_e from tritium diffusion testing and 0.33×10^{-10} to 1.75×10^{-10} m^2/s when assuming n_e based on oven-drying. D_R was generally found to increase slightly with increasing water-to-cement ratio; this was likely due to increased diffusive transport in mixtures with higher porosities. Furthermore, D_R also generally increased based on contaminant in the following order $D_{RBenzene} > D_{RTrichloroethylene} > D_{REthylbenzene}$ which can be largely attributed to the different levels of sorption observed for the three VOCs.

Table 5.9 compares the calculated τ for all mixtures considering both assumptions for the value of n_e. Overall, the tortuosity was found to range from 0.13 to 0.25 when using n_e determined from tritium diffusion testing and 0.19 to 0.33 when determining n_e from oven-drying. For comparison, tortuosities from tritium diffusion testing (discussed in Chapters 3 and 4) on the three mixtures ranged from 0.10 to 0.25. As with the determination of D_e, small changes in tortuosity may be more difficult to detect in VOC diffusion testing relative to tritium diffusion testing. This may explain the apparent lack of trend of tortuosity with increasing n_e for the VOCs.

Table 5.9 — Comparison of tortuosities determined from VOC diffusion testing program to tortuosities determined from diffusion testing on tritiated water (Chapters 3 and 4).

Mixture	Tortuosity, τ				
	Benzene	Trichloroethylene		Ethylbenzene	Tritium
		Group	Alone		
	n_e from Tritium Diffusion Testing				
c	0.15	0.18	0.18	0.16 to 0.19	0.20 to 0.25
h	0.13 to 0.19	0.15 to 0.18	0.20 to 0.23	0.16 to 0.22	0.12 to 0.16
g	0.17 to 0.19	0.18 to 0.20	0.20 to 0.23	0.22 to 0.25	0.10 to 0.12
	n_e from Oven-Drying				
c	0.19 to 0.22	0.25	0.25	0.22 to 0.25	-
h	0.19 to 0.26	0.20 to 0.25	0.30	0.25 to 0.30	-
g	0.24 to 0.26	0.23 to 0.25	0.28 to 0.30	0.30 to 0.33	-

The three VOCs tested have relatively high solubility compared to other non-polar organic compounds (e.g., naphthalene) and hence the relatively low values of K_d measured in both batch testing and diffusion testing are not surprising. It is interesting to note the similarity in K_d values obtained from batch and diffusion testing; Figure 5.5 plots average values of K_d determined from batch testing against average values of K_d obtained from diffusion testing for each mixture and each VOC.

The values of K_d determined from diffusion testing presented in this plot were attained using n_e determined from tritium diffusion testing. A line with a slope of 1:1 is presented on Figure 5.5, this line represents the case where K_d determined from batch testing and diffusion testing are equal. This observation is useful when trying to examine the influence of VOC sorption on contaminant migration. Batch testing is a relatively quick and simple approach to establish values of K_d compared to double-reservoir diffusion testing. As will be shown later in the chapter, the contaminant migration from cement-based S/S monoliths may be very dependent on the level of sorption assumed during modeling. Overall, the value of K_d was generally found to decrease with increasing water-to-cement ratio and based on compound in the following order $K_{dEthylbenzene}$ > $K_{dTrichloroethylene}$ > $K_{dBenzene}$. There was no substantial difference in the values of K_d obtained when trichloroethylene was tested in isolation and those when trichloroethylene was tested simultaneously with the other organic compounds. This suggests that under the specific conditions of this study (e.g., concentration) there was negligible interaction between trichloroethylene and the other VOCs in solution (i.e., there were negligible competition effects).

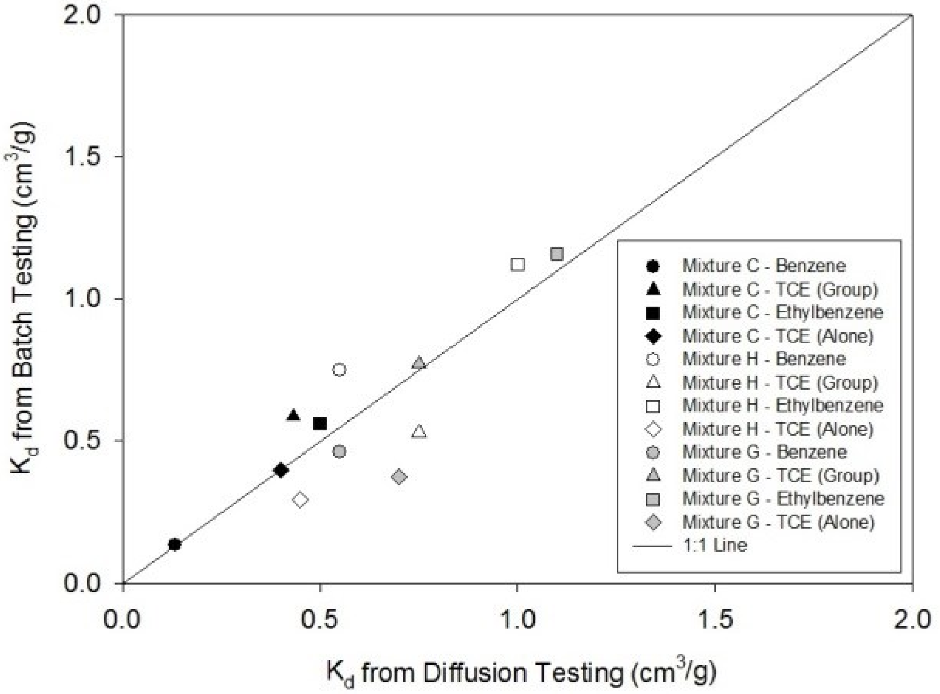

Figure 5.5 — Average K$_d$ from determined from batch testing vs. average K$_d$ obtained from diffusion testing for a given mixture and VOC (using the assumption that the effective porosity, n$_e$, was equal to the average value determined from tritium diffusion testing on the same mixture when analyzing the diffusion tests).

For organic compounds, K$_d$ [M^{-1}L^3] may be normalized to the fraction of organic carbon, f$_{oc}$ [-], to produce the organic carbon-water partition coefficient, K$_{oc}$ [M^{-1}L^3], as shown in Equation 5-6 (Karickhoff et al. 1979; Schwarzenbach et al. 2003).

$$K_{OC} = \frac{K_d}{f_{OC}} \qquad (5\text{-}6)$$

Furthermore, Karickhoff et al. (1979) present an empirical correlation to predict K_{oc} (cm^3/g) for a particular organic compound based on the octanol-water partition coefficient, K_{ow} (-) (Equation 5-7).

$$\log K_{OC} = \log K_{OW} - 0.21 \tag{5-7}$$

Equations 5-6 and 5-7 may be used to calculate an expected value of K_d for each compound if the f_{oc} is known. Afshar (2008) evaluated the f_{oc} of the materials used in the current study and the results are repeated in Table 5.10.

Table 5.10 — Organic carbon content of materials used in this study (Afshar 2008)

Material	**% Organic Carbon**
Sand	0.031
Kaolinite	0.401
Type 10 Portland Cement	0.270
Weighted Average	0.127

The weighted average f_{oc} of the solids (sand, kaolinite, and cement) for each of the three soil-cement mixtures used in this study is 0.13%. Using the values of K_{OW} presented in Table 5.3 and the weighted average f_{oc}, the expected values of K_d were determined to be 0.11, 1.10, and 0.21 cm^3/g for benzene, ethylbenzene, and trichloroethylene, respectively. These values are presented alongside average values of K_d from batch testing and diffusion testing for each compound in Table 5.11. The results show that experimentally measured and calculated theoretical values of K_d compare relatively well. This provides not only a quick check on laboratory results but also provides some confidence in using the relationships presented in Equations 5-6 and 5-7 to assume values of K_d for use in pre-design modeling assessments.

The VOC diffusion test results for the three soil-cement mixture tested in this study have shown that D_e for monolithic soil-cement specimens with low hydraulic conductivity are similar to those obtained for other low hydraulic conductivity materials such as compacted clay and geosynthetic clay liners. This suggests that if the hydraulic characteristics of the soil-cement material are maintained, the long-term contaminant migration out of a soil-cement monolith may be predicted relatively well using conventional contaminant transport approaches such as those applied to compacted clay liners (e.g., Lake and Rowe 2005).

Table 5.11 — Comparison of calculated and average measured values of K_d for benzene, ethylbenzene, and trichloroethylene.

VOC	K_d (cm^3/g)			
	Calculated based on f_{oc} and K_{ow} (Karickhoff et al., 1979)	**Average determined from batch Testing**	**Average determined from diffusion testing assuming n_e from tritiated water diffusion tests**	**Average determined from diffusion testing assuming n_e from oven-drying**
Benzene	0.11	0.42	0.37	0.32
Ethylbenzene	1.10	0.92	0.81	0.70
Trichloroethylene	0.21	0.35[a]/0.65[b]	0.61[a] /0.52[b]	0.45[a] /0.53[b]

[a]When benzene, ethylbenzene, trichloroethylene, and naphthalene were being tested simultaneously.
[b]When trichloroethylene was the only compound being tested.

During pre-design, where decisions may be made about the type of containment technologies employed, values from literature (such as those presented in this chapter), are often relied on in the absence of test data on the specific mixture. Contaminant transport modeling can show the relative effects of how a change in the value of a given parameter influences contaminant migration. The next section demonstrates how contaminant migration modeling may be performed and shows the relative effects of the three parameters studied (n_e, D_e, and K_d) over a range of values through the use of an illustrative example.

5.5. MODELING

The results of diffusion testing and batch testing of benzene, ethylbenzene, and trichloroethylene for several soil-cement mixtures have been discussed above. This section is concerned with the relative effects of the parameters n_e, D_e, and K_d and with illustrating how these parameters may be used in contaminant migration modeling. A theoretical site, which is used as an illustrative example, is shown in Figure 5.6.

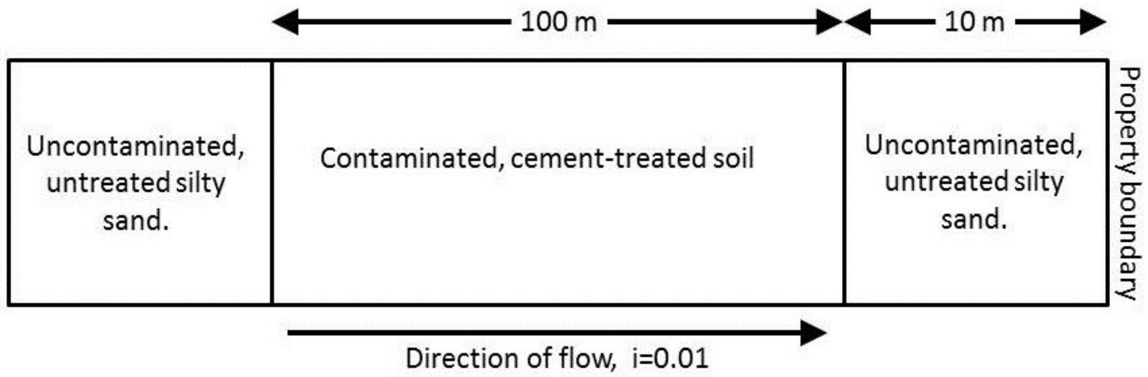

Figure 5.6 — Theoretical site used in example contaminant migration analyses.

The following assumptions were used in all modeling presented in this chapter:

- The potential for contaminant migration is only lateral (i.e., one-dimensional) and the horizontal gradient, i, is a constant 1%.
- The neighbouring soil consists of a silty sand with the following properties, $k = 1\times10^{-7}$ m/s, $n_e = 0.40$, $D_e = 5.0\times10^{-10}$ m^2/s, and $K_d = 0$).
- The impacted portion of the site has a uniform initial concentration of trichloroethylene of 3.4 g/m^3.
- There is no volume increase of the soil due to cement-based S/S treatment.
- The properties of the soil beyond the property line (i.e., to the right in Figure 5.6) are constant to an infinite extent.

- There is no biological degradation, volatilization, or transformation of contaminants.

- The soil-cement material will maintain constant material properties for at least 1000 years.

Nine different cases were modeled and a summary of the transport properties used in each case is provided in Table 5.12.

Table 5.12 — Contaminant transport parameters used in modeling and the modeled concentration of trichloroethylene at the property boundary after 1000 years for the theoretical site.

Case	**Mixture**	**W:C**	**Soil-Cement Monolith Properties**				**Concentration at boundary**
			n_e	**D_e (m^2/s)**	**k (m/s)**	**K_d (cm^3/g)**	**after 1000 Years (µg/L)**
1	c	2.0	0.34	2.5×10^{-10}	3.3×10^{-9}	0	164
2	h	1.5	0.30	2.6×10^{-10}	4.2×10^{-10}	0	49
3	g	1.0	0.27	2.6×10^{-10}	4.6×10^{-10}	0	52
4	c	2.0	0.34	2.5×10^{-10}	3.3×10^{-9}	0.4	70
5	h	1.5	0.30	2.6×10^{-10}	4.2×10^{-10}	0.6	18
6	g	1.0	0.27	2.6×10^{-10}	4.6×10^{-10}	0.7	16
7	c	2.0	0.48	1.8×10^{-10}	3.3×10^{-9}	0.3	70
8	h	1.5	0.42	1.9×10^{-10}	4.2×10^{-10}	0.5	18
9	g	1.0	0.37	2.0×10^{-10}	4.6×10^{-10}	0.7	15

The nine cases consider results of diffusion testing (i.e., D_e and K_d) for the three mixtures using both the assumption that n_e is equal to the value determined from tritium diffusion testing (cases 1-6) and the assumption that n_e is equal to the value determined based on oven-drying (cases 7-9). Cases 1-3 are modeled without sorption (i.e., K_d=0) while cases 4-9 are modeled with sorption. The hydraulic conductivity used in each case was equal to the average hydraulic conductivity determined for each mixture (presented in Chapter 4).

Figure 5.7 shows the concentration of trichloroethylene at the property boundary (10 m downgradient from the soil-cement monolith) for times up to 1000 years and Table 5.12 summarizes the concentration at the property boundary after 1000 years for each case.

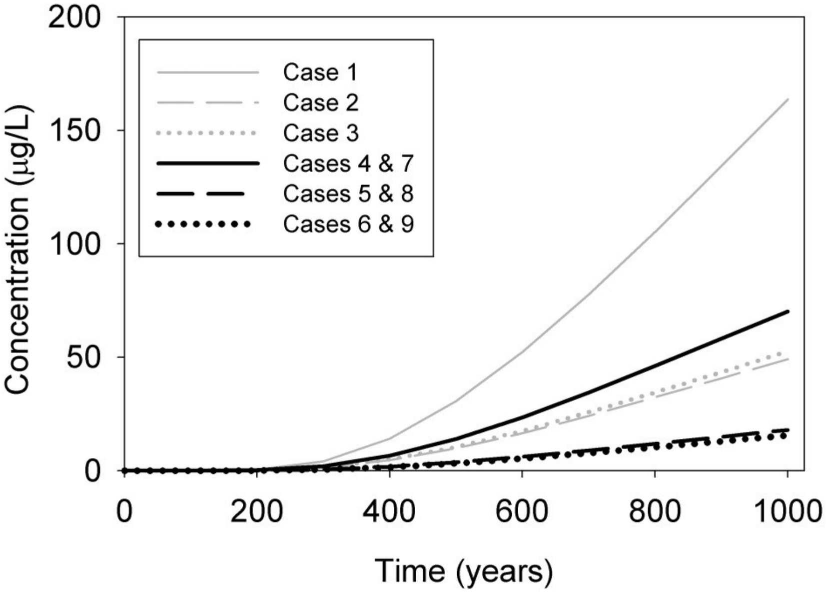

Figure 5.7 — Concentration at the property boundary for the theoretical site for modeling cases 1 to 9.

The concentrations at the property boundary for the cases representing soil-cement material with the highest water-to-cement ratio (cases 1, 4, and 7) are substaintially higher than those representing the other two mixtures. Considering the cases modeled without sorption (cases 1, 2, and 3), the higher values of k and D_e in case 1 results in a concentration of 164 µg/L after 1000 years compared to the 49 and 53 µg/L observed for cases 2 and 3, respectively. Figure 5.7 shows the effect of considering a moderate amount of sorption (K_d = 0.4 to 0.7 cm^3/g) for the soil-cement monolith on the concentration at the property boundary. When this relatively low level of sorption is considered (cases 4 to 6), concentrations at the property boundary after 1000 years are reduced to 70, 18, and 16 µg/L from 164, 49, and 53 µg/L when no sorption is modeled (cases 1-3).

Table 5.12 also illustrates that the assumption used to define n_e in the interpretation of the diffusion tests has a negligible effect on the modeled concentrations. When using n_e

determined from tritium diffusion testing and the associated D_e and K_d, the modeled concentrations at the property boundary after 1000 years were 70, 18, and 16 μg/L for mixtures c, h, and g, respectively. When using n_e determined from oven-drying (and the associated D_e and K_d) the concentrations were correspondingly 70, 18, and 15 μg/L.

5.6. PRACTICAL APPLICATIONS

It has been illustrated above that the choice of n_e does not have a substantial effect on the interpretation of the VOC diffusion tests. Therefore, for simplicity, when interpreting diffusion test results from double-reservoir diffusion tests, it is likely sufficient to estimate the n_e based on the porosity obtained from oven-drying.

Considering the relative influence of K_d on the results of contaminant migration modeling, presented above, when developing a contaminant migration model, it may often be sufficient to conservatively estimate D_e (e.g., based on the results of the testing performed in this thesis) and to measure K_d using batch tests or to estimate it from established relationships (e.g., Karickhoff et al. 1979). This approach may offer significant efficiency as batch testing or measuring the fraction of organic content of the soil is substaintially less time- and material-intensive than diffusion testing. In many cases this approach may be sufficient to estimate the contaminant migration from a particular site with sufficient accuracy to guide decision-making related to the selection of the cement-based S/S versus other treatment options. In cases where more investigation is warranted, such as in detailed design, diffusion testing may be performed as outlined above to estimate the diffusive and sorptive parameters based on site-specific details (mix design, contaminants of interest, etc.). Furthermore, the relative influence of K_d on the results of contaminant migration modeling suggests that the use of additives that promote sorption (e.g. fly ash) may be an efficient way to decrease contaminant migration from soil-cement systems used in source-control remediation. For instance, Lake et al. (2013) examined the potential for beneficial resue of fly ash as a sorbent for benzene, trichloroethylene, and ethylbenzene in soil-cement materials and concluded that the addition of fly ash can potentially reduce the rate of migration of trichloroethylene and ethylbenzene from contaminanted sites due to increased sorption (i.e. increased values of K_d due to the inclusion of fly ash). The effect of sorption is further investigated in Chapter 6.

5.7. SUMMARY AND CONCLUSIONS

To understand the long-term performance of cement-based S/S materials it is essential to have methods to reliably estimate contaminant migration parameters. This includes methods to measure or estimate parameters describing diffusion and sorption (i.e., n_e, D_e, and K_d). To date, there has been insufficient research investigating the diffusion of VOCs through soil-cement materials. From a design perspective, there is currently a lack of published values of D_e and K_d for soil-cement materials which makes it necessary to assume values based on those published for other materials; this study has provided some assistance in this regard.

Thirteen diffusion tests were performed on three different laboratory-prepared mixtures of water, Portland cement, silica sand, and kaolinite using benzene, ethylbenzene, and trichloroethylene as tracers. Double-reservoir diffusion tests performed in glass diffusion apparatuses were adapted from those developed for clayey soils. The one-dimensional contaminant migration equation was solved using a finite layer computer program and the best-fit parameters were determined by using a trial-and-error method. In this analysis, two different assumptions were used for the value of n_e: a) that it was equal to the value n_e determined from tritium diffusion testing and b) that it was equal to the total porosity determined from oven-drying).

Values of D_e determined from diffusion testing ranged from 1.5×10^{-10} to 3.0×10^{-10} m^2/s for the three water-to-cement ratios and three VOCs tested. No trends of D_e or $n_e\times D_e$ were apparent based on VOC or based on the water-to-cement ratio. K_d determined from batch testing and diffusion testing were found to range from 0 to 1.3 cm^3/g and compare relatively well to each other and to theoretical estimates based on f_{oc} and K_{ow}. Results of diffusion and batch testing using solutions of trichloroethylene in isolation and trichloroethylene in solution with the other organic compounds were similar and reveal no evidence of interaction or competition effects.

Contaminant migration modeling of a theoretical site was performed to show the relative importance of the diffusive and sorptive parameters obtained from testing (i.e., n_e, K_d, and D_e). For the range of values modeled K_d had the largest influence on the results (assuming that the hydraulic conductivity remains constant). The porosity selected in diffusion test analyses was shown to have a negligible effect when applying the results of testing to a theoretical site.

5.8. ACKNOWLEDGEMENTS

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CHAPTER 6: NAPHTHALENE DIFFUSION AND SORPTION COEFFICIENTS FOR CEMENT SOLIDIFIED-STABILIZED MATERIALS[3]

6.1. INTRODUCTION

This chapter discusses naphthalene diffusion and sorption testing that was performed in conjunction with the volatile organic compound (VOC) diffusion and sorption testing presented in Chapter 5. Naphthalene is discussed separately as it has substantially different physical and chemical properties than the VOCs. Naphthalene has a higher boiling temperature, a lower solubility in water, and a higher free-solution diffusion coefficient (D_o) than the VOCs (Table 6.1).

Table 6.1 — Summary of physical and chemical properties of naphthalene.

	Molecular Weight[a]	**Boiling Temperature[a]**	**Solubility in Water[a] @20°C**	**Log K_{ow}[a] @25°C**	**Dielectric Constant[a] @20°C**	**D_o[b] @25°C**	**Specific Density[a] @20°C**
	(g/mol)	**(°C)**	**(g/L)**	**(-)**	**(-)**	**(m^2/s)**	**(g/cm^3)**
Naphthalene	128.2	218	0.031	3.36	2.5	7.63×10^{-10}	1.14

[a] Schwarzenbach et al. (2003).
[b] Yaws (2010).

In this chapter, laboratory determined values of the effective diffusion coefficient (D_e) and distribution coefficient (K_d) of naphthalene for three different soil-cement mixtures are presented. Batch testing is performed to provide an estimate of K_d independent of diffusion testing. Additionally, the results of contaminant transport modeling on a theoretical site are presented to show the relative effects of the parameters determined from this testing (i.e., D_e and K_d).

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[3] A modified and condensed version of this chapter has been published:
Goreham, V., and Lake, C.B., 2013b, "Naphthalene Diffusion and Sorption Coefficients for Cement Solidified/Stabilized Materials", *Proceedings of the 5th International Young Geotechnical Engineers' Conference,* Marne-la-Vallée, France, pp. 98–101.

6.2. BACKGROUND

Naphthalene ($C_{10}H_8$) is an organic compound comprised of two fused benzene rings (Figure 6.1) that has been been noted as a contaminant of concern in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (Agency for Toxic Substances & Disease Registry 2007). Naphthalene has been used in a number of industrial applications including as a wetting agent and fumigant as well as in the production of plastics, insecticides, pesticides, plasticizers, dyes, and tanning agents (USEPA 2010). Furthermore, naphthalene contamination is prominent on sites containing petroleum products (Sawatsky et al. 1997). Naphthalene is a potential human carcinogen and has been shown or is suspected of having a number of possible adverse health effects which include: anemia, cataracts, and damage to red blood cells (USEPA 2010).

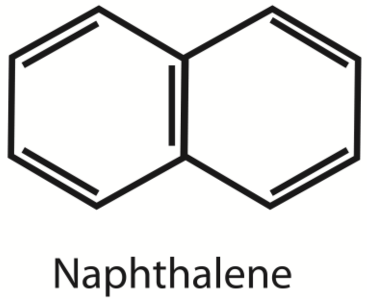

Figure 6.1 — Chemical Structure of naphthalene (Brown and Poon 2005).

The United Stated Environmental Protection Agency does not define a Maximum Contaminant Level (MCL) for naphthalene. The Canadian Council of Ministers of the Environment (1999d) defines the Water Quality Guideline for the Protection of Aquatic Life to be 0.090 mg/L.

One notable case of cement-based solidification/stabilization (S/S) of naphthalene contaminated soil and sediments is the Sydney Tar Ponds and Coke Ovens Site in Cape Breton, Nova Scotia. This site contains over 1.2 million tonnes of soils and sediments impacted by many pollutants (including naphthalene) from historical industrial activities (AMEC 2004).

There is a paucity of research investigating diffusion of organic compounds such as naphthalene for soil-cement materials. Hebatpuria et al. (1999) investigated the leaching of naphthalene from cement-based S/S materials (some treated with reactivated carbon). This study determined that the retarded diffusion coefficient, $D_{R,}$ for naphthalene and the cement-based S/S material utilized was approximately 4.0×10^{-10} m^2/s and generally increased over the seven day duration of the test which implies the actual diffusion coefficient was not established and that the results were influenced by some mechanism other than diffusion. As discussed in Chapter 2, the parameter D_R includes the effects of sorption and may be defined by Equation 6-1.

$$D_R = \frac{D_e}{1 + \frac{\rho K_d}{n_e}} \tag{6-1}$$

Where: D_R is the retarded diffusion coefficient $[L^2T^{-1}]$, D_e is the effective diffusion coefficient $[L^2T^{-1}]$, ρ_d is the dry density of the soil-cement $[ML^{-3}]$, K_d is the distribution coefficient $[M^{-1}L^3]$, and n_e is the effective porosity [-]. In this chapter, square brackets denote the fundamental dimensions mass [M], length [L], and time [T] for dimensionally consistent equations. Scale units such as kilogram (kg), metre (m), and second (s) are presented in round brackets for equations that are dimensionally inconsistent.

6.3. EXPERIMENTAL METHOD

Diffusion and batch testing methodology are discussed in detail in Chapter 5 and thus are not repeated in full detail in the current chapter. For completeness, a summary is provided in the following subsections.

6.3.1. Specimen Preparation and Testing Program

A mixture of 80% silica sand and 20% kaolinite (by dry mass) was mixed in a 20 L bucket and sufficient water was added to result in a water content of 13 %. This mixture has been referred to as "soil A" in Chapters 4 and 5. This soil was mixed with cement (CSA Type 10, general use, normal Portland cement provided by Holcim Canada) grout at three different water-to-cement ratios which resulted in three unique soil-cement mixtures. Sufficient grout was added in each of the three mixtures to result in a 15 % cement content (by dry mass). Specimens were promptly cast in 69-mm diameter by 30-mm long cylindrical polyvinylchloride molds and subject to evenly distributed tamping with pressure just sufficient to ensure uniform filling of the molds. Specimens were stored in separate, tightly sealed, plastic bags at 21 ± 2 °C for 56 days before being extruded and returned to the bags for an additional 28 days (84 days total curing time) before testing.

The three mixtures (mixtures c, h, and g) are identical to three mixtures used in the tritiated water diffusion testing program discussed in Chapter 4 and hence the sample naming and numbering system used in that chapter is continued. Table 6.2 summarizes the proportions of soil, water, and cement in each mixture.

Table 6.2 — Summary of soil-cement mixtures tested with naphthalene.

Mixture	Soil	Cement[a] (%)	Total W:C[b]	Grout W:C[c]	Total Fraction		
					Cement	Soil	Water
c	A	15	2.87	2	0.10	0.63	0.27
h	A	15	2.37	1.5	0.10	0.66	0.24
g	A	15	1.87	1	0.10	0.70	0.20

Note: Tests include benzene, ethylbenzene, and trichloroethylene as co-solutes.

[a] Cement content as a percentage of dry soil mass.

[b] Total water-to-cement ratio including water content of soil at mixing (13%).

[c] Water-to-cement ratio of cement grout.

6.3.2. Diffusion Testing

Diffusion testing was performed using a double-reservoir diffusion apparatus built of glass. A photograph of a typical diffusion apparatus is shown in Figure 6.2. Details on the apparatus and the experimental method are presented in detail in Chapter 5 and are not repeated in full in this chapter. In general the test method is adapted from a procedure presented by Rowe et al. (1988) developed for clayey soils. Diffusion testing on mixture ‘c’ was performed in triplicate and diffusion testing on mixture ‘h’ and mixture ‘g’ were performed in duplicate.

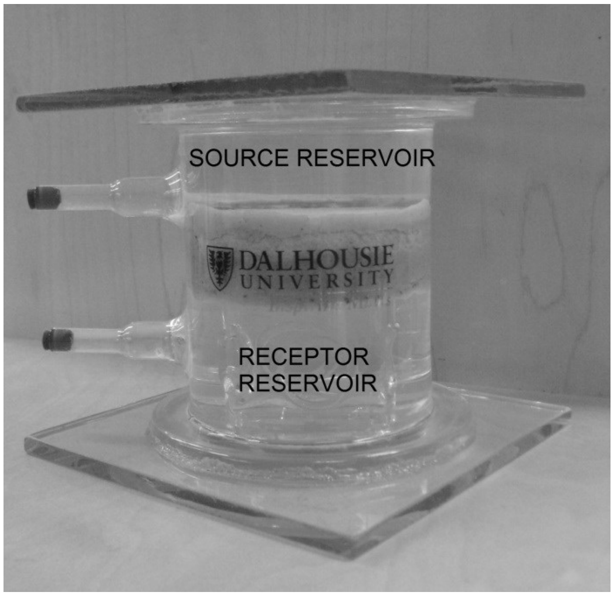

Figure 6.2 — Photograph of a typical glass double-reservoir diffusion apparatus.

For each diffusion test, a reservoir with a known initial concentration was on one side of the specimen (in the source reservoir) while Type 1 ultrapure water (i.e., Milli-Q water) was initially on the other side (in the receptor reservoir). The concentrations in each reservoir were monitored intermittently (typically twice-weekly) as the test progressed. During the test the concentration in the source reservoir decreased and the concentration in the receptor reservoir increased as naphthalene migrated from the source reservoir, though the specimen, and into the receptor reservoir.

For the seven diffusion tests, the initial concentration of naphthalene in the source reservoir ranged from 3.8 to 5.3 mg/L. The source reservoir also contained benzene (26.0 to 50.9 mg/L), trichloroethylene (11.7 to 47.9 mg/L), and ethylbenzene (10.4 to 49.4 mg/L). The initial concentration of each compound and the source and receptor reservoir volumes for each diffusion test are summarized in Table 6.3.

Table 6.3 — Initial concentrations and reservoir volumes for naphthalene diffusion tests.

	Volume		**Initial concentration, C_o**			
Specimen	**Source (mL)**	**Receptor (mL)**	**Benzene (mg/L)**	**TCE (mg/L)**	**Ethylbenzene (mg/L)**	**Naphthalene (mg/L)**
c4	132.0	175.0	28.2	11.7	11.3	5.3
c5	131.0	170.0	26.5	13.7	10.4	5.0
c6	145.4	166.5	26.0	21.1	12.0	5.1
h4	128.9	168.3	50.0	47.0	46.7	4.2
h5	120.9	173.3	46.8	43.2	41.7	3.8
g4	138.9	165.1	50.1	47.8	49.0	3.9
g5	134.7	173.6	50.9	47.9	49.4	3.8

6.3.3. Batch Testing

Batch testing was performed on each of the three soil-cement mixtures to allow for an estimation of K_d independent of diffusion testing. The methodology is described in detail in Chapter 5 and is briefly outlined below. Generally, procedures similar to those described by Afshar (2008) were employed.

Batch tests were performed on specimens that were cured for a minimum of 84 days. Prior to testing, the specimens were pulverized, sieved through a 2 mm sieve, and oven-dried to a constant mass at 60°C.

Sorption isotherms were developed using solutions with naphthalene concentrations of 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 2.5, and 5.0 mg/L. Each solution contained benzene, trichloroethylene, and ethylbenzene at concentrations approximately ten times that of naphthalene. Batch tests were performed in triplicate; however, only duplicate results are available for mixture g at the 1 mg/L concentration level due to a vial breaking in the centrifuge.

Three grams of soil-cement were placed in each 50-mL pyrex centrifuge tube. The tubes were sealed with open-top caps lined with polytetrafluoroethylene septa. The centrifuge tubes were filled with ultrapure water and spiked with a known amount of stock solution containing benzene, ethylbenzene, trichloroethylene, and naphthalene. All solutions contained 1.0 g/L of sodium azide to act as a biocide. The centrifuge tubes were sealed with open-top caps lined with polytetrafluoroethylene septa and agitated end-over-end for 24 ±2 hours at (21±2 °C) before liquids and solids were separated using centrifugation. Three aliquots of the liquid were sampled from each tube and placed with ultrapure water (as required) in three separate 2-mL gas chromatograph auto sampler vials. Gas chromatography was used to analyze the concentration in each vial. A group of vials without any soil-cement, containing solutions at each concentration level, and subject to the same procedures presented above was used as a control.

6.3.4. Diffusion Coefficient Estimation

The experimental data obtained from diffusion testing was compared to the results of theoretical modeling using the 1D contaminant migration program POLLUTE v6 (Rowe et al. 1998). The best-fit parameters (i.e., D_e and K_d) were determined from the values which resulted in the lowest root-mean-square error (RMSE) when comparing the experimental and theoretical concentrations.

Finite-mass boundary conditions (Rowe et al. 2004) were used to represent the source and receptor reservoirs. Finite-mass boundary conditions represent the case where the concentration at the boundary is constantly changing with time due to mass transfer through the specimen. For a finite-mass boundary condition, Equation 6-2 may be used to describe the concentration in the source reservoir at any time $c_t(t)$ (Rowe et al. 2004).

$$c_t(t) = c_o - \frac{1}{H_r}\int_0^t f_t(t)dt - \frac{q_c}{H_r}\int_0^t c_t(t)dt \qquad (6\text{-}2)$$

Where: c_o is the initial concentration in the source solution [ML^{-3}], H_r is the equivalent height of source fluid (volume of source fluid per unit area) [L]; $f_t(t)$ is the mass flux of contaminant into the soil-cement at any time t [$ML^{-2}T^{-1}$]; q_c is the fluid collected for sampling per unit area, per unit time [LT^{-1}].

Similarly, Equation 6-3 may be used to express the concentration in the receptor reservoir at any time $c_b(t)$ (Rowe et al. 2004).

$$c_b(t) = c_{bo} + \frac{1}{H_b}\int_0^t f_b(t)dt - \frac{q_c}{H_b}\int_0^t c_b(t)dt \qquad (6\text{-}3)$$

Where: c_{bo} is the initial concentration in the receptor solution [ML^{-3}], H_b is the equivalent height of the receptor reservoir (volume of receptor reservoir per unit area) [L], and $f_b(t)$ is the mass flux of contaminant into the receptor reservoir at any time t [$ML^{-2}T^{-1}$].

Transient one-dimensional contaminant transport (without decay) through porous media (e.g., soil-cement) may be described by Equation 6-4 (Rowe et al. 2004).

$$n_e\frac{\partial c}{\partial t} = n_e D_e\frac{\partial^2 c}{\partial z^2} - n_e v\frac{\partial c}{\partial z} - \rho_d K_d\frac{\partial c}{\partial t} \qquad (6\text{-}4)$$

Where: c is the concentration in the pore space of the soil-cement at depth z and time t [ML^{-3}], n_e is the effective porosity of the soil-cement [-], D_e is the effective diffusion coefficient [L^2T^{-1}], v is the Darcy velocity [LT^{-1}], ρ_d is the dry density of the soil-cement [ML^{-3}], and K_d is the distribution coefficient [$M^{-1}L^3$].

Equations 6-2 to 6-4 were solved using POLLUTE v.6 (Rowe et al. 1998) by applying a trial-and-error approach to match theoretical source and receptor concentrations to experimental data. Trial values of D_e were varied by increments of 0.25×10^{-10} m^2/s and trial values of K_d were varied by 0.1 cm^3/g. The best-fit values were taken as those that resulted in the least RMSE when comparing experimental data with the theoretical results.

In the previous chapter, when investigating diffusion of the VOCs, the diffusion tests were analyzed using two different assumptions for the value of n_e. Firstly it was assumed that for each soil-cement mixture, the value of n_e was equal to the average n_e determined from tritiated water diffusion testing on that mixture (i.e., from Chapter 4). Secondly, it was assumed that the value of n_e was equal to the average porosity determined from oven-drying of that mixture. For each assumption, the best-fit values of D_e and K_d were determined using trial-and-error based on lowest RMSE. The same approach is used in this chapter to interpret naphthalene diffusion.

6.4. RESULTS AND DISCUSSION

The results of a typical naphthalene diffusion test (on mixture c) analyzed using the assumption that n_e is equal to the value determined from diffusion testing of tritiated water are presented in Figure 6.3.

In Figure 6.3, the upper data points (starting at $c/c_o=1$) show the decrease in naphthalene concentration with time in the source reservoir due to contaminant migration into the soil-cement specimen. The lower data points (starting at $c/c_o=0$) show the corresponding increase in contaminant concentration in the receptor reservoir with time. The theoretical best-fit results are shown as dashed lines. Figure 6.4 shows the same experimental data analyzed assuming that n_e was equal to the average total porosity determined from oven-drying of all samples of mixture c. Plots showing the experimental data and theoretical best fits for all the naphthalene diffusion tests performed in this study are included in Appendix C.

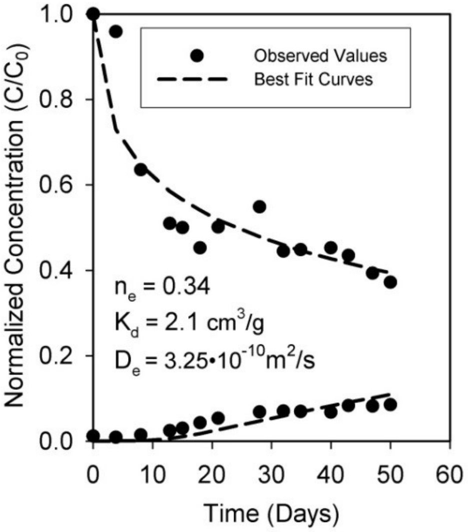

Figure 6.3 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c4.

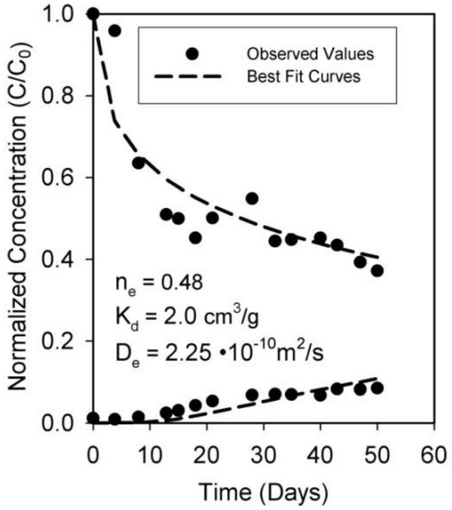

Figure 6.4 — Naphthalene concentration profiles from laboratory diffusion experiments and best-fit curves (assuming n_e from oven-drying) for specimen c4.

Table 6.4 summarizes the results of the naphthalene diffusion and batch testing. When using n_e determined from tritium diffusion testing, D_e was found to range from 2.25×10^{-10} to 3.50×10^{-10} m^2/s. When assuming n_e was equal to the average porosity determined from oven-drying, D_e was found to range from 1.50×10^{-10} to 2.75×10^{-10} m^2/s.

These values are comparable to those determined in Chapter 5 for benzene, ethylbenzene, and trichloroethylene. As was observed in Chapter 5 for the three VOCs examined, the values of D_e determined assuming n_e from tritium diffusion testing were always less than those determined assuming n_e based on oven-drying.

Table 6.4 — Summary of naphthalene batch and diffusion test results.

	Batch Testing	**n_e from Tritium Diffusion Testing**					**n_e from Oven-Drying**				
Specimen	**K_d (95% CI)**	**n_e**	**K_d**	**D_e ×10^{10}**	**D_R ×10^{10}**	**RMSE[a]**	**n_e**	**K_d**	**D_e ×10^{10}**	**D_R ×10^{10}**	**RMSE[a]**
	(cm^3/g)	**(-)**	**(cm^3/g)**	**(m^2/s)**	**(m^2/s)**	**(-)**	**(-)**	**(cm^3/g)**	**(m^2/s)**	**(-)**	**(-)**
c4	1.3 – 1.5	0.34	2.1	3.25	0.35	0.055	0.48	2.0	2.25	0.34	0.054
c5	1.3 – 1.5	0.34	1.9	3.00	0.35	0.048	0.48	1.7	2.25	0.39	0.049
c6	1.3 – 1.5	0.34	2.5	3.25	0.30	0.069	0.48	2.5	2.25	0.28	0.069
h4	1.5 – 2.0	0.30	1.5	2.75	0.33	0.034	0.42	1.5	1.75	0.28	0.034
h5	1.5 – 2.0	0.30	1.6	2.25	0.25	0.025	0.42	1.6	1.50	0.23	0.026
g4	1.7 – 1.9	0.27	2.3	3.50	0.24	0.037	0.37	2.1	2.75	0.27	0.037
g5	1.7 – 1.9	0.27	1.6	3.00	0.28	0.025	0.37	1.5	2.25	0.30	0.025

[a] Root-mean-square error for best-fit parameters and laboratory diffusion test results.

The value of $n_e \times D_e$, which is directly related to the diffusive flux, was found to range from 6.8×10^{-11} to 1.1×10^{-10} m^2/s when using the values of n_e from tritium diffusion testing and 7.2×10^{-11} to 1.2×10^{-10} m^2/s when using values of n_e determined from oven-drying. No trend in D_e or $n_e \times D_e$ was apparent with water-to-cement ratio.

Table 6.5 compares the calculated tortuosities for the naphthalene diffusion tests to those determined for tritium (Chapters 3 and 4) and benzene, ethylbenzene, and trichloroethylene (Chapter 5).

Table 6.5 — Comparison of tortuosities determined from naphthalene diffusion to those determined from diffusion testing on tritiated water, benzene, trichloroethylene, and ethylbenzene.

Mixture	n_e from oven-drying		n_e from tritium diffusion testing		
	$\tau_{Naphthalene}$	$\tau_{Benzene}$, $\tau_{Ethylebenzene}$, $\tau_{Trichloroethylene}$	$\tau_{Naphthalene}$	$\tau_{Benzene}$, $\tau_{Ethylebenzene}$, $\tau_{Trichloroethylene}$	$\tau_{Tritium}$
c	0.29 – 0.29	0.15 – 0.19	0.39 – 0.43	0.19 – 0.25	0.20 – 0.25
h	0.23 – 0.20	0.13 – 0.22	0.29 – 0.36	0.19 – 0.30	0.12 – 0.16
g	0.29 – 0.36	0.17 – 0.25	0.39 – 0.46	0.23 – 0.33	0.10 – 0.12

Using n_e determined from tritium diffusion testing, the tortuosity ranged from 0.29 to 0.46, and using n_e determined from oven-drying the tortuosity varied from 0.20 to 0.36. The calculated tortuosities for naphthalene were generally higher than those observed for tritiated water and the three VOCs. Naphthalene tends to sorb at higher levels than the other contaminants investigated in this thesis and it is postulated that the higher levels of sorption (i.e., increased value of K_d) observed for naphthalene may have influenced the interpreted values of D_e. As will be illustrated in the following section, the level of sorption observed for naphthalene has a more substantial effect on contaminant transport than D_e does over the range of values observed throughout this thesis.

Average values of K_d from diffusion testing on mixtures c, h, and g were 2.2, 1.6, and 2.0 cm^3/g, respectively when n_e was from tritium diffusion testing was used and 2.1, 1.6, and 1.8 cm^3/g, respectively when n_e was determined oven-drying was used. From the above results, it is apparent that the choice of n_e doesn't have a large effect on the value of K_d determined from diffusion testing.

Interpretation of the batch tests using linear sorption isotherms resulted in values of K_d of 1.4, 1.7, and 1.8 cm^3/g for mixtures c, h, and g, respectively. Figures showing the linear sorption isotherms for all three soil-cement mixtures are included in Appendix D. The values of K_d determined from diffusion testing and the 95% confidence interval of the determined from batch testing are presented in Table 6.4. Generally, the values of K_d determined from the two methods compare well.

As expected based on the higher K_{ow} and lower solubility of naphthalene, measured values of K_d for naphthalene were larger than those determined for the VOCs discussed in the previous chapter. As with the VOCs, no trend in the value of K_d was observed with water-to-cement ratio.

The retarded diffusion coefficient, D_R, was found to range from 0.24×10^{-10} to 0.35×10^{-10} m^2/s when using n_e determined from tritium diffusion testing and from 0.23×10^{-10} to 0.39×10^{-10} m^2/s when using n_e determined from oven-drying.

As discussed in Chapter 5, and shown in Equation 6-5, K_d may be normalized with respect to the fraction of organic carbon in the soil, f_{oc} [-] to produce the organic carbon-water partition coefficient, K_{oc} [$M^{-1}L^3$] (Karickhoff et al. 1979; Schwarzenbach et al. 2003).

$$K_{OC} = \frac{K_d}{f_{OC}} \tag{6-5}$$

Furthermore, K_{oc} (cm^3/g) may be estimated based on the octanol-water partition coefficient, K_{ow} (-), (Equation 6-6; Karickhoff et al. 1979).

$$\log K_{OC} = \log K_{OW} - 0.21 \tag{6-6}$$

The materials utilized to create the specimens used in this study had a weighted-average f_{oc} of 0.13% (Afshar 2008). Using this f_{oc}, a log K_{OW} of 3.36 for naphthalene (Schwarzenbach et al. 2003), and applying Equations 6-5 and 6-6 results in a calculated K_d of 1.8 cm^3/g. This value is in general agreement with the values determined from diffusion and batch testing (Table 6.3).

6.5. MODELING

In Chapter 5, contaminant migration modeling was performed to illustrate how the properties of the three different mixtures affect contaminant transport of an organic contaminant (trichloroethylene) through a theoretical site. In this chapter, similar modeling is performed to investigate the relative effects of D_e and K_d on contaminant transport. The theoretical site conditions used for the modeling in Chapter 5 (shown in Figure 5.5) are reused for this investigation. Furthermore, the assumptions used in this modeling are similar to those made for the modeling discussed in Chapter 5:

- The potential for contaminant migration is only lateral (i.e., one-dimensional) and the horizontal gradient, i, is a constant 1% for all cases.
- The neighbouring soil consists of a silty sand with the following properties, $k = 1\times10^{-7}$ m/s, $n_e = 0.40$, $D_e = 5.0\times10^{-10}$ m^2/s, and $K_d = 0$.
- The portion of the site impacted by naphthalene has a uniform initial concentration of 3.4 g/m^3.
- There is no volume increase of the soil due to cement-based S/S treatment.
- The properties of the soil beyond the property line (i.e., to the right in Figure 5.5) are constant to an infinite extent.
- There is no biological degradation, volatilization, or transformation of contaminants.
- The soil-cement material will maintain its material properties for at least 1000 years.

Six different cases were modeled; the assumed contaminant transport properties (i.e., k, n_e, D_e, and K_d) for each case are summarized in Table 6.6. Two different values of D_e

(2.0 and 3.5×10^{-10} m^2/s) and three different values of K_d (0, 0.5, 2.5 cm^3/g) were modeled. A constant value of k was assumed in all models (4.2×10^{-10} m/s).

Table 6.6 — Summary of contaminant transport parameters used in contaminant migration modeling.

Case	Soil-Cement Monolith Properties			Concentration at Boundary
	n_e (-)	D_e (m^2/s)	K_d (cm^3/g)	after 1000 Years ($\mu g/L$)
1	0.30	2.0×10^{-10}	0	45
2	0.30	2.0×10^{-10}	0.5	19
3	0.30	2.0×10^{-10}	2.5	6
4	0.30	3.5×10^{-10}	0	54
5	0.30	3.5×10^{-10}	0.5	21
6	0.30	3.5×10^{-10}	2.5	7

These values represent the approximate range of values obtained from diffusion testing on the organic contaminants (i.e., benzene, ethylbenzene, trichloroethylene, and naphthalene) discussed in this thesis. Other properties (e.g., n_e, k, i) were held constant for all six cases.

Figure 6.5 shows the concentration of naphthalene at the property boundary (10 m downgradient from the soil-cement monolith) for times up to 1000 years.

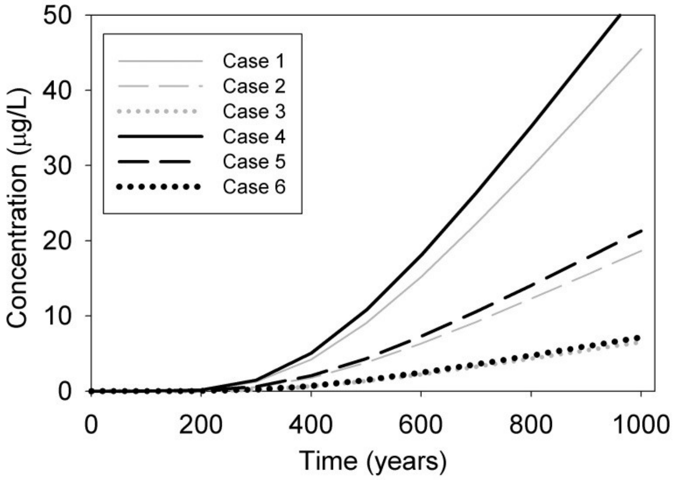

Figure 6.5 — Concentration at the property boundary for the theoretical site for cases 1-6.

Table 6.5 and Figure 6.6 present the concentration at the property boundary after 1000 years for each of the six cases. It can be seen that for the range of D_e and K_d modeled, K_d has a more significant effect on contaminant migration (e.g., concentration at the property boundary after 1000 years) than D_e. An increase in diffusion coefficient from 2.0 to 3.5×10^{-10} m^2/s (with all other parameters being held constant) resulted in an increase in concentration at the property boundary after 1000 years from 45, 19, and 6 mg/L to 54, 21, and 7 mg/L respectively (an increase of 10 to 18%). In comparison, a decrease in the value of K_d from 2.5 to 0 cm^3/g resulted in increase in concentration of 6 and 7 mg/L to 45 and 54 mg/L, respectively (an increase of 599 to 651 %).

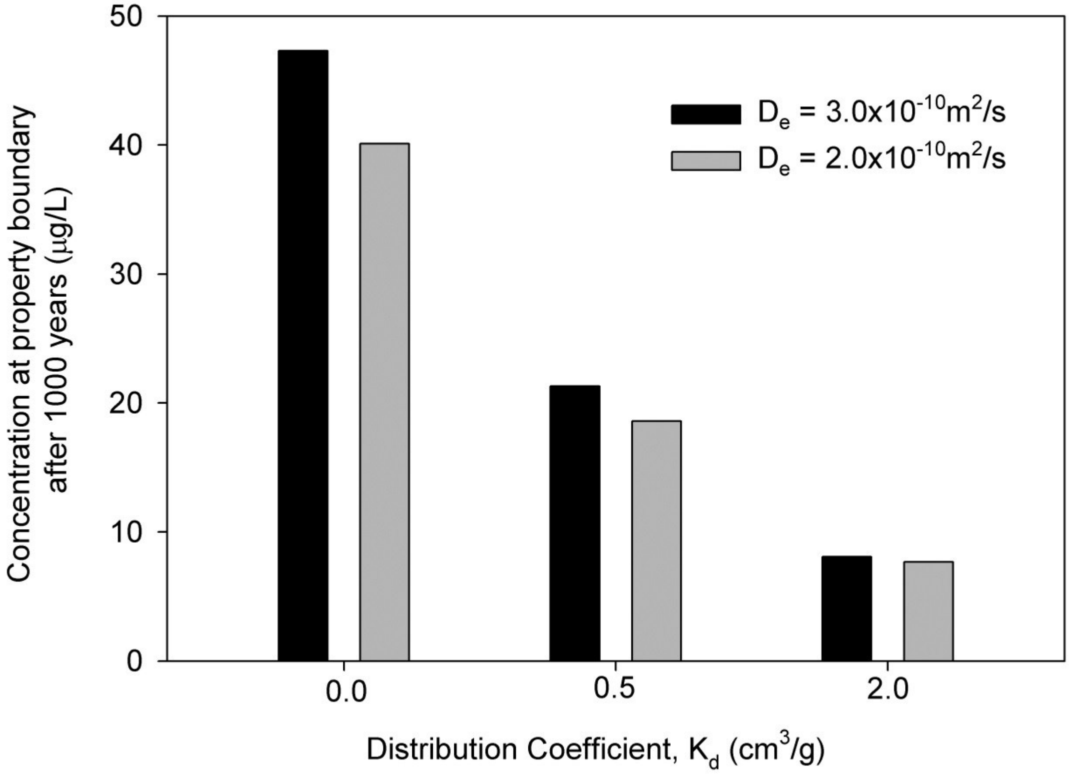

Figure 6.6 — Results of contaminant migration modeling on a theoretical site: concentration at the property boundary after 1000 years.

6.6. PRACTICAL APPLICATIONS

In many cases (such as the theoretical site modeled above) contaminant transport of compounds in low-hydraulic conductivity, monolithic, soil-cement materials that experience substantial sorption (e.g., naphthalene with the cement-based S/S materials studied herein) may be more influenced by sorption than by diffusion. Under these conditions an accurate estimate of D_e, may be of secondary importance compared to an accurate estimate of K_d.

In the modeled examples, a change in the diffusion coefficient from 2.0 to 3.5×10^{-10} m^2/s resulted in concentrations (at the property boundary, after 1000 years) that increased 10 to 18%. It is unlikely that this level of inaccuracy will influence the selection of cement-based S/S treatment over other treatment options. A much smaller change in K_d would be required to effect similar change. Therefore, when substantial levels of sorption are expected, it may be efficient to allocate more resources to the estimation and control of K_d rather than D_e during the predesign (feasibility and technology selection) stage. Contaminant transport modeling (as performed above) may be used as a tool to determine which parameters are likely to have the greatest effect on contaminant fate for a given site and site-specific conditions.

The modeling presented above supports the findings of Chapter 5 which indicate that for the pre-design stage it may be sufficient to conservatively estimate D_e (e.g., from the results presented in this thesis) and estimate K_d from batch testing or conservative estimates based on established relationships (e.g., Karickhoff et al. 1979). In cases where more investigation is warranted (e.g., detailed design, sensitive sites), diffusion testing performed as outlined above to estimate the diffusive parameters based on project-specific parameters may be performed.

Additionally, due to the illustrated importance of sorption in contaminant migration analyses, it may often be efficient to reduce contaminant migration from a site by increasing their capacity to sorb contaminants. This may be done by using additves that encourage sorption. For instance, Lake et al. (2013) have shown that the addition of fly ash can potentially reduce off-site migration of benzene, ethylbenzene, and trichloroethylene by increasing the sorptive capacity (i.e. K_d) of cement-treated soils. However, this approach may be more effective for contaminants that typically have a higher affinitty to sorb (i.e. those with a high $\log K_{ow}$) such as naphthalene than those with a low affinity for sorption such as benzene.

6.7. CONCLUSIONS

This chapter discussed naphthalene diffusion and sorption testing of three laboratory-prepared soil-cement mixtures. The three soil-cement mixtures were identical to three mixtures used in the tritiated water diffusion testing program and the VOC diffusion testing program discussed in previous chapters.

A glass, double-reservoir diffusion testing apparatus was used to perform diffusion testing. Two values of n_e were used in the interpretation of the diffusion tests (n_e determined from oven-drying and n_e determined from the tritium diffusion testing). D_e was found to range from 2.25×10^{-10} to 3.50×10^{-10} m^2/s when using n_e determined from the tritium diffusion testing program and 1.50×10^{-10} to 2.75×10^{-10} m^2/s when using n_e determined from oven-drying. The value of $n_e\times D_e$ was found to range from 6.8×10^{-11} to 1.1×10^{-10} m^2/s when interpreting the diffusion tests using n_e determined from tritium diffusion testing and 7.2×10^{-11} to 1.2×10^{-10} m^2/s when using n_e determined from oven-drying.

Measured values of the distribution coefficient ranged from 1.4 to 2.5 cm^3/g. Values of the distribution coefficient determined from diffusion testing, batch testing, and based on theoretical estimates based on the fraction of organic content were in general agreement.

The results of contaminant migration modeling of a theoretical site illustrate the relative effects of D_e and K_d on contaminant transport over the approximate range of values obtained from testing. This modeling revealed that for the range of D_e and K_d modeled, changes in K_d generally have a more appreciable effect on contaminant transport than changes in D_e.

CHAPTER 7: CONCLUSION

7.1. SUMMARY AND CONCLUSIONS

In summary, the work described in this thesis has:

- Developed a laboratory testing apparatus and methodology to assess the effective diffusion coefficient (D_e) and effective porosity (n_e) of conservative inorganic chemicals (e.g., tritiated water) for monolithic soil-cement specimens. This methodology was used to:
    - Evaluate n_e and D_e of tritiated water for 14 different soil-cement mixtures.
    - Assess the influence of curing time on the diffusive properties of a soil-cement material.
    - Investigate the influence of a number of different mixture properties on n_e and D_e including curing time, water-to-cement ratio, cement content, and grain-size distribution.
- Adapted a double-reservoir diffusion testing apparatus and methodology to be used in the evaluation of D_e and the distribution coefficient (K_d) of organic compounds for soil-cement specimens. This methodology was used to:
    - Evaluate D_e and K_d of benzene, ethylbenzene, trichloroethylene, and naphthalene for three different soil-cement mixtures.
- Used contaminant migration analysis to illustrate the relative effects of the contaminant migration parameters determined (i.e., n_e, D_e, and K_d) from diffusion and sorption testing on contaminant transport of a theoretical site.

To properly assess how cement-based S/S materials will perform in the long-term it is essential to be able to model how contaminants will migrate through soil-cement materials. Previous research indicates that in many cases contaminant transport through these low-hydraulic conductivity materials may be governed by diffusion. In this thesis it was shown that traditional diffusion testing techniques may be used to measure contaminant migration of dissolved inorganic (e.g., tritiated water) and dissolved organic (e.g., benzene, ethylbenzene, trichloroethylene, and naphthalene) compounds for soil-cement materials. This testing was performed using methods consistent with conventional design parameters used for contaminant migration assessments of other source-control remediation options. Furthermore, it was shown that material and mixture properties (e.g., water-to-cement ratio, water content) influenced the diffusive properties of the cured soil-cement specimens.

The work discussed in this thesis represents a substantial amount of diffusion testing which may be used as a baseline for future studies. The results of 51 individual single-reservoir diffusion tests on tritiated water and 13 individual tests (representing 34 separate diffusion profiles) on dissolved organic compounds (i.e., benzene, ethylbenzene, trichloroethylene, and naphthalene) are presented. Tests were performed in duplicate or triplicate and replicates generally provided consistent results. This study presents a number of findings that provide insight which may be used by both practicing engineers and researchers alike:

- Tritium diffusion testing on specimens from 14 different soil-cement mixtures resulted in values of n_e that ranged from 0.21 to 0.41 and values of D_e that ranged from 2.5×10^{-10} to 7.0×10^{-10} m^2/s. These values are similar to those previously determined for saturated inactive clays.

- VOC (benzene, ethylbenzene, and trichloroethylene) diffusion testing on specimens from three different soil-cement mixtures resulted in values of D_e that ranged from 1.50×10^{-10} to 3.00×10^{-10} m^2/s. Diffusion and batch testing on samples from these mixtures resulted in values of K_d that ranged from 0 to 1.3 cm^3/g. Naphthalene diffusion and sorption testing on specimens from the same three soil-cement mixtures resulted in values of D_e that ranged from 1.50×10^{-10} m^2/s to 3.50×10^{-10} m^2/s and values of K_d that ranged from 1.4 to 2.5 cm^3/g.

- Results of diffusion testing using tritiated water indicated that curing times of greater than 70 days were found to be sufficient to allow a reasonable assessment of the longer-term diffusion coefficients of a soil-cement mixture.

- When analyzing a tritiated water diffusion profile through a soil-cement specimen (i.e., as performed in the single-reservoir diffusion test) the best assumption is that only a portion of the water in the specimen is accessible to the diffusing compound (i.e., the effective porosity, n_e, is less than the total porosity, n). However, as no diffusion profile was measured through the specimen in the double-reservoir diffusion tests, the value of n_e assumed does not have a substantial effect on the interpretation of the diffusion test.

- Both the n and n_e were shown to increase with increasing water content of the initial soil-cement mixture.

- For the four different soils tested, soil gradation was not found to have a substantial effect on the values of n_e or D_e obtained for the cured specimens.

- Values of K_d determined from diffusion testing, batch testing, and based on theoretical estimates from the fraction of organic content (e.g., Karickhoff et al. 1979) were in general agreement.

- When the diffusing species experiences substantial sorption (e.g., naphthalene with the cement-based S/S materials studied herein), contaminant transport may be influenced by sorption to a greater degree than by diffusion. Under these conditions an accurate estimate of D_e may be of secondary importance compared to an accurate estimate of K_d.

Practical applications derived from these findings include:

- The contents of this thesis may be used to develop estimates of diffusive properties for contaminant migration models. For instance:
    - In the pre-design (technology selection) stage it may be sufficient to conservatively estimate n_e and D_e (e.g., from the results presented in this thesis) and estimate K_d from batch testing or from conservative estimates based on established relationships (e.g., Karickhoff et al. 1979).
    - In cases where comprehensive investigation is warranted (e.g., detailed design, sensitive sites), diffusion testing, performed as outlined in this thesis, may be undertaken to estimate the parameters related to diffusion (i.e., n_e, D_e) and sorption (i.e., K_d) using site-specific conditions and parameters.
- Designs aiming to minimize diffusive transport should generally aim to reduce the water content of the initial mixture to the minimum allowed by other constraints (e.g., mixability). Implications of this include:
    - When trying to reduce contaminant transport through soil-cement materials, increasing the ratio of the volume of grout to the volume of treated soil may not be as effective as maintaining that ratio while reducing the water-to-cement ratio of the grout.

  - Conservative values of n_e and D_e may be obtained by performing diffusion tests on the mixtures with the highest expected porosity (i.e., highest initial water content) of all mixtures that meet the other performance criteria.

- Testing was performed on soil-cement samples using soil ranging from a poorly graded sand with 0% “fines” (silt and clay sized particles) to a clayey sand with 40% fines. The fines content did not have a large effect on n_e nor D_e and thus minor variations in grain-size (such as those investigated) are unlikely to have a substantial effect on n_e and D_e for a given mix design.

- For simplicity, when interpreting diffusion test results from double-reservoir diffusion tests on organic contaminants for soil-cement specimens, it is likely sufficient to estimate n_e based on the total porosity estimated from oven-drying.

7.2. RECOMMENDATIONS FOR FUTURE WORK

The following recommendations provide suggestions for additional research that would complement the work presented herein:

- Diffusion tests were performed using five contaminants on specimens of fourteen different soil-cement mixtures that generally represented cement-based S/S materials. Future work could examine diffusion of additional contaminants for a wide range of different soil-cement mixtures.

- Soil-cement diffusion testing was performed on relatively small specimens (~ 70 mm diameter) over relatively short time periods (< 52 days). Future work could investigate on larger laboratory scale or full-scale field-testing over longer time periods. This work could provide information on the effect of time, temperature, geochemical conditions, and the influence of the material variability.

- Diffusion testing in this thesis was performed on saturated or near-saturated specimens. Future work could investigate the effect of partially saturated soil-cement materials and their diffusive behavior for both organic and inorganic contaminants.

- All laboratory tests undertaken in this work were performed at room temperature. Future work could examine the effect of temperature on the diffusion and sorption of organic and inorganic contaminants for soil-cement materials.

- The effects of curing were investigated in Chapter 2. However, specimens were only cured for a maximum of 126 days which is much shorter than the design life of a typical cement-based S/S system. Future work could examine the effect of longer-term aging on the diffusive properties of soil-cements using accelerated-aging techniques.

- Future work could investigate the effect of environmental processes such as physical (thermal stress, frost, salt crystallization, drying) and biochemical weathering on transport parameters such as k, K_d, and D_e for soil-cement materials. This work could include an investigation of the effects of matrix diffusion on samples that have been damaged (i.e. cracked) due to these processes.

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APPENDIX A: TRITIUM DIFFUSION TESTING RESULTS

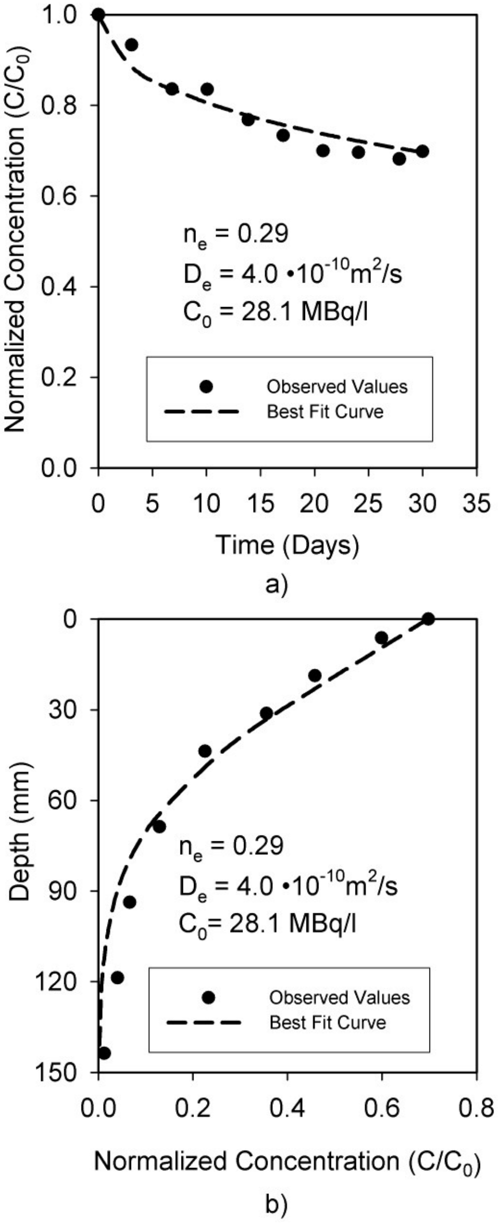


Figure A.1 — Concentration profiles for specimen a1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

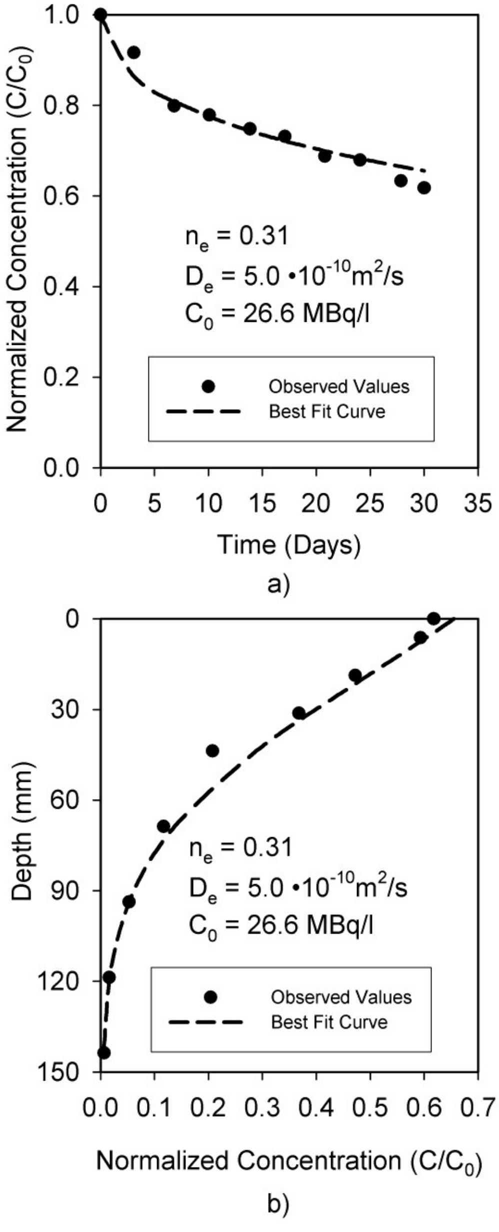
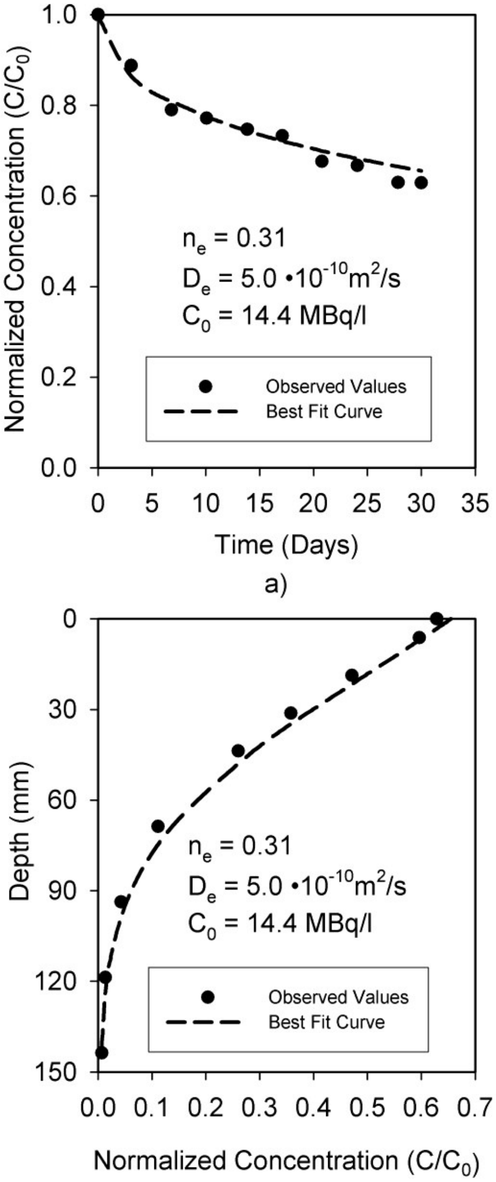


Figure A.2 — Concentration profiles for specimen a2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.3 — Concentration profiles for specimen a3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

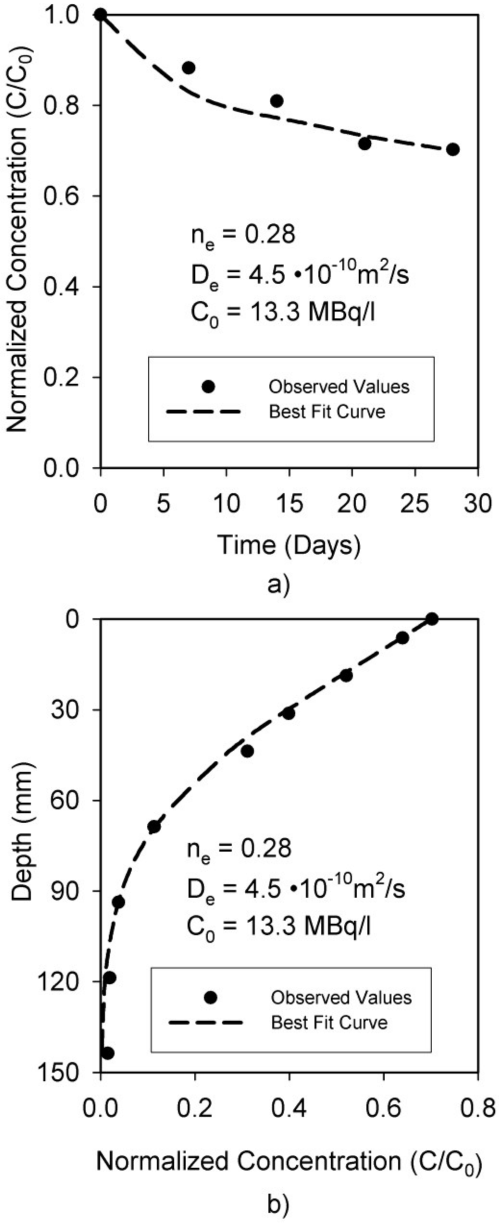


Figure A.4 — Concentration profiles for specimen b1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

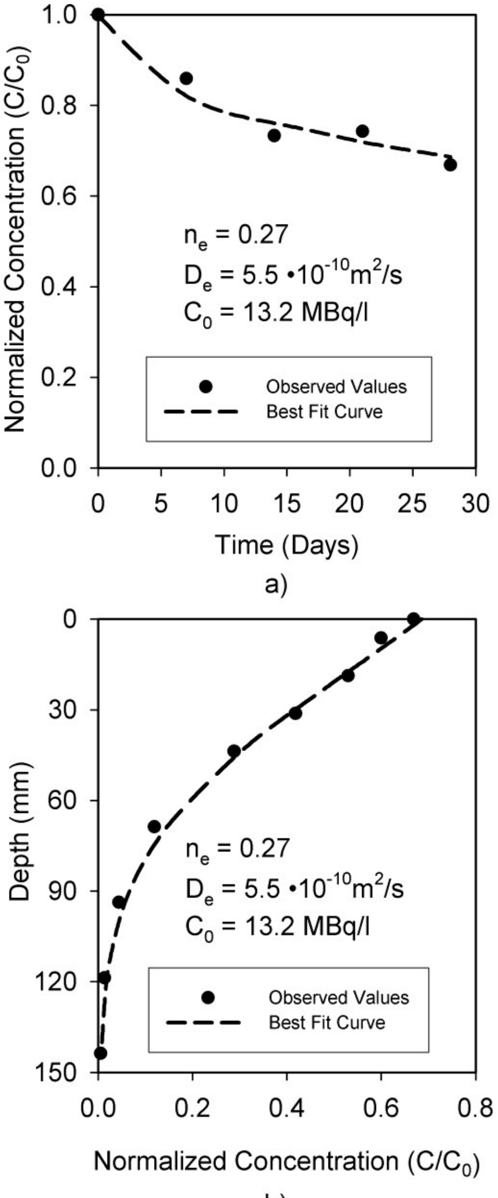
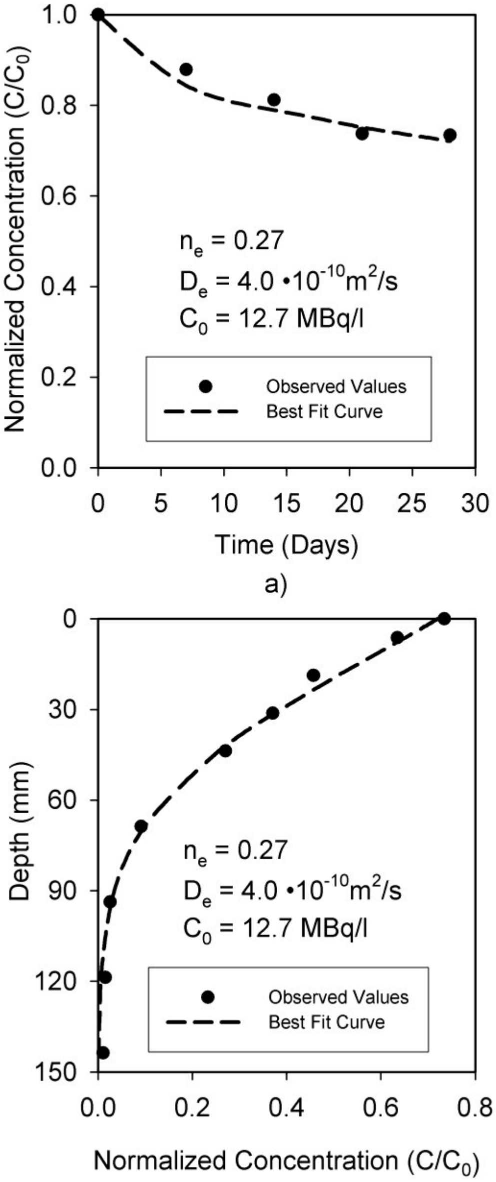


Figure A.5 — Concentration profiles for specimen b2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.6 — Concentration profiles for specimen b3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

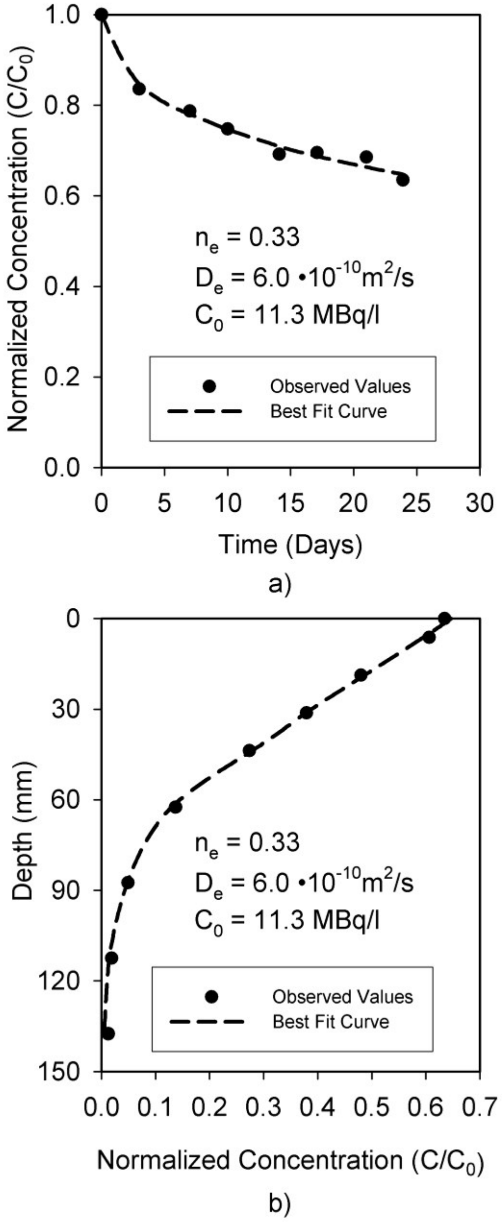
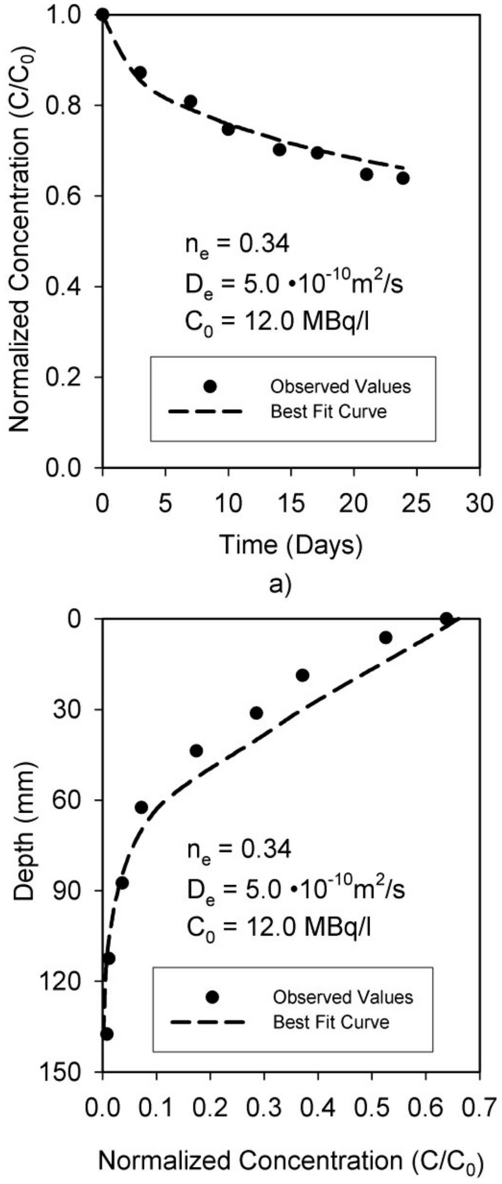


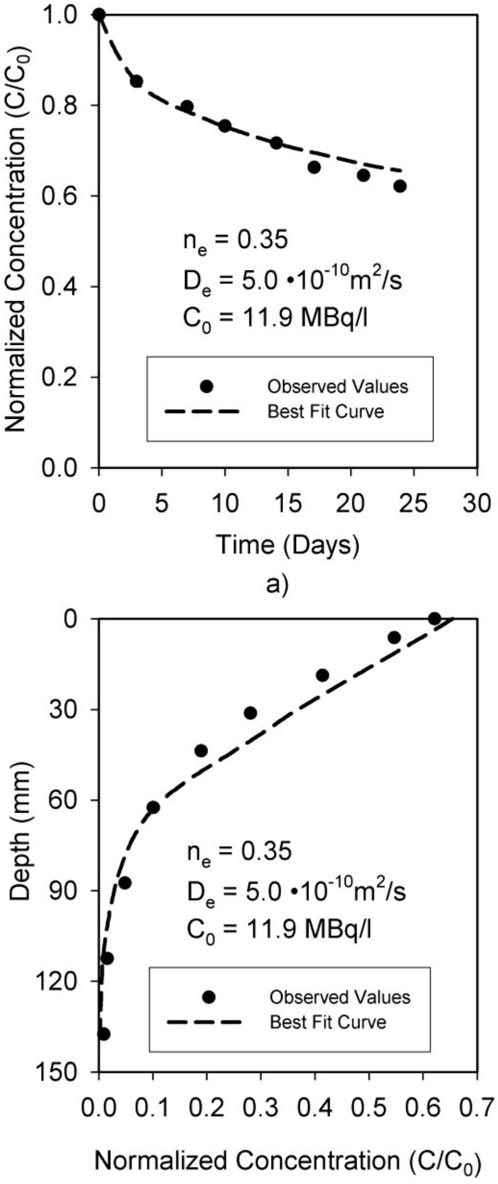
Figure A.7 — Concentration profiles for specimen c1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.8 — Concentration profiles for specimen c2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.9 — Concentration profiles for specimen c3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

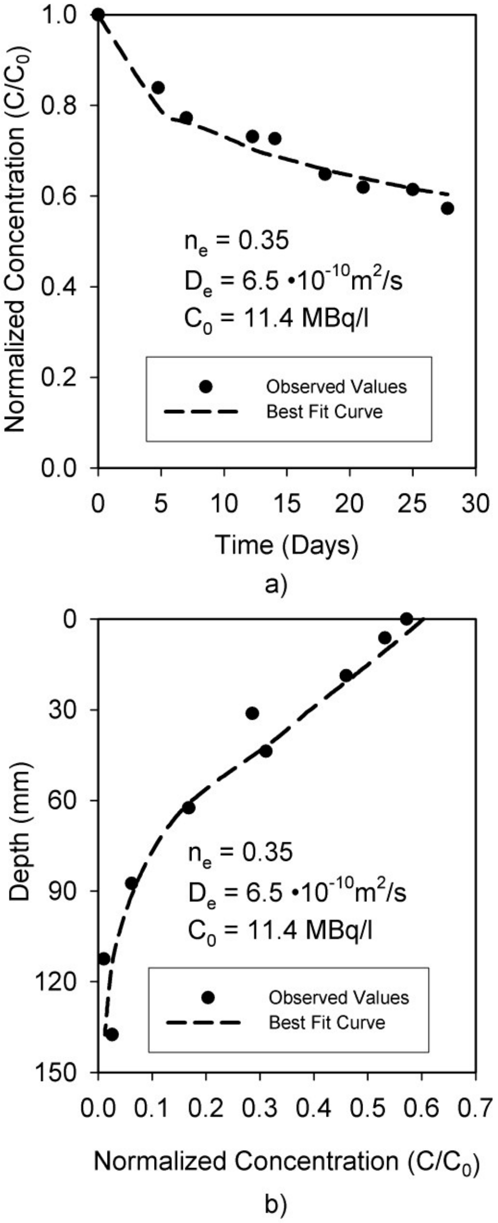
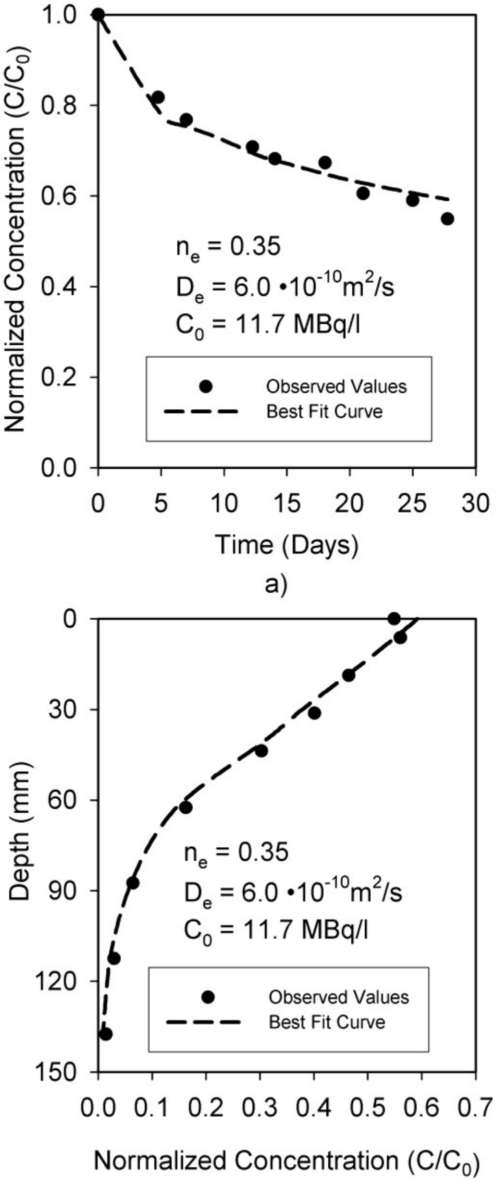
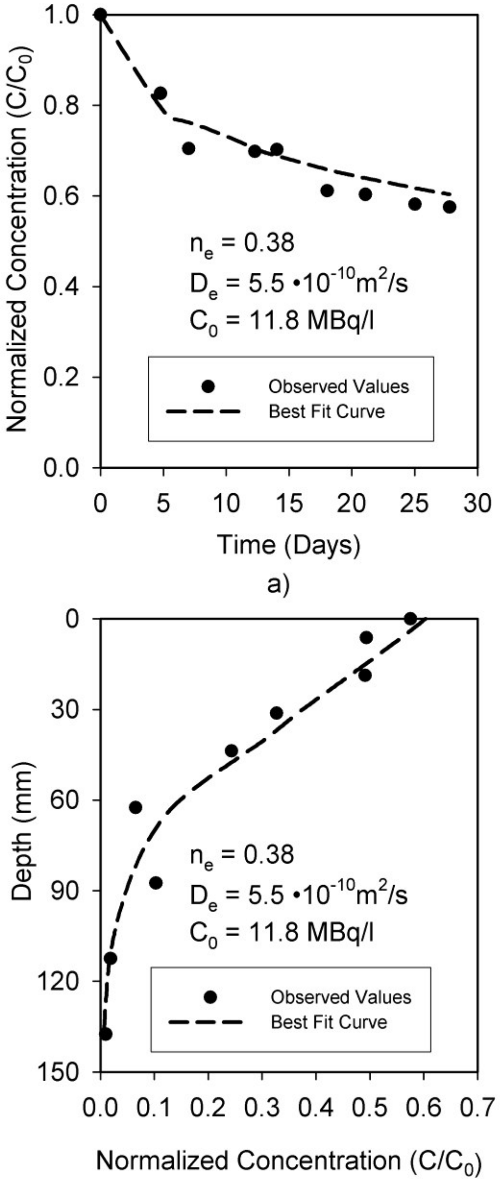


Figure A.10 — Concentration profiles for specimen d1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



b)

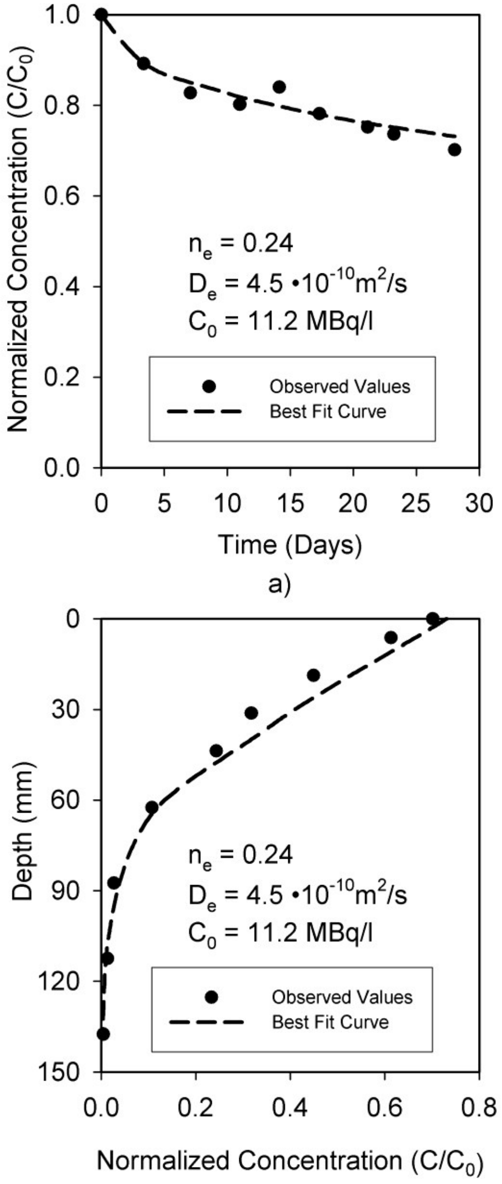
Figure A.11 — Concentration profiles for specimen d2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

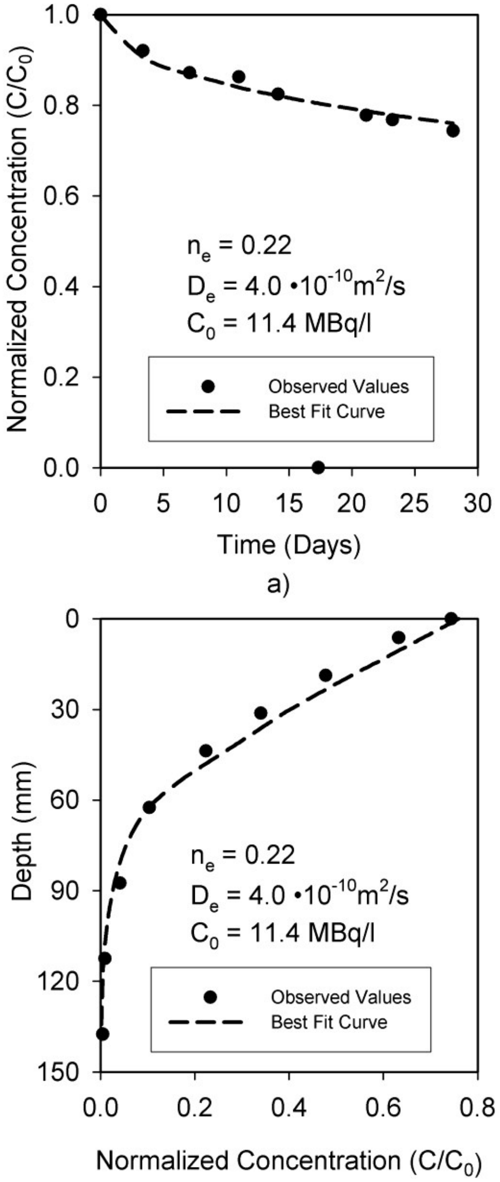
Figure A.12 — Concentration profiles for specimen d3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

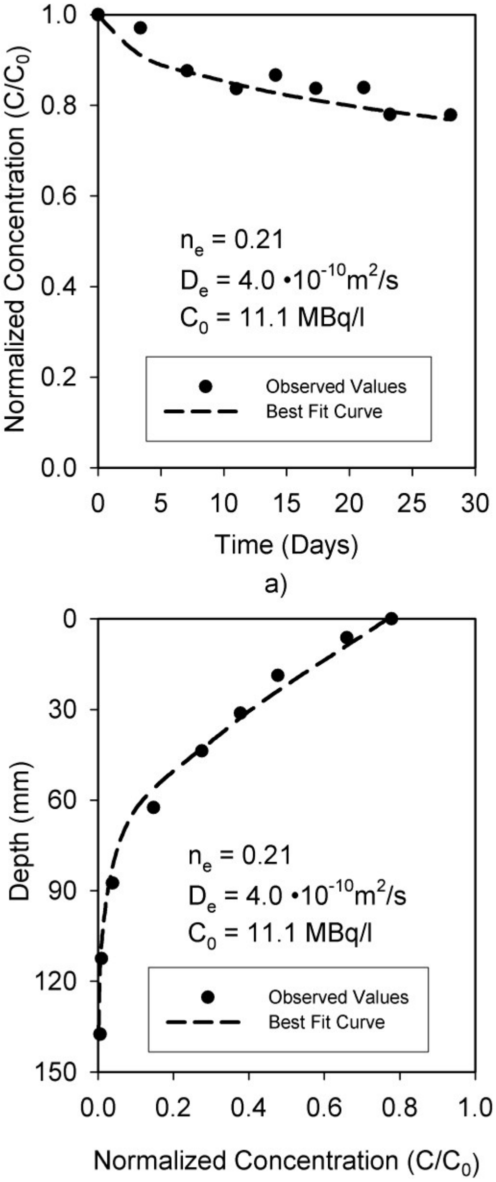
b)

Figure A.13 — Concentration profiles for specimen e1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



b)

Figure A.14 — Concentration profiles for specimen e2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.15 — Concentration profiles for specimen e3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

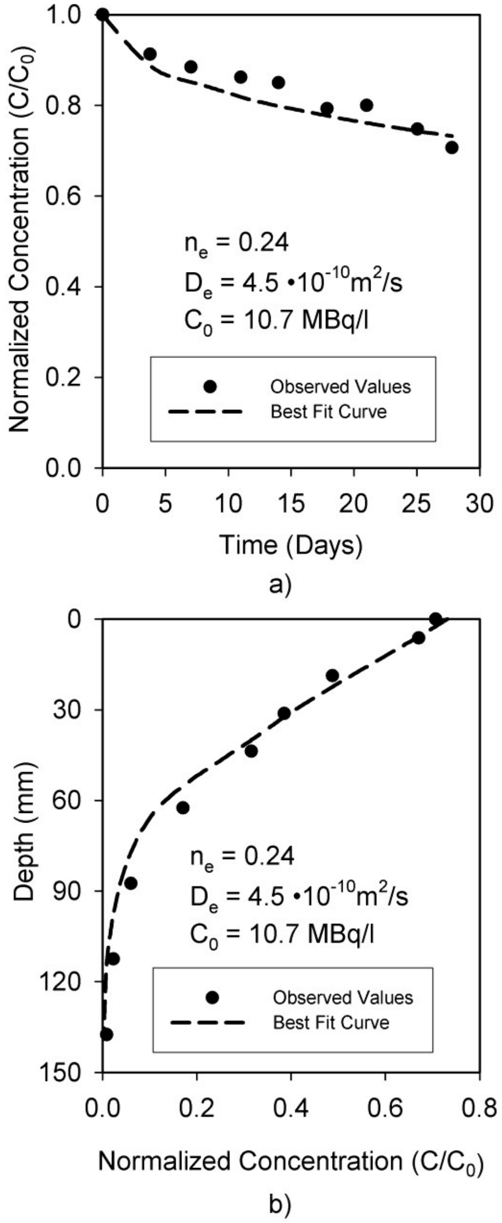
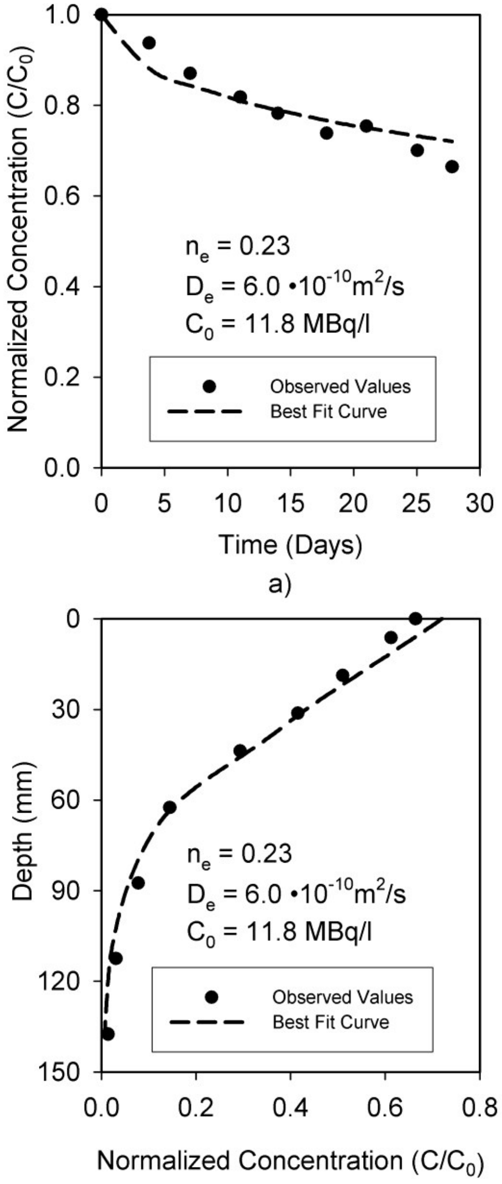
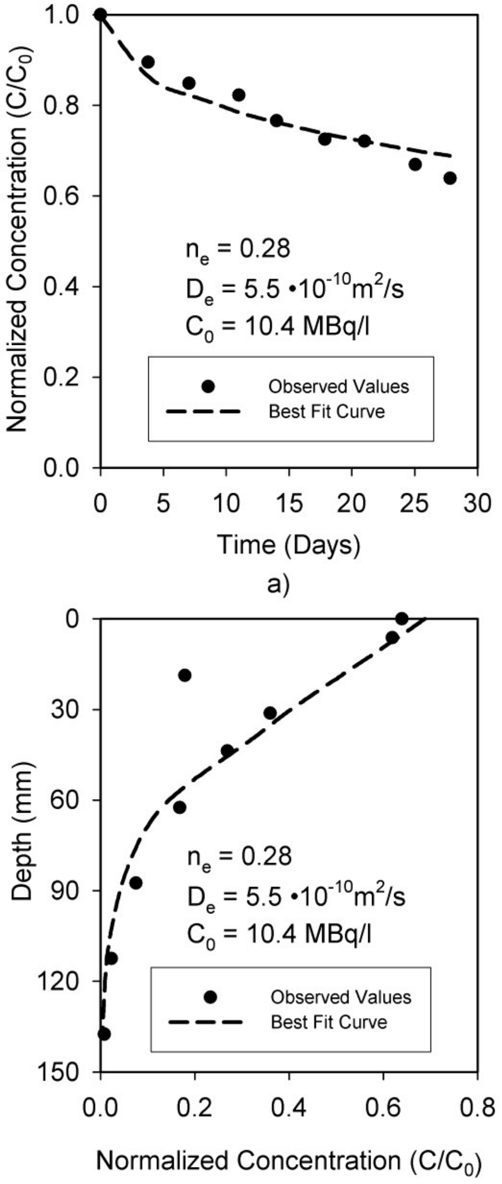


Figure A.16 — Concentration profiles for specimen f1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



b)

Figure A.17 — Concentration profiles for specimen f2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.18 — Concentration profiles for specimen f3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

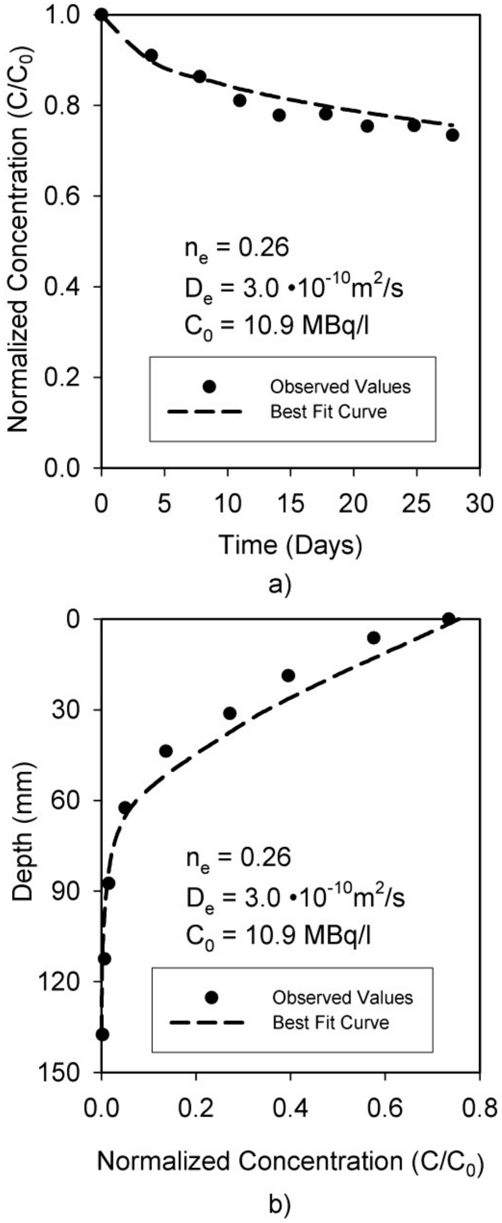
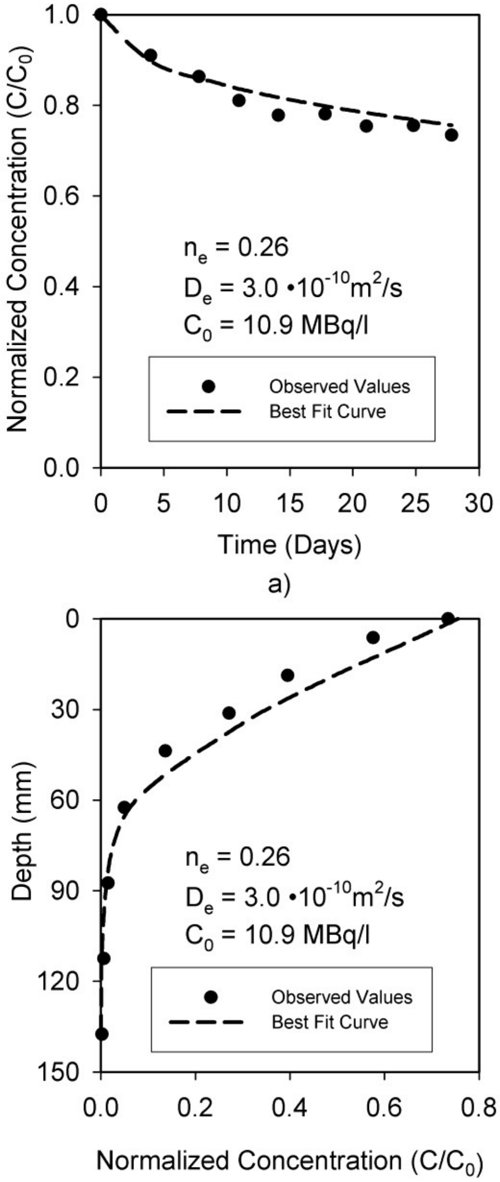


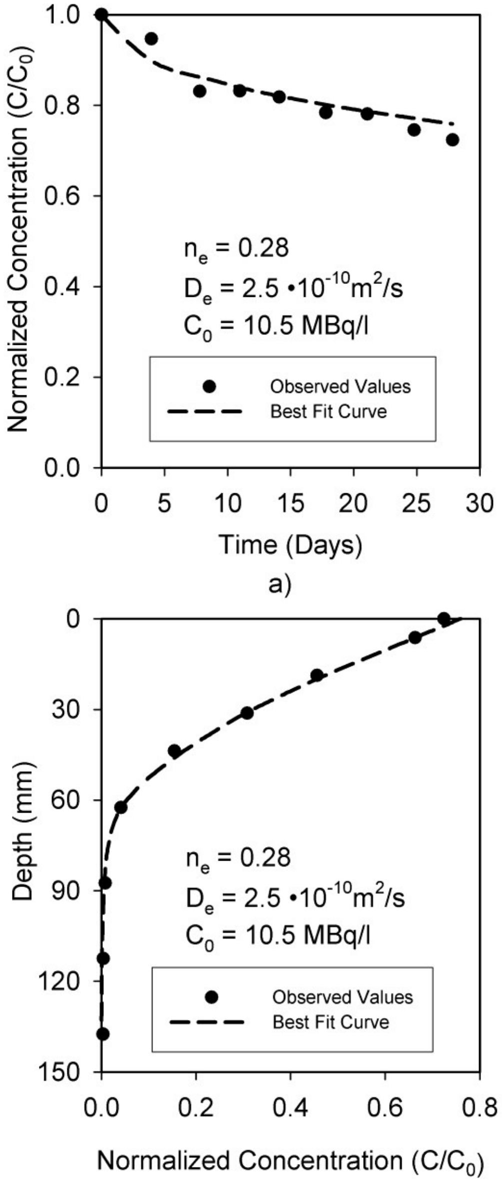
Figure A.19 — Concentration profiles for specimen g1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.20 — Concentration profiles for specimen g2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.21 — Concentration profiles for specimen g3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

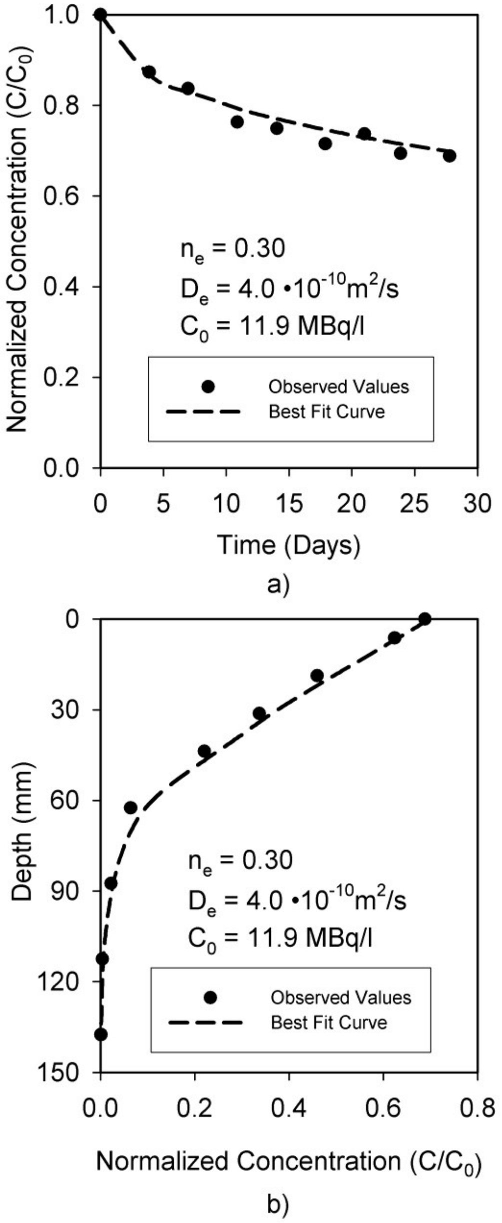


Figure A.22 — Concentration profiles for specimen h1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

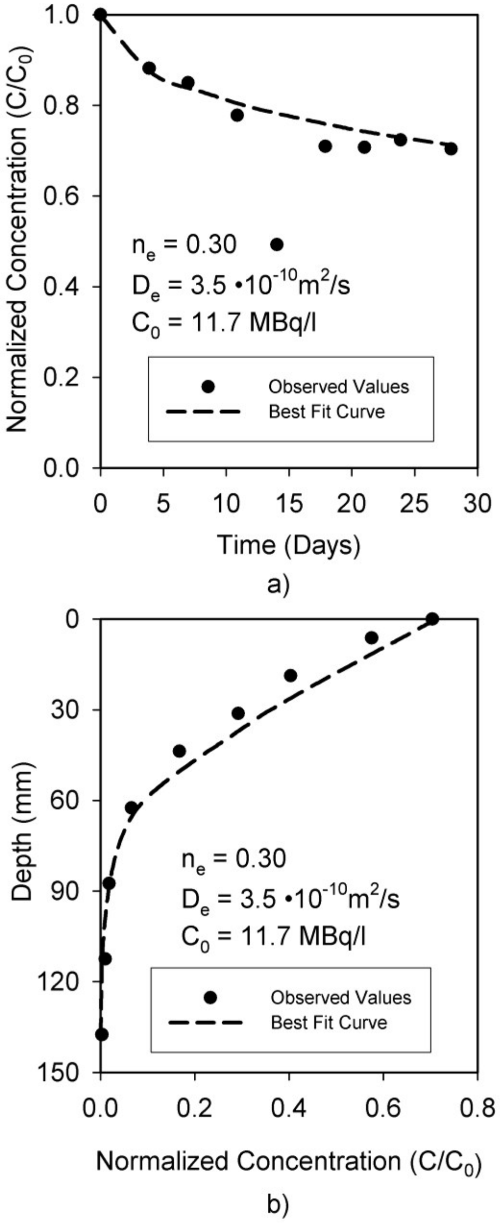
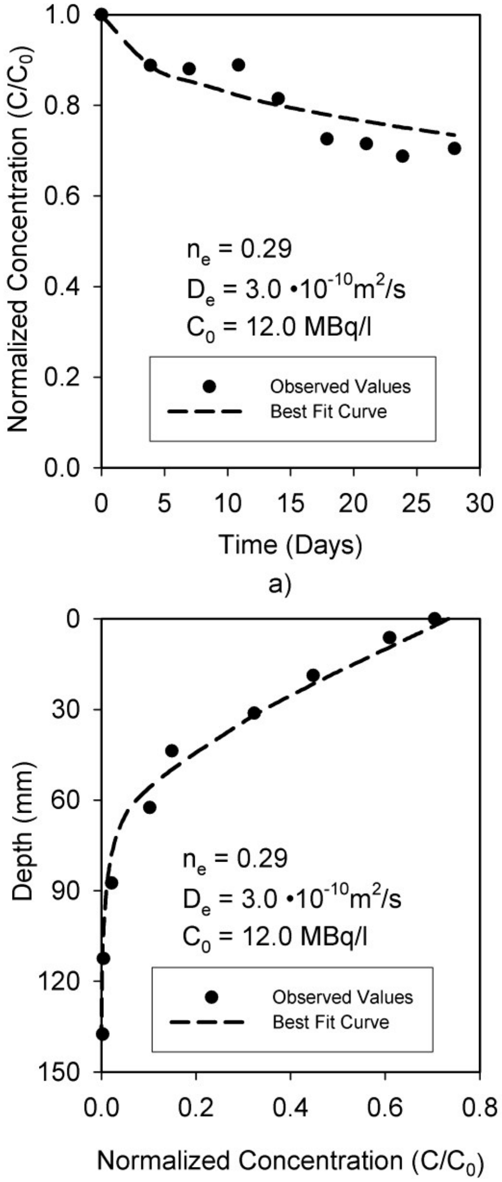


Figure A.23 — Concentration profiles for specimen h2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.24 — Concentration profiles for specimen h3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

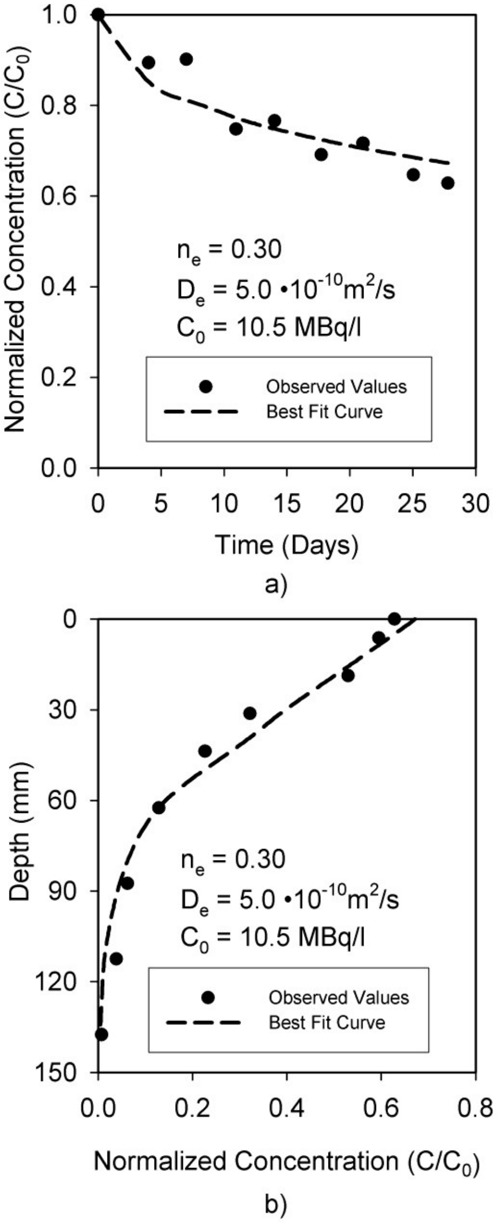
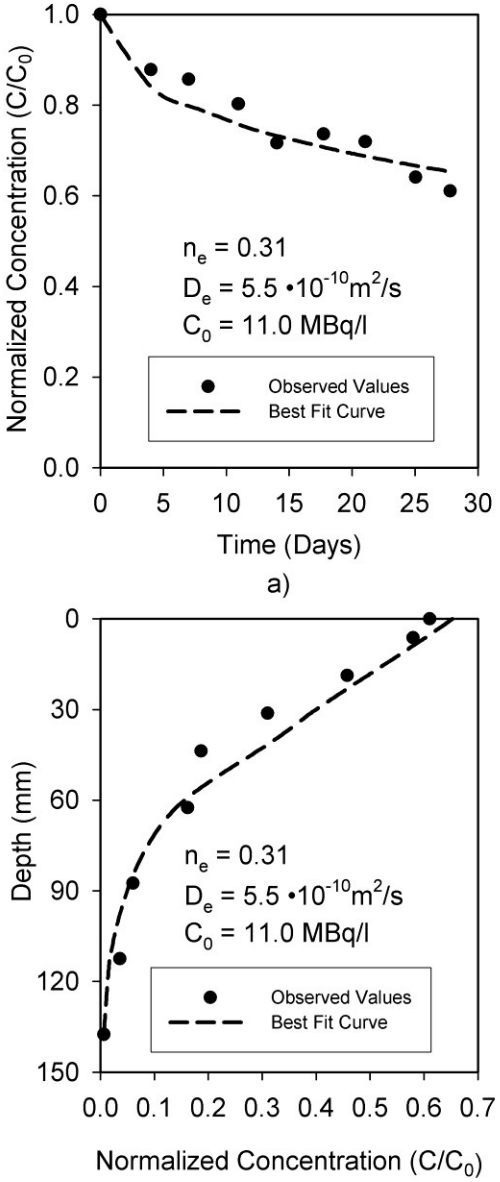


Figure A.25 — Concentration profiles for specimen i1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.26 — Concentration profiles for specimen i2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

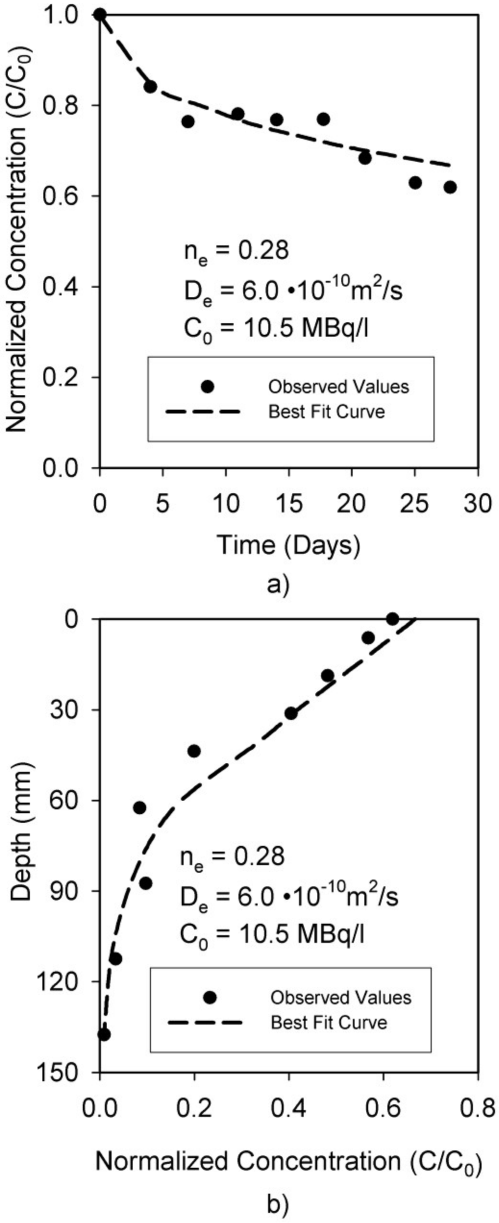
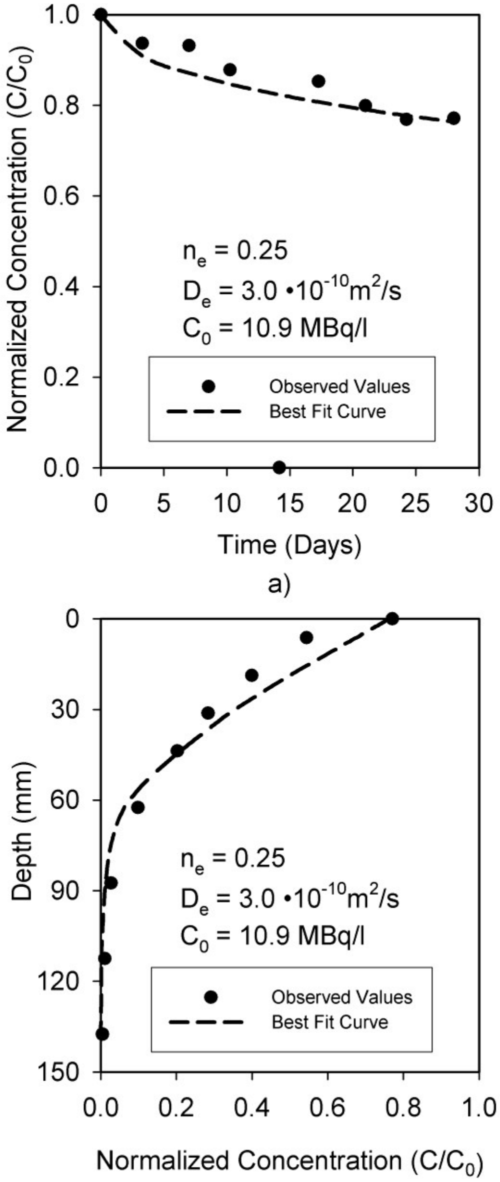


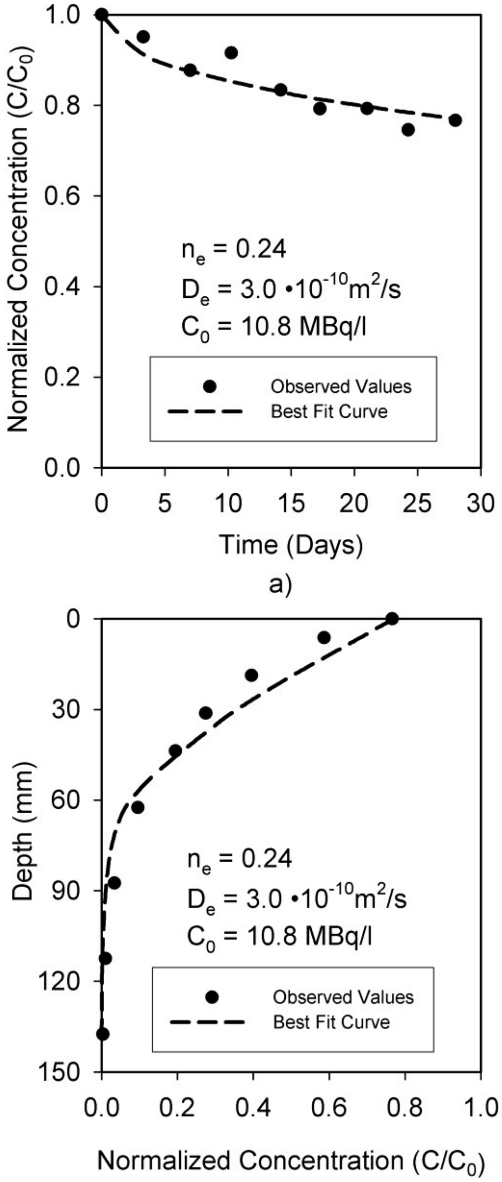
Figure A.27 — Concentration profiles for specimen i3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

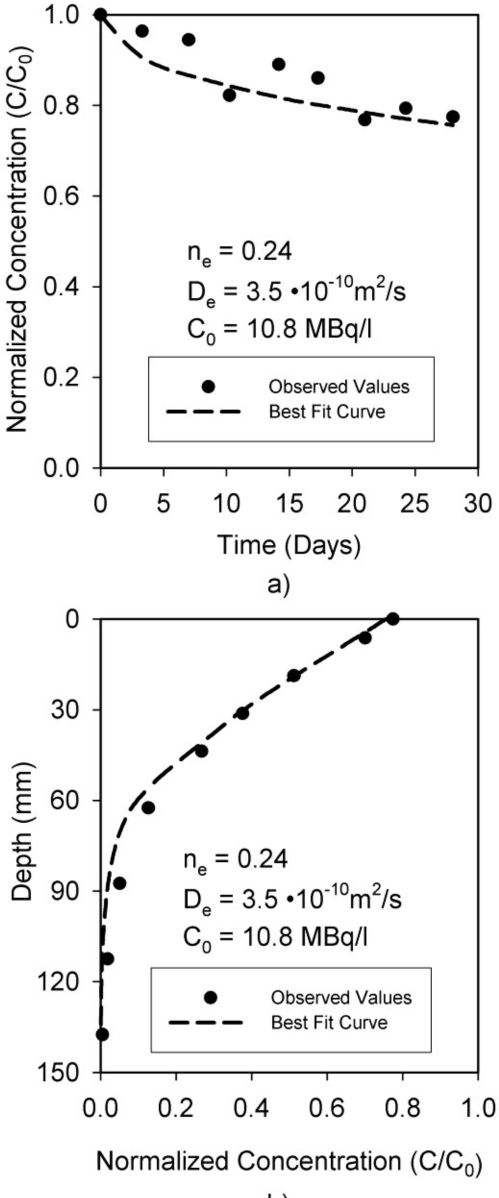
Figure A.28 — Concentration profiles for specimen j1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

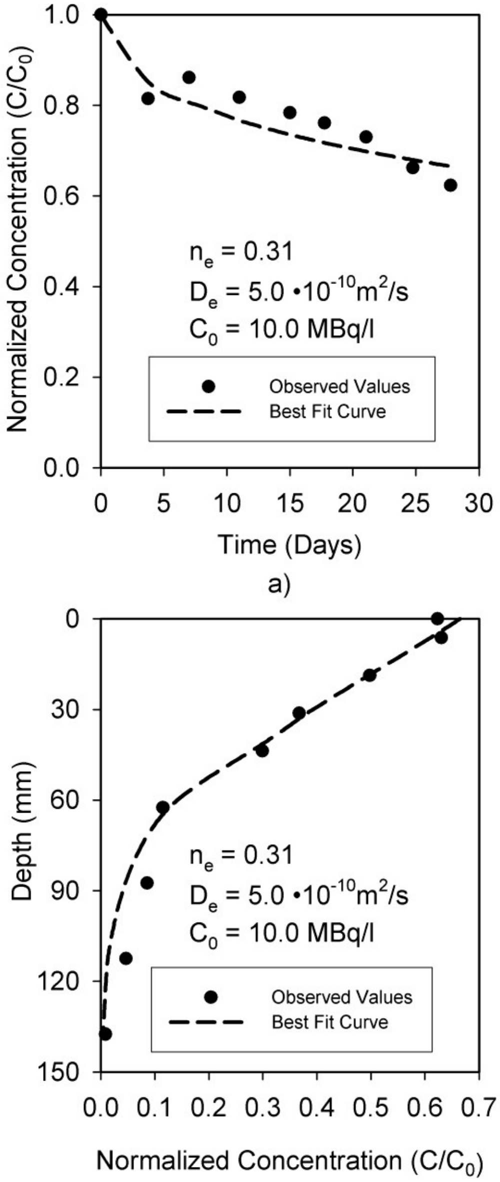
Figure A.29 — Concentration profiles for specimen j2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.30 — Concentration profiles for specimen j3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.31 — Concentration profiles for specimen k1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

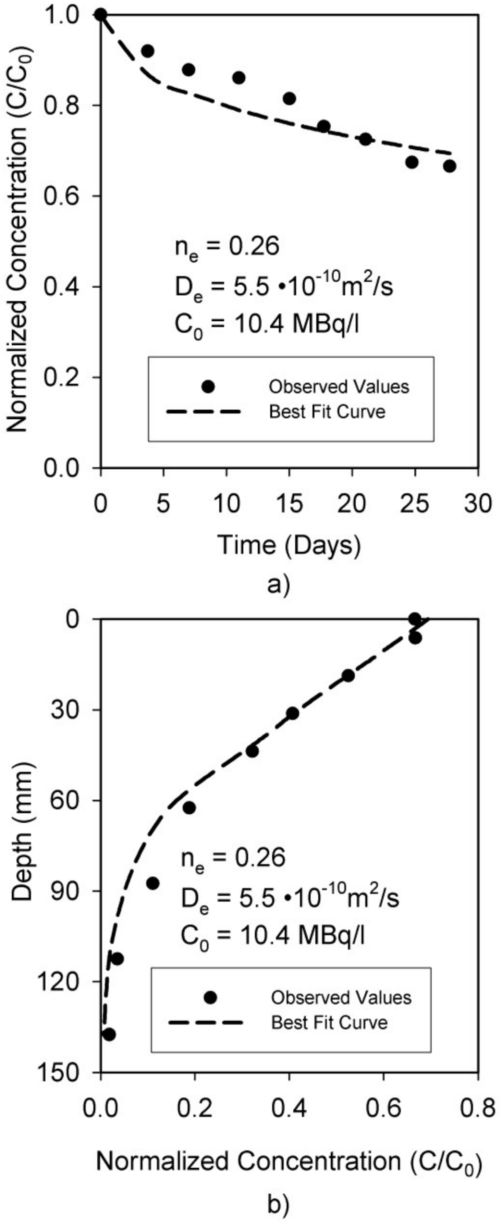
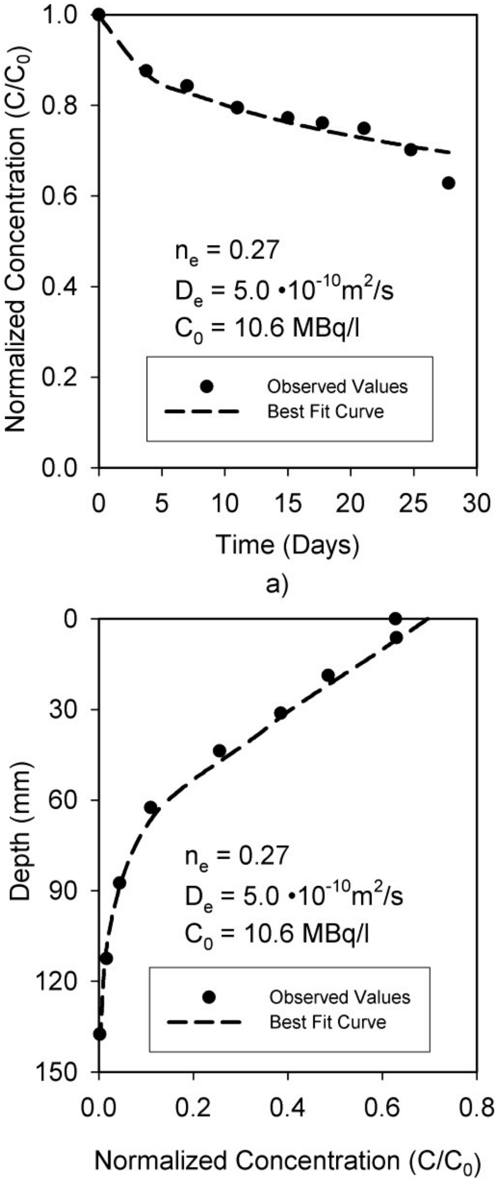


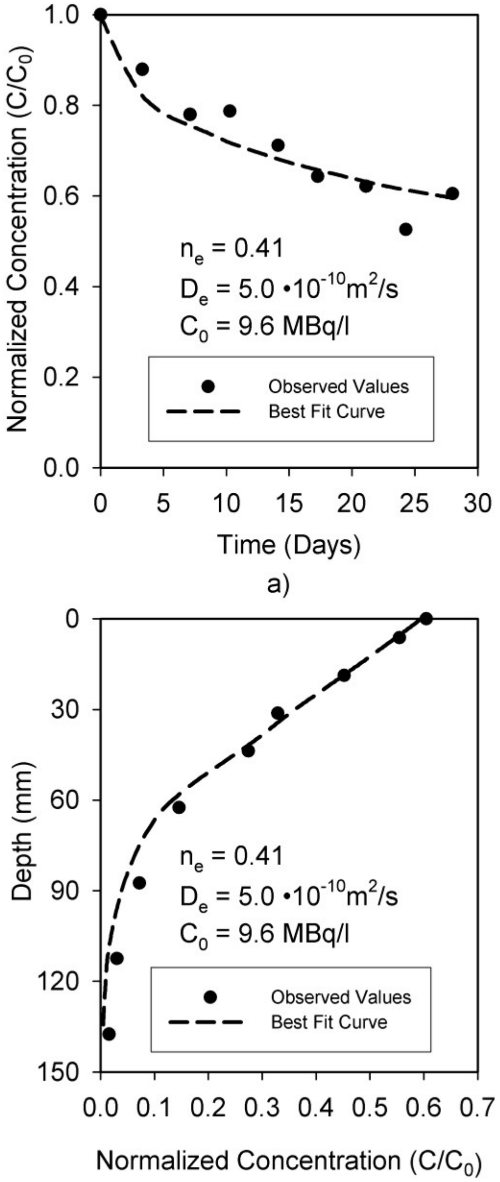
Figure A.32 — Concentration profiles for specimen k2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

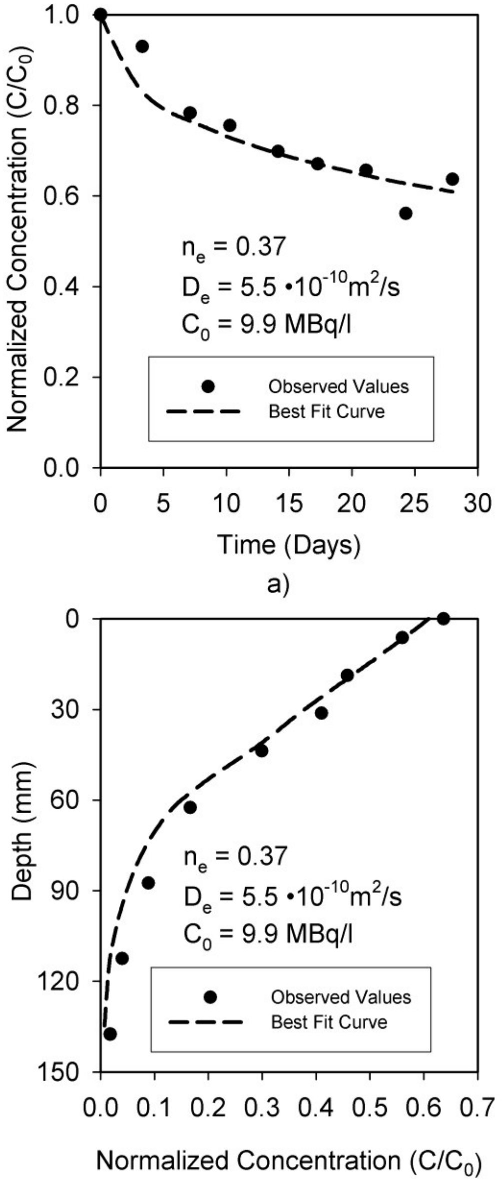
Figure A.33 — Concentration profiles for specimen k3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.34 — Concentration profiles for specimen l1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.35 — Concentration profiles for specimen l2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

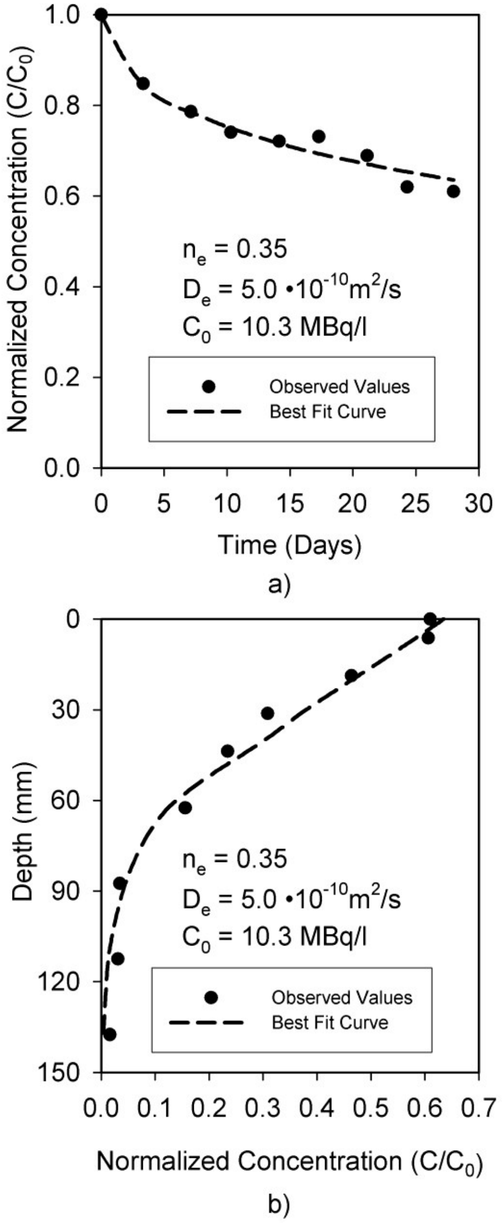
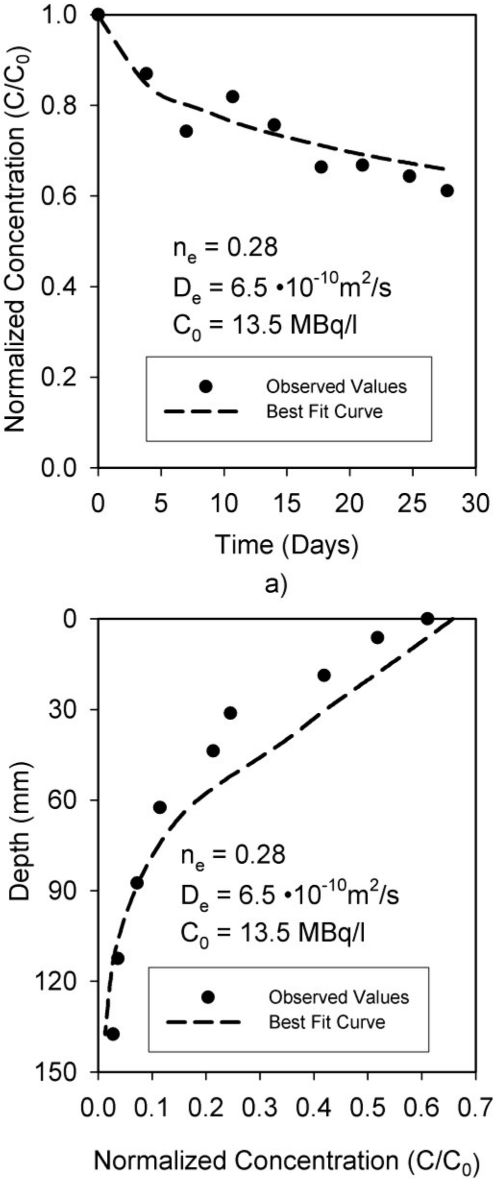


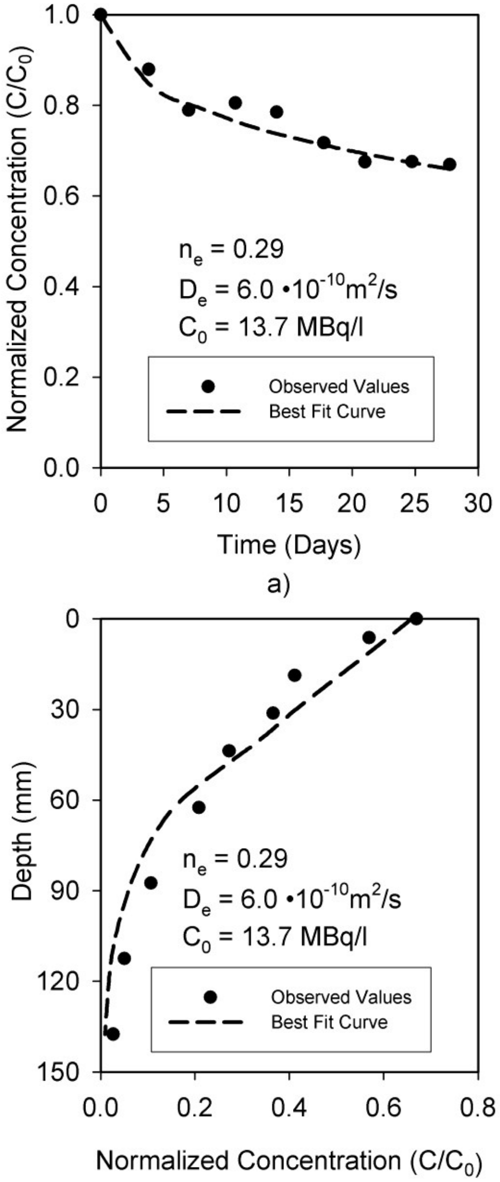
Figure A.36 — Concentration profiles for specimen l3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.37 — Concentration profiles for specimen m1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.38 — Concentration profiles for specimen m2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

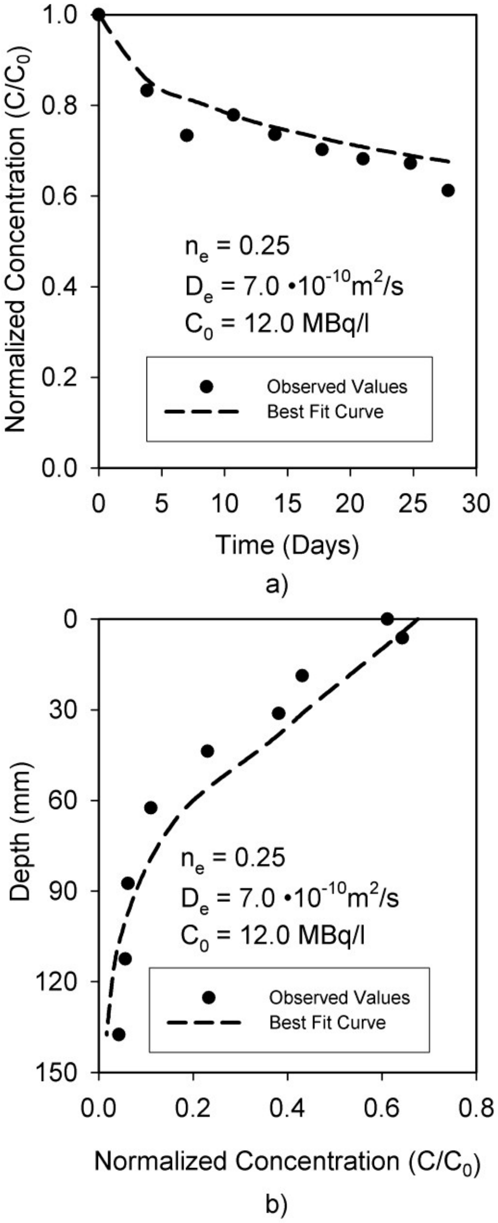


Figure A.39 — Concentration profiles for specimen m3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

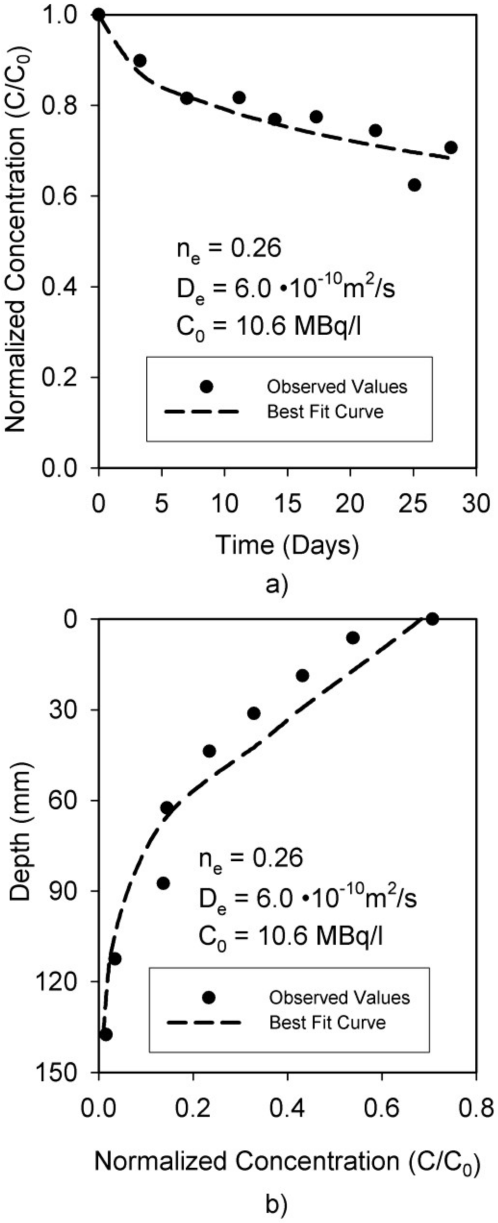
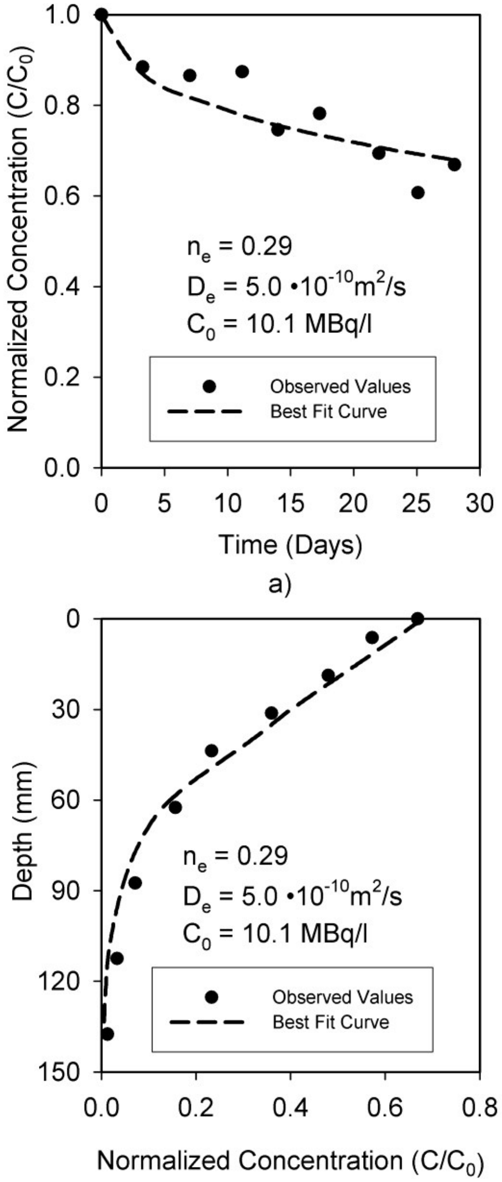


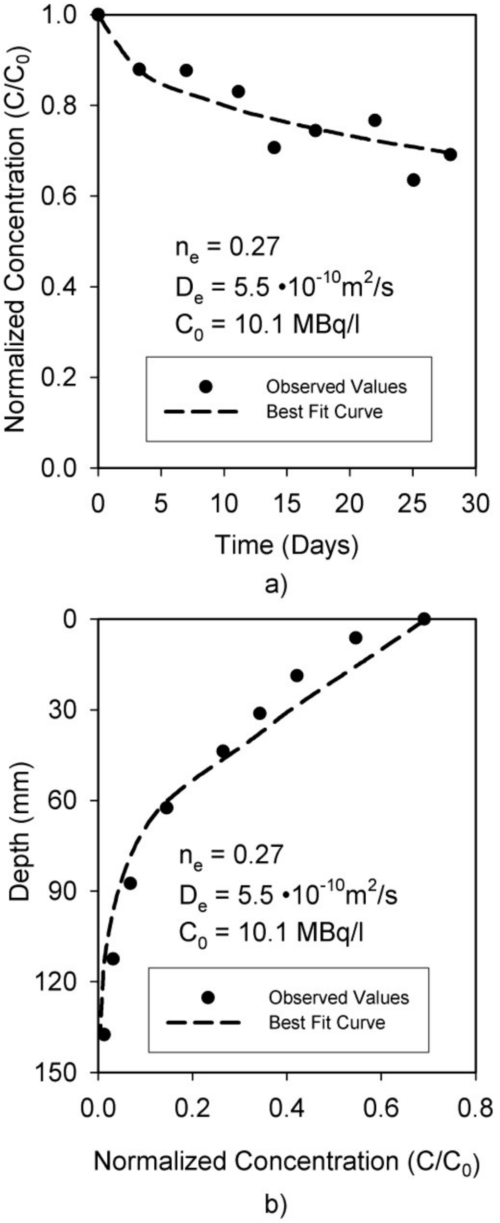
Figure A.40 — Concentration profiles for specimen n1: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.41 — Concentration profiles for specimen n2: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.



a)

b)

Figure A.42 — Concentration profiles for specimen n3: a) in the source reservoir with time and b) through the soil-cement specimen at the end of the test.

APPENDIX B: EXAMPLE ANALYSIS - TRITIUM DIFFUSION TESTING

The following example uses the results of diffusion testing on one of the replicates from Chapter 3 (labelled as specimen g1 in Chapter 4) to illustrate the methodology used to fit theoretical curves to the laboratory diffusion test results. The following example uses the "effective porosity method" but analysis using the "total porosity method" follows a similar procedure.

1) The measured tritium concentrations of the source solution with time are presented in Table B1 and the measured tritium concentrations of the supernatant from the wash extract for each of the eight sections used to develop the concentration profile are shown in Table B2.

Table B.1 — Measured tritium concentration in the source reservoir for specimen g1.

Source Reservoir		
Time (days)	Concentration (kBq/L)	C/C_o -
0.0	9797	1.00
4.0	9206	0.94
7.8	8748	0.89
11.0	8031	0.82
14.1	7684	0.78
17.8	7685	0.78
21.1	7404	0.76
24.8	6991	0.71
27.8	7038	0.72

Table B.2 — Measured tritium concentrations of the supernatants from the wash extracts of the eight sections used to determine the diffusion profile through specimen g1.

Average Depth of Section (mm)	C_{Wash} (kBq/L)
6.25	719
18.75	491
31.25	356
43.75	187
62.5	67
87.5	37
112.5	16
137.5	9

2) The concentration of tritium in the accessible portion of the specimen, C_{AW}, may be calculated from the measured supernatant concentrations using Equations 3-5, 3-7, 3-8, and 3-9. This analysis utilizes the measured value of the water content ($w = 0.225$) to calculate the total porosity ($n = 0.37$) and requires an assumption

for the value of n_e. In the analysis a number of values of n_e were analyzed but for the purposes of continuing this example n_e is assumed to be 0.27.

$$M_W = \frac{wM_T}{1+w} = \frac{(0.225)20g}{1+0.225} = 3.67\ g \qquad \text{(Equation 3-5)}$$

$$M_{AW} = M_W \frac{n_e}{n} = 3.67\ g\ \frac{0.27}{0.37} = 2.68\ g \qquad \text{(Equation 3-7)}$$

$$M_{IW} = M_W \frac{n - n_e}{n} = 3.67\ g\ \frac{0.37 - 0.27}{0.37} = 0.99\ g \qquad \text{(Equation 3-8)}$$

$$C_{AW} = C_{Wash} \frac{V_{AW} + V_{IW} + V_{DW}}{V_{AW}} \qquad \text{(Equation 3-9)}$$

$$= C_{Wash} \frac{\frac{M_{AW}}{\gamma_W} + \frac{M_{IW}}{\gamma_W} + \frac{M_{DW}}{\gamma_W}}{\frac{M_{AW}}{\gamma_W}}$$

$$= C_{Wash} \frac{M_{AW} + M_{IW} + M_{DW}}{M_{AW}}$$

$$= C_{Wash} \frac{(2.68\ g + 0.99\ g + 20\ g)}{2.68\ g} = 8.83\ C_{Wash}$$

For each section, the concentrations in the accessible portion of the specimen, C_{AW}, calculated from wash extract concentrations, $C_{Wash,}$ are presented in Table B.3.

Table B.3 — Calculated concentration in the accessible portion of specimen g1 assuming $n_e = 0.27$.

Concentration Profile	
Average Depth of Section (mm)	Concentration (kBq/L)
6.25	6347
18.75	4337
31.25	3146
43.75	1653
62.50	590
87.50	330
112.50	145
137.50	76

3) For each assumption of n_e, POLLUTE v6 (Rowe et al. 1998) was used to generate theoretical diffusion profiles for a number of different values of D_e. The current example continues using the assumption that $D_e = 3.0\times10^{-10}$ m^2/s. The model accounts for other specifics such as source and receptor reservoir volumes, specimen length, specimen diameter, and rate of sampling. The concentrations determined from the theoretical analysis with $n_e = 0.27$ and $D_e = 3.0\times10^{-10}$ m^2/s are presented in Table B.4. This table also presents a comparison of laboratory and theoretical results. The root-mean-square error (RMSE) of the theoretical concentration profile to the observed concentration profile is also presented.

4) To capture the best-fit parameters, steps 2) and 3) are repeated for a number of values of n_e and D_e and the best-fit parameters are taken as the combination which yield the least RMSE. For specimen g1 the assumed values of n_e ranged from 0.26 to 0.31 and assumed values of D_e ranged from 1.5×10^{-10} to 4.0×10^{-10} m^2/s. The calculated RMSE for each combination of n_e and D_e is presented in Table B.5. In this case the minimum RMSE (and thus the best-fit parameters) resulted in the case where $n_e = 0.27$ and $D_e = 3.0\times10^{-10}$ m^2/s. It is important to note that the

minimum value of RMSE occurs near the centre of the studied range and not at the boundary to ensure that the best-fit parameters are captured.

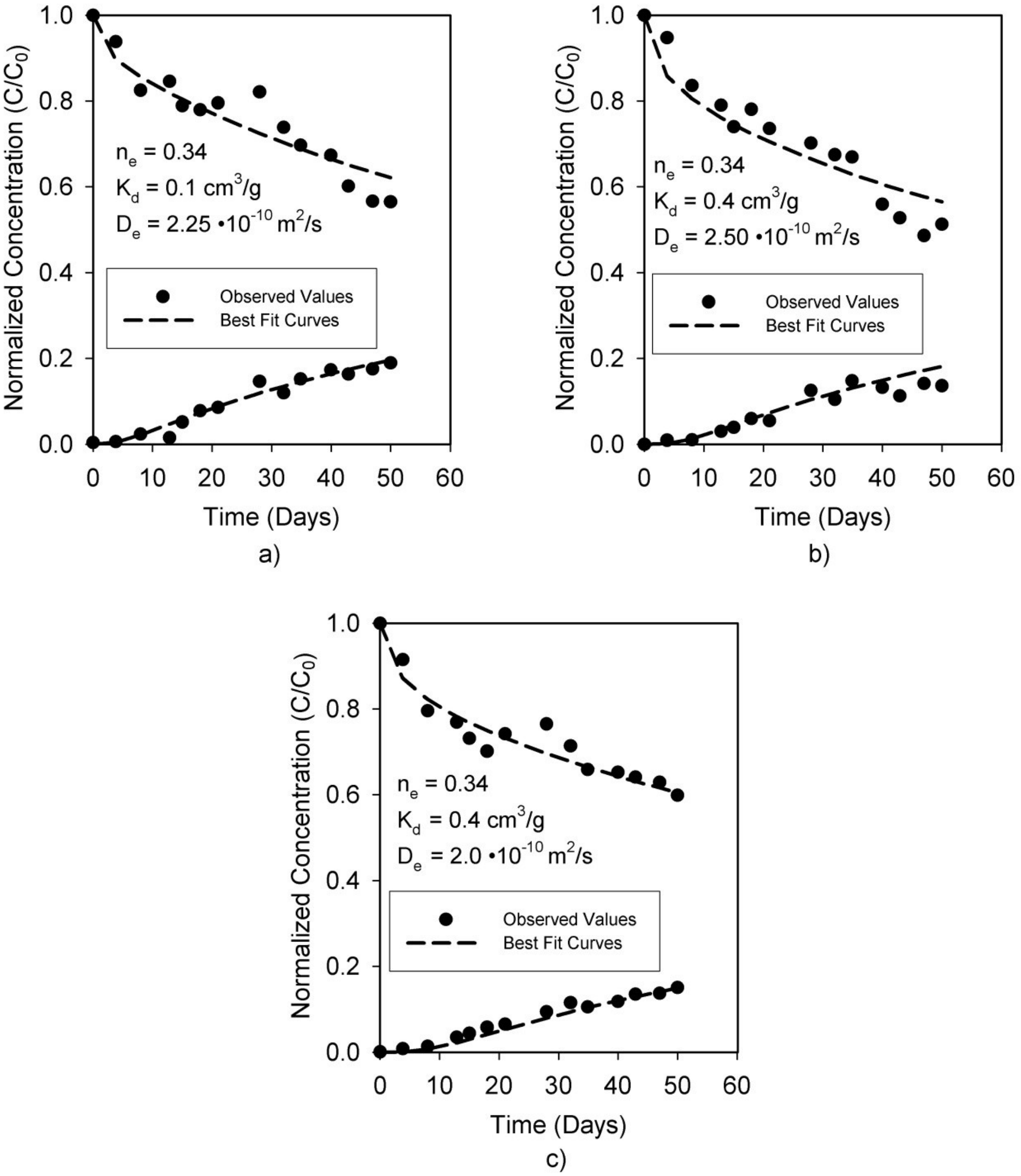
Table B.4 — Comparison of laboratory observed and theoretical concentration for the tritiated water diffusion test on specimen g1.

Source Reservoir					
Time	Laboratory Results		Pollute Model		$(C/C_{oLab}-C/C_{oModel})^2$
	Conc.	C/C_o	Conc.	C/C_o	
(days)	(kBq/L)	-	(kBq/L)	-	-
0.0	9797	1.00	9797	1.00	0.0E+00
4.0	9206	0.94	8748	0.89	2.2E-03
7.8	8748	0.89	8376	0.86	1.4E-03
11.0	8031	0.82	8141	0.83	1.3E-04
14.1	7684	0.78	7955	0.81	7.7E-04
17.8	7685	0.78	7759	0.79	5.7E-05
21.1	7404	0.76	7602	0.78	4.1E-04
24.8	6991	0.71	7455	0.76	2.2E-03
27.8	7038	0.72	7338	0.75	9.3E-04
Concentration Profile					
Depth	Laboratory Results		Pollute Model		-
	Conc	C/C_o	Conc.	C/C_o	-
(mm)	(kBq/L)	-	(kBq/L)	-	-
0	7038	0.72	7338	0.75	-
6.25	6347	0.65	4214	0.66	2.6E-04
18.75	4337	0.44	2134	0.49	2.4E-03
31.25	3146	0.32	1051	0.33	1.7E-04
43.75	1653	0.17	344	0.21	1.5E-03
62.5	590	0.06	36	0.06	1.5E-07
87.5	330	0.03	4	0.01	4.7E-04
112.5	145	0.01	0	0.00	1.7E-04
137.5	76	0.01	0	0.00	5.8E-05
				RMSE	**0.02808**

Table B.5 — Values of root-mean-square error (RMSE) of the observed and theoretical results for each combination of n_e and D_e analyzed for specimen g1.

	$D_e \times 10^{10}$ m^2/s					
n_e	**1.5**	**2.0**	**2.5**	**3.0**	**3.5**	**4.0**
0.25	0.07139	0.05154	0.03783	0.03028	0.02874	0.03182
0.26	0.06615	0.04663	0.03409	0.02809	0.02862	0.03337
0.27	0.06165	0.04305	0.03164	**0.02808**	0.03061	0.03645
0.28	0.05807	0.04041	0.03088	0.02946	0.03368	0.04044
0.29	0.05505	0.03874	0.03143	0.03207	0.03743	0.04472
0.30	0.05256	0.03799	0.03295	0.03535	0.04165	0.04922
0.31	0.05091	0.03801	0.0352	0.03928	0.04596	0.05377

APPENDIX C: ORGANIC DIFFUSION TESTING RESULTS

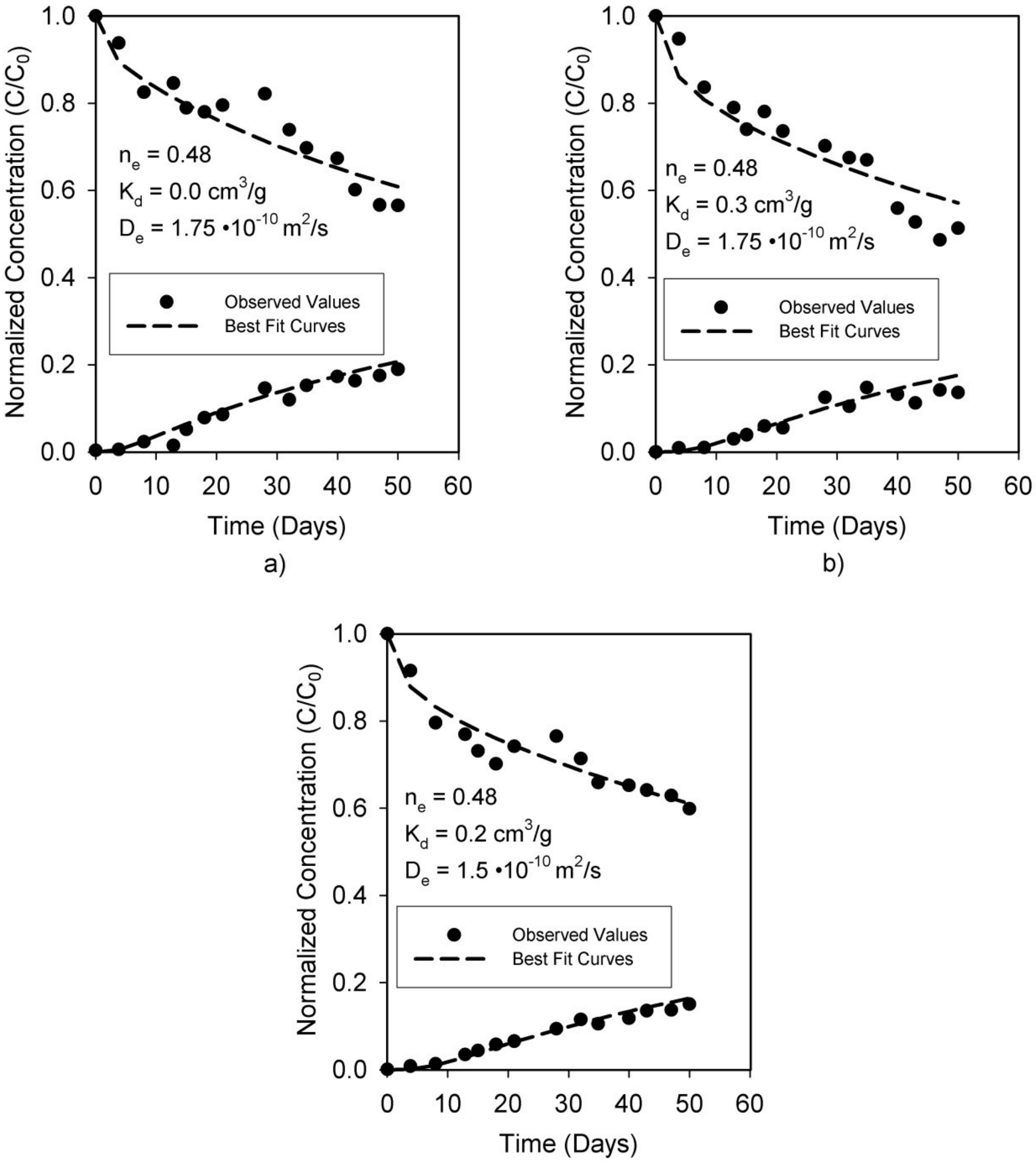


a)

b)

c)

Figure C.1 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen c4: a)benzene, b)trichloroethylene, c)ethylbenzene.



a)

b)

c)

Figure C.2 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c4: a)benzene, b)trichloroethylene, c)ethylbenzene.

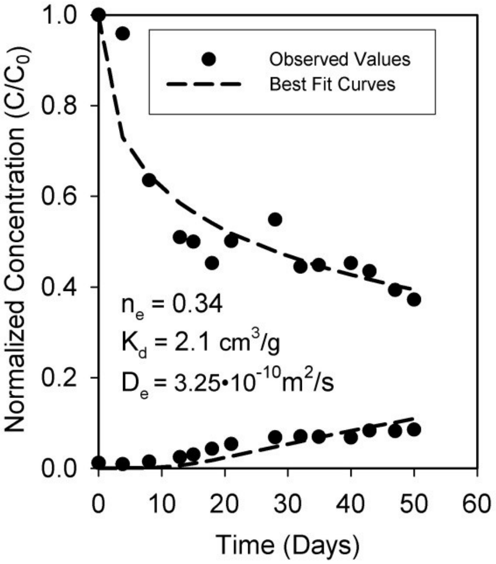


Figure C.3 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c4.

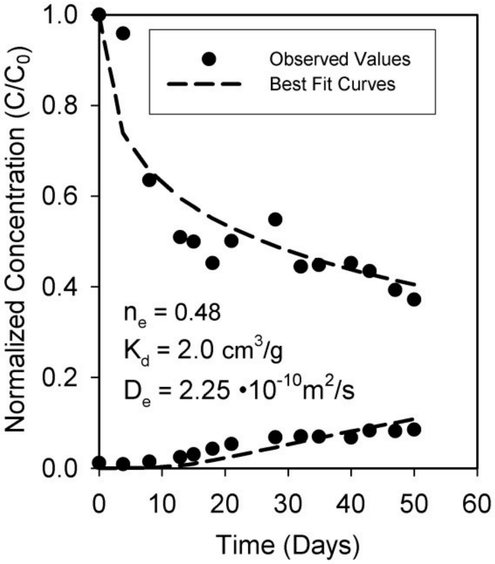
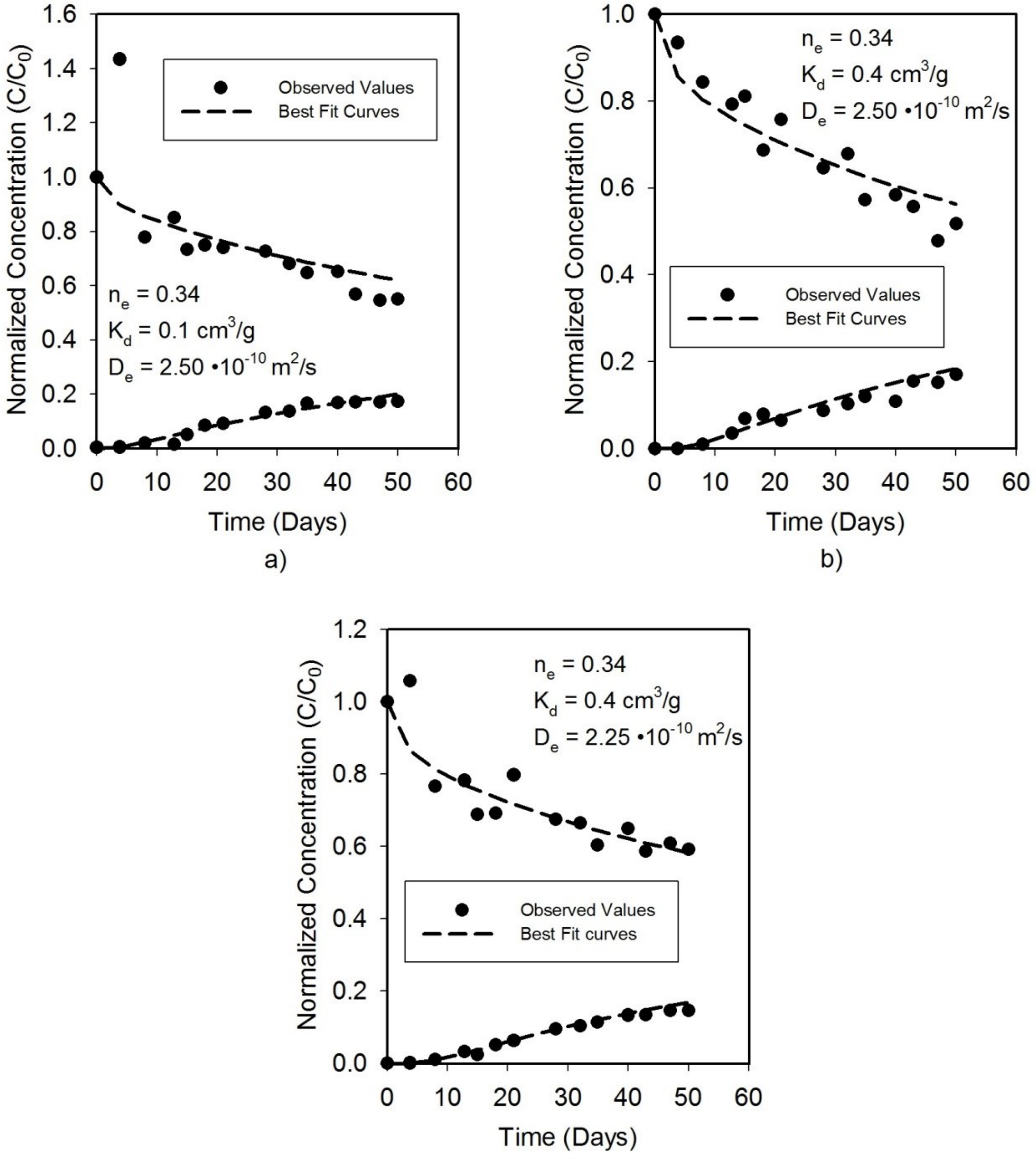


Figure C.4 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c4.

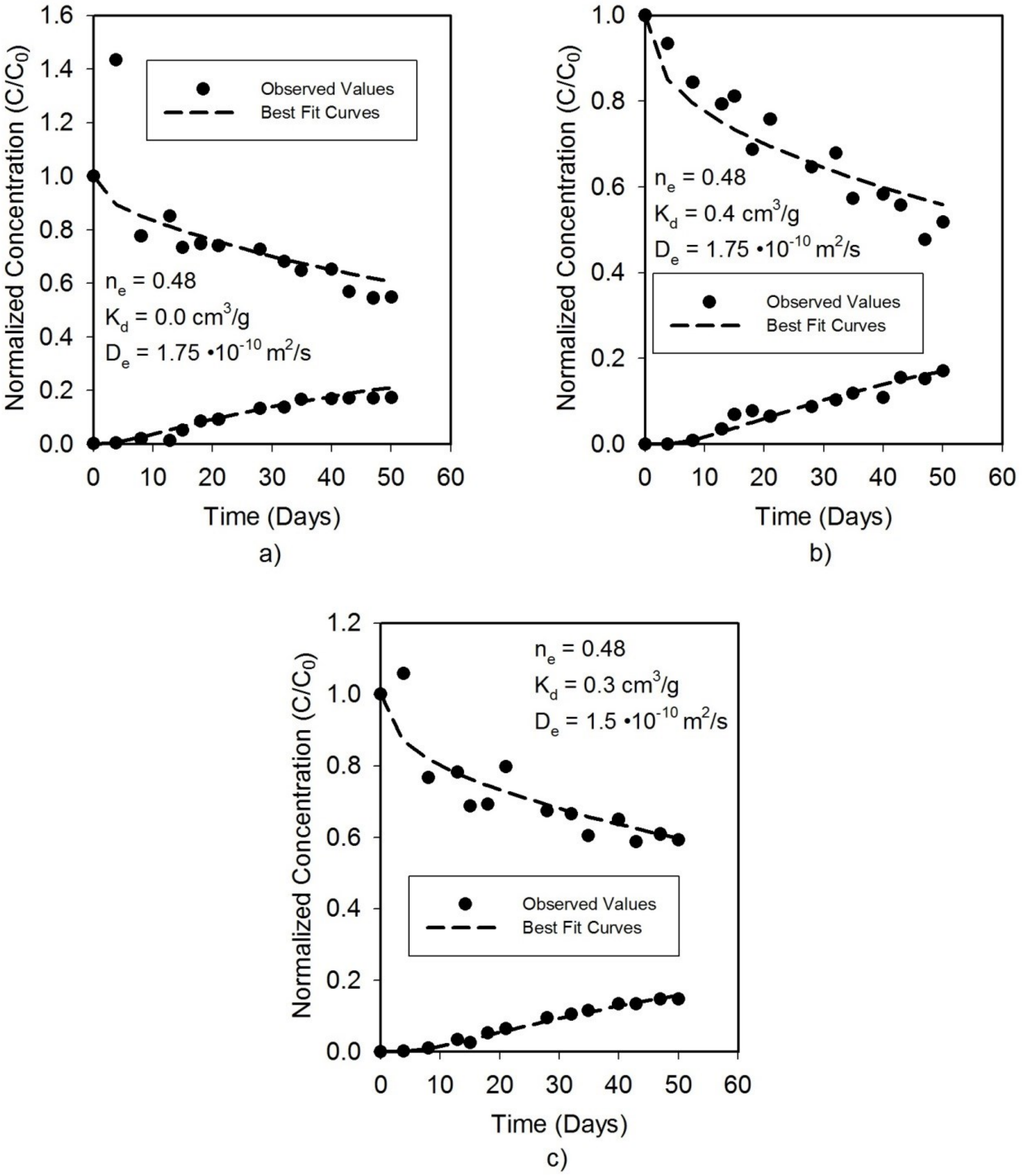


a)

b)

c)

Figure C.5 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen c5: a)benzene, b)trichloroethylene, c)ethylbenzene.



a)

b)

c)

Figure C.6 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c5: a)benzene, b)trichloroethylene, c)ethylbenzene.

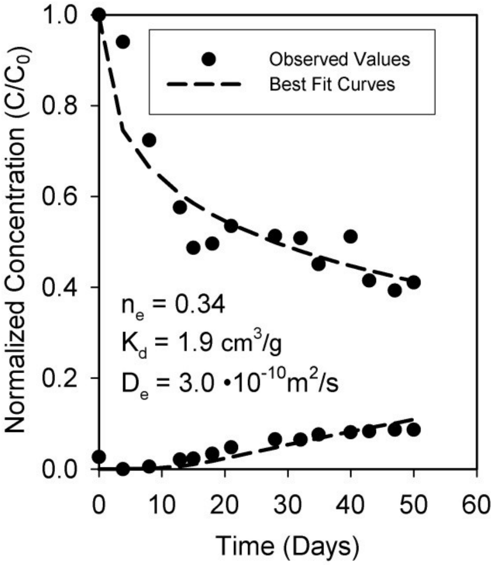


Figure C.7 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c5.

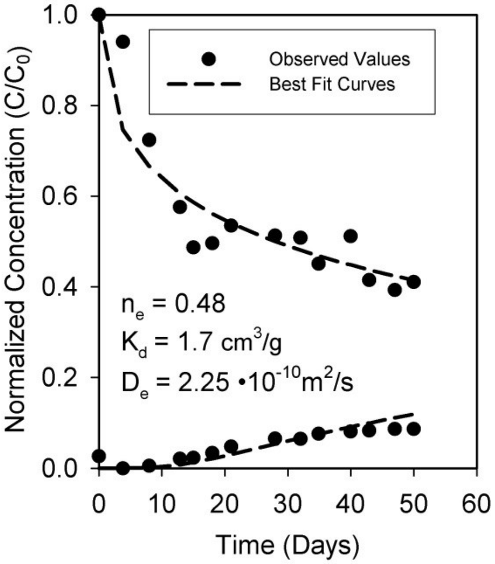
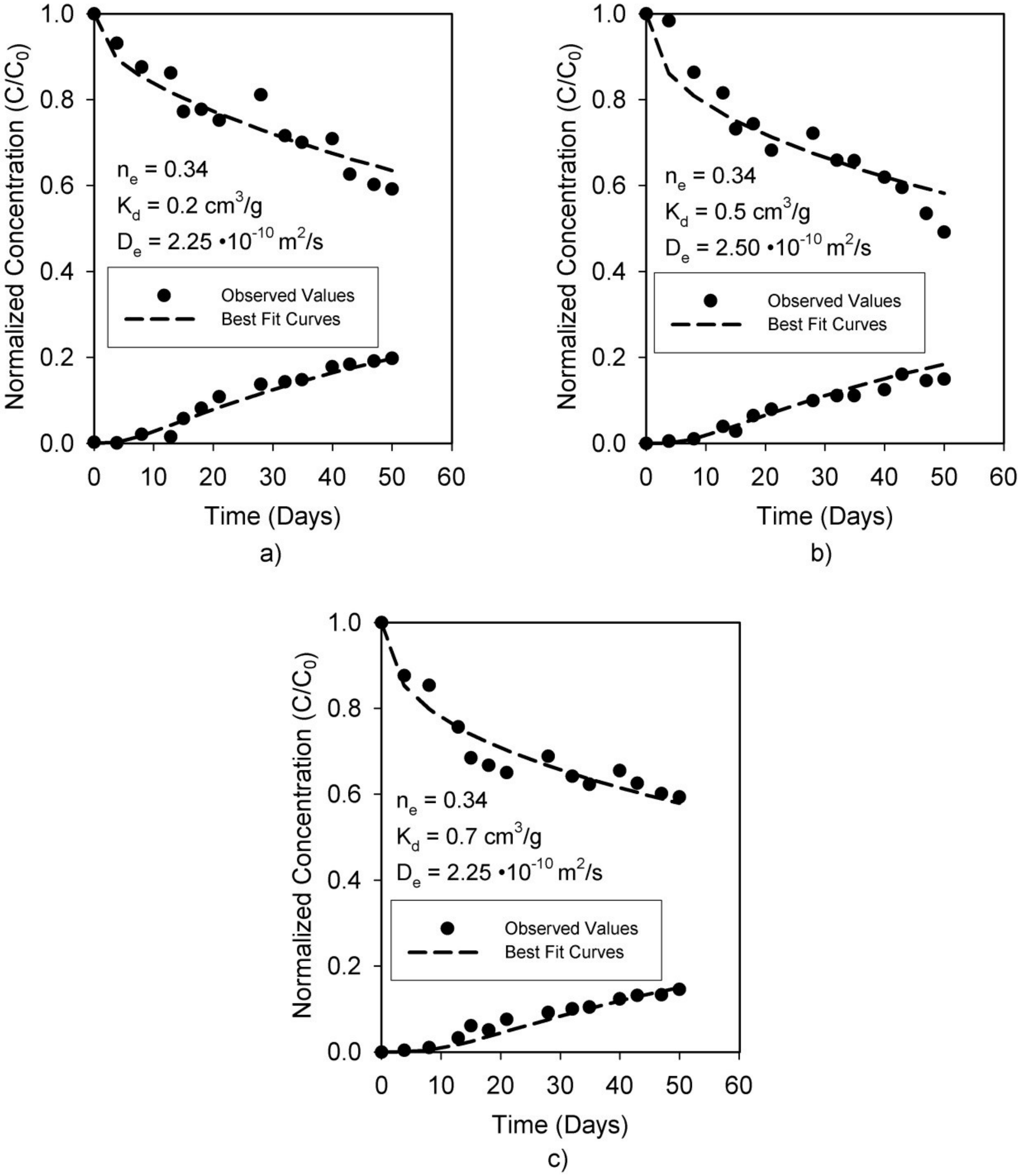


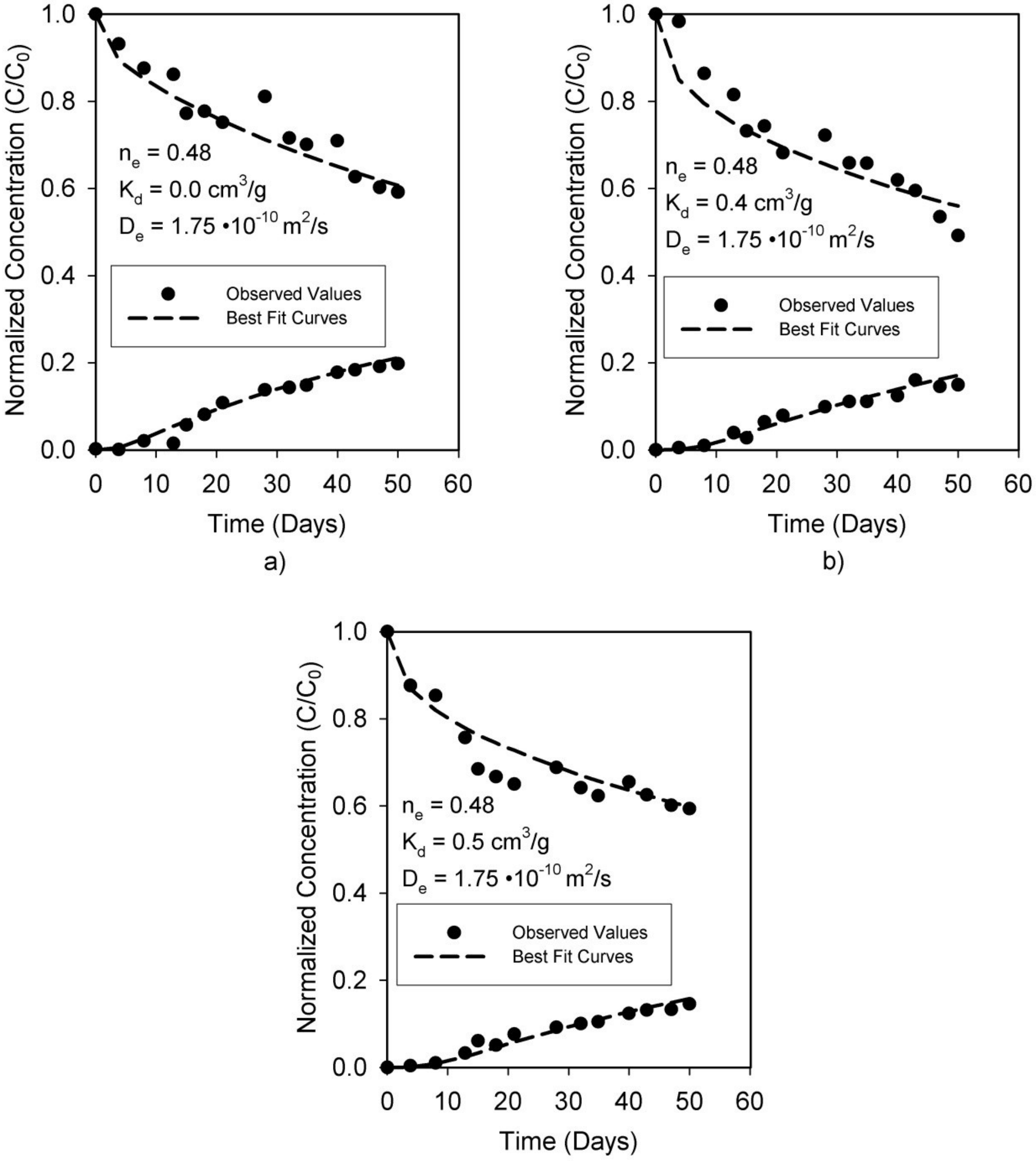
Figure C.8 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c5.



a) b)

c)

Figure C.9— Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen c6: a)benzene, b)trichloroethylene, c)ethylbenzene.



a)

b)

c)

Figure C.10 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c6: a)benzene, b)trichloroethylene, c)ethylbenzene.

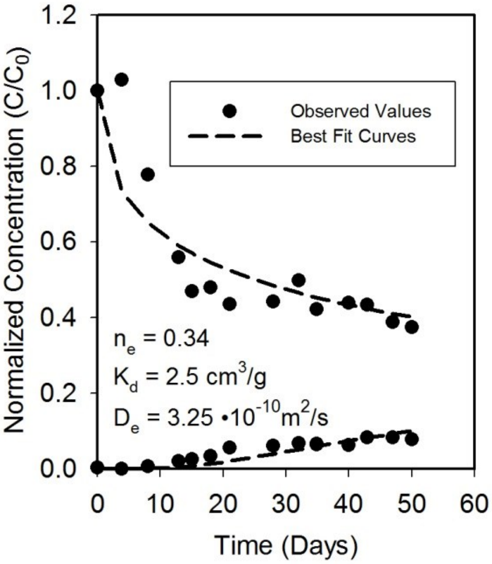


Figure C.11 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c6.

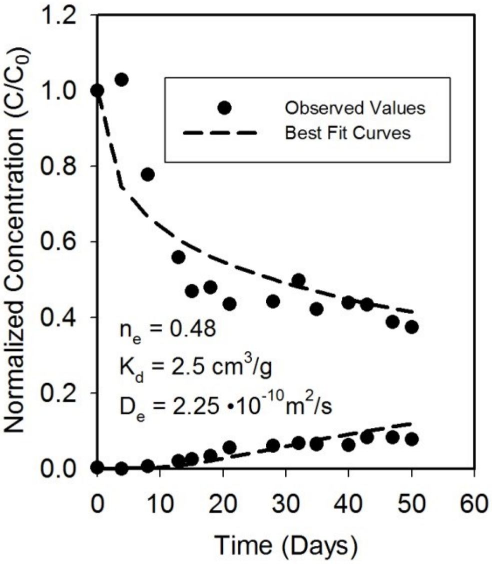


Figure C.12 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c6.

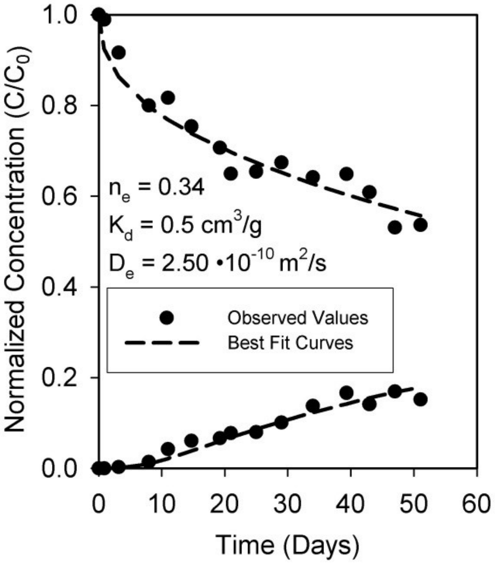


Figure C.13 — Concentration Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c7.

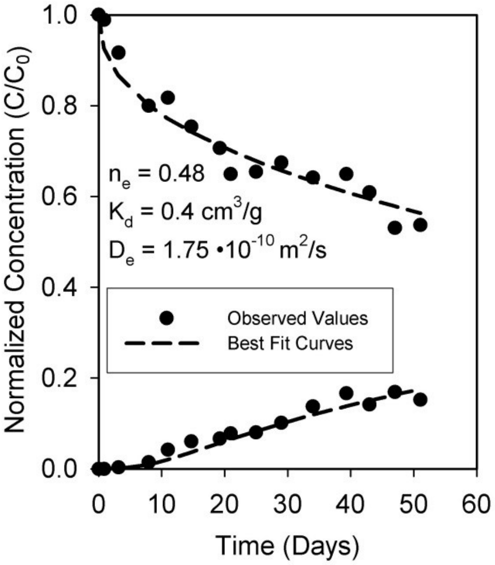


Figure C.14 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c7.

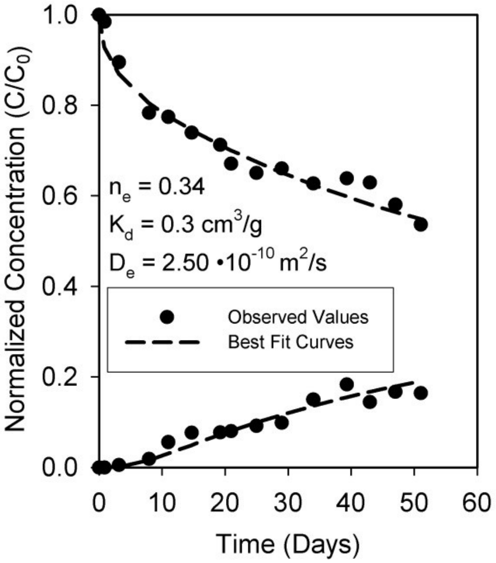


Figure C.15 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen c8.

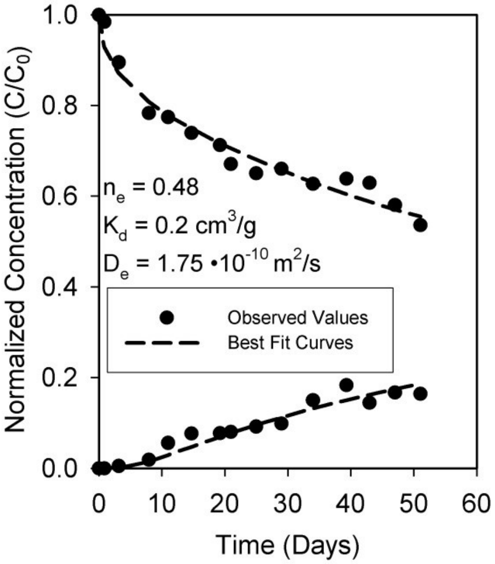
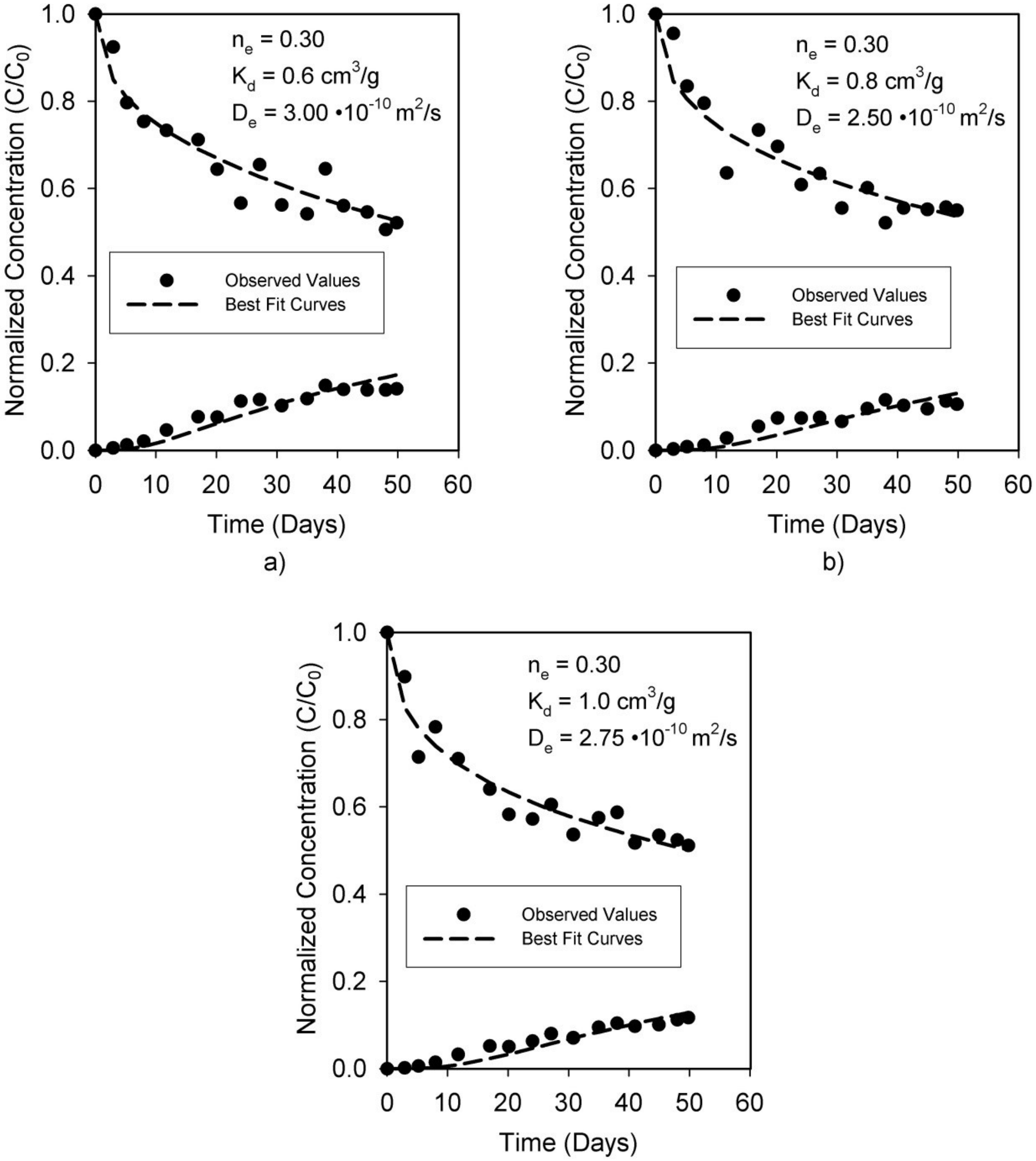


Figure C.16 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen c8.



a)

b)

c)

Figure C.17 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen h4: a)benzene, b)trichloroethylene, c)ethylbenzene.

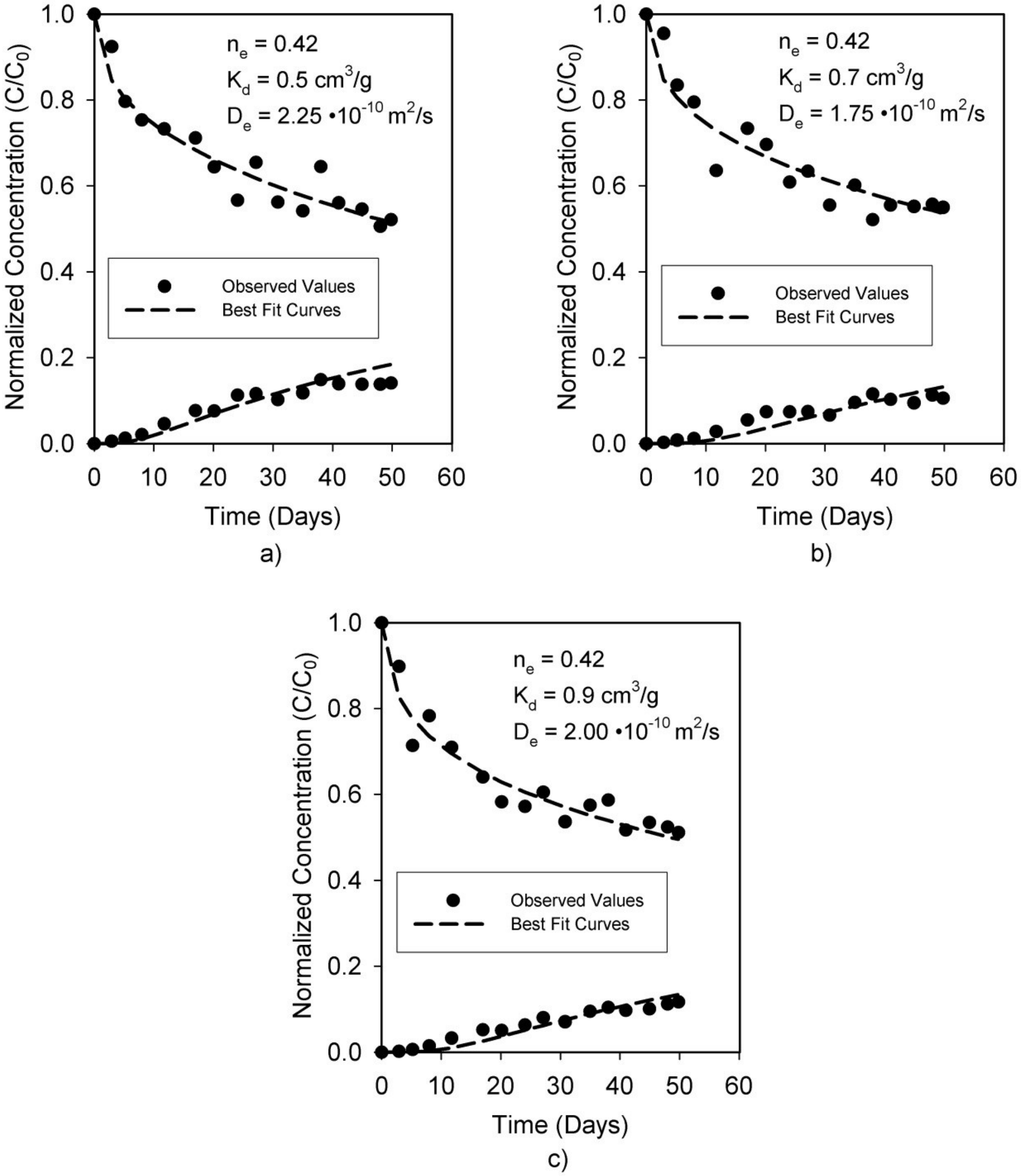


Figure C.18 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h4: a)benzene, b)trichloroethylene, c)ethylbenzene.

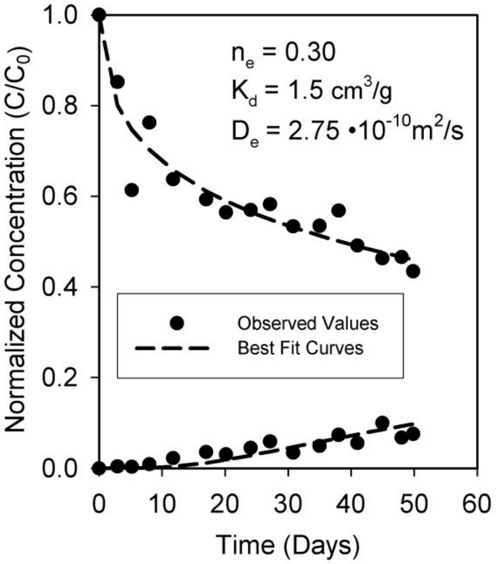


Figure C.19 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen h4.

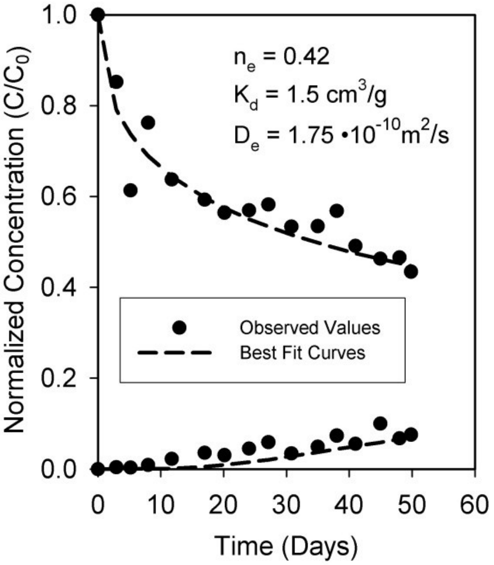
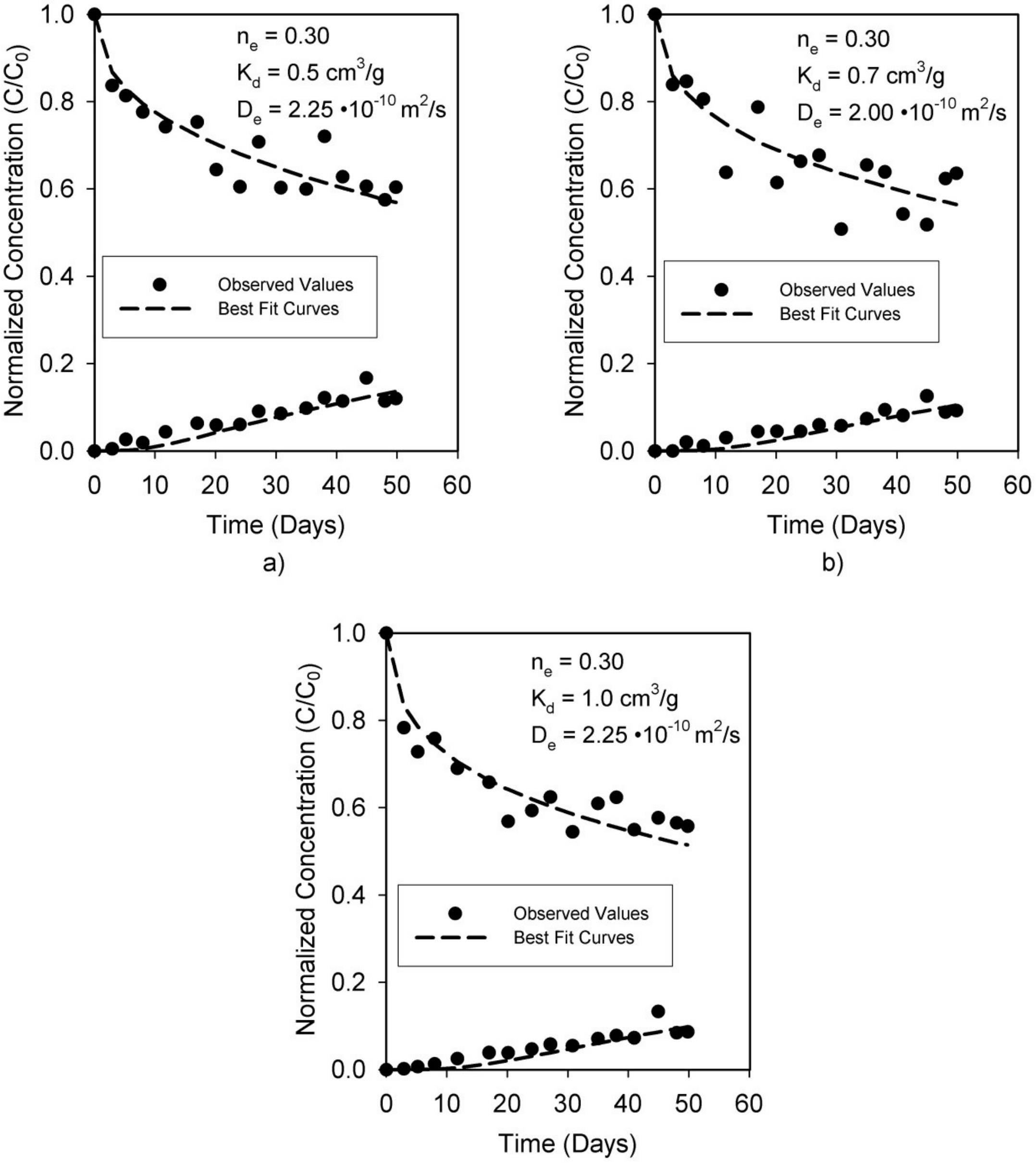


Figure C.20 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h4.



a)

b)

c)

Figure C.21 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen h5: a)benzene, b)trichloroethylene, c)ethylbenzene.

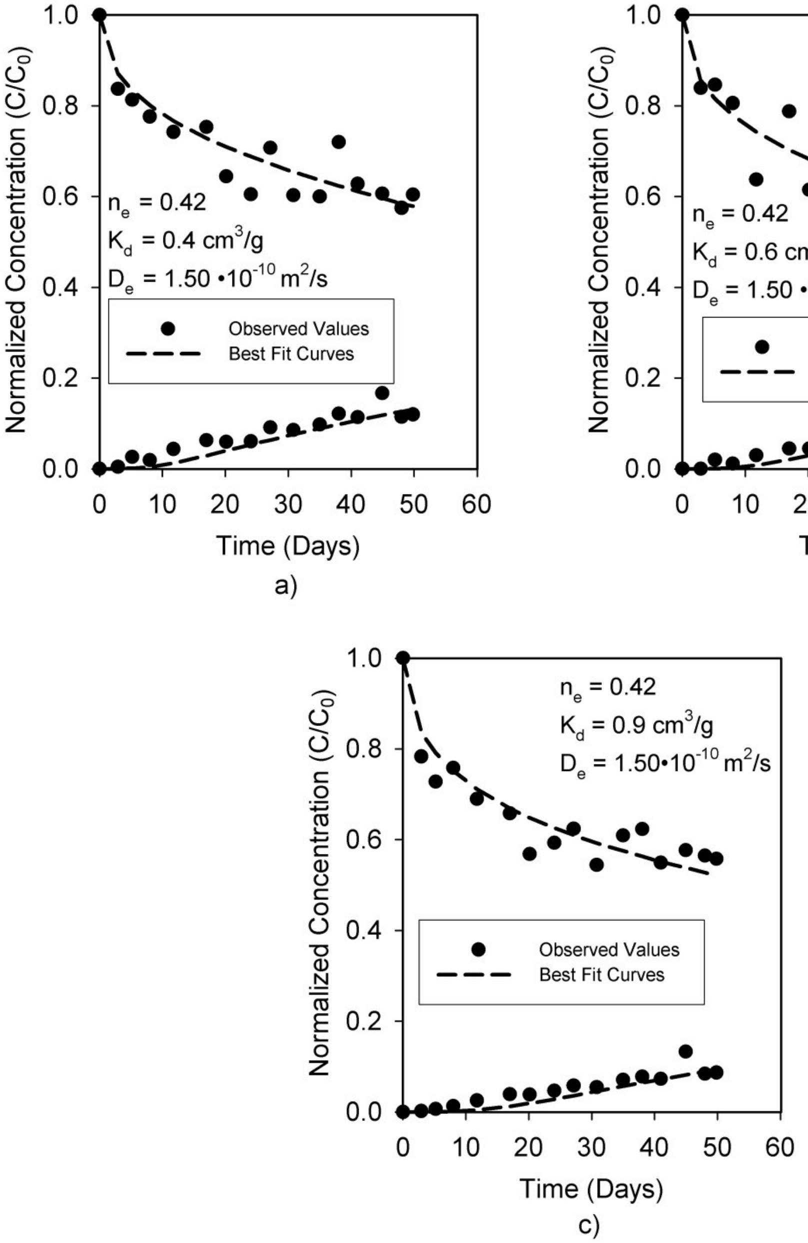


Figure C.22 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h5: a)benzene, b)trichloroethylene, c)ethylbenzene.

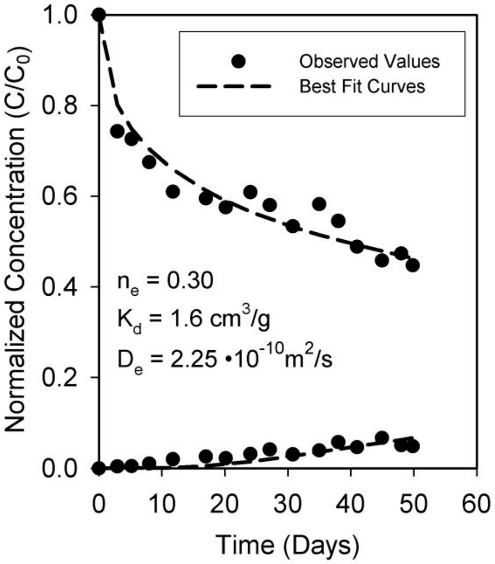


Figure C.23 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen h5.

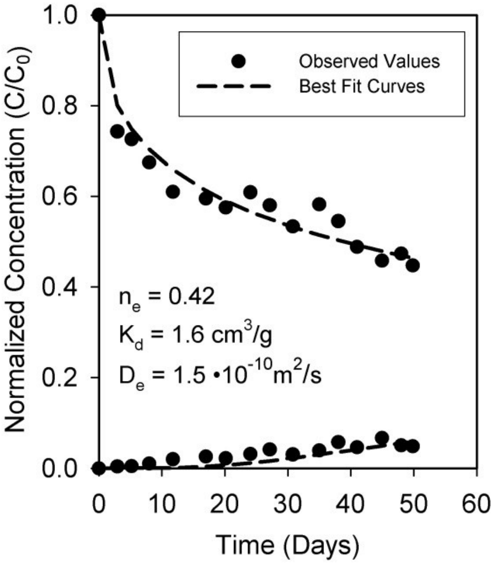


Figure C.24 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h5.

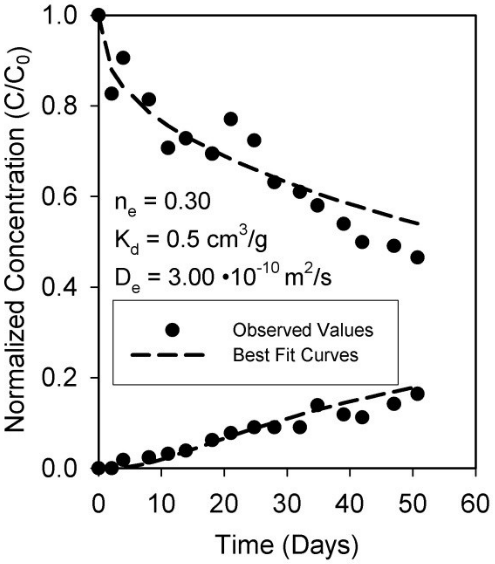


Figure C.25 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen h6.

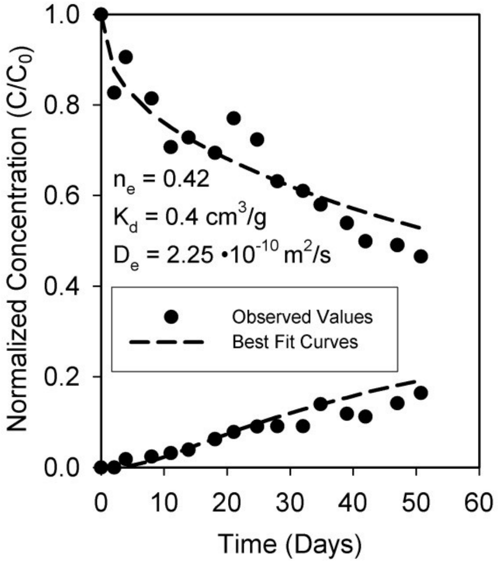


Figure C.26 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h6.

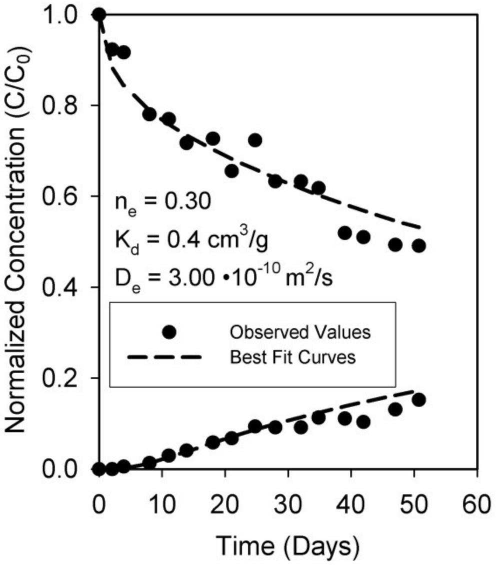


Figure C.27 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen h7.

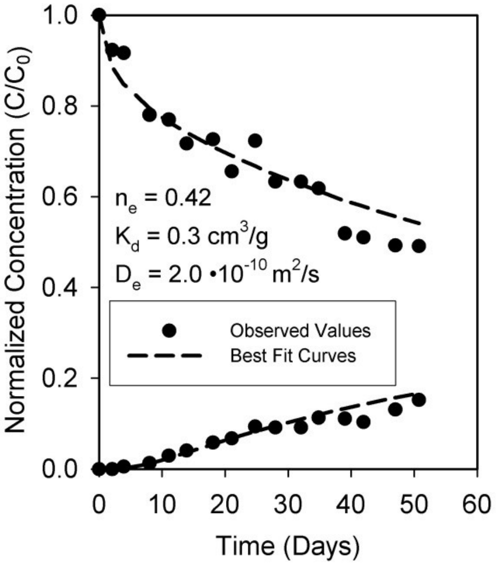
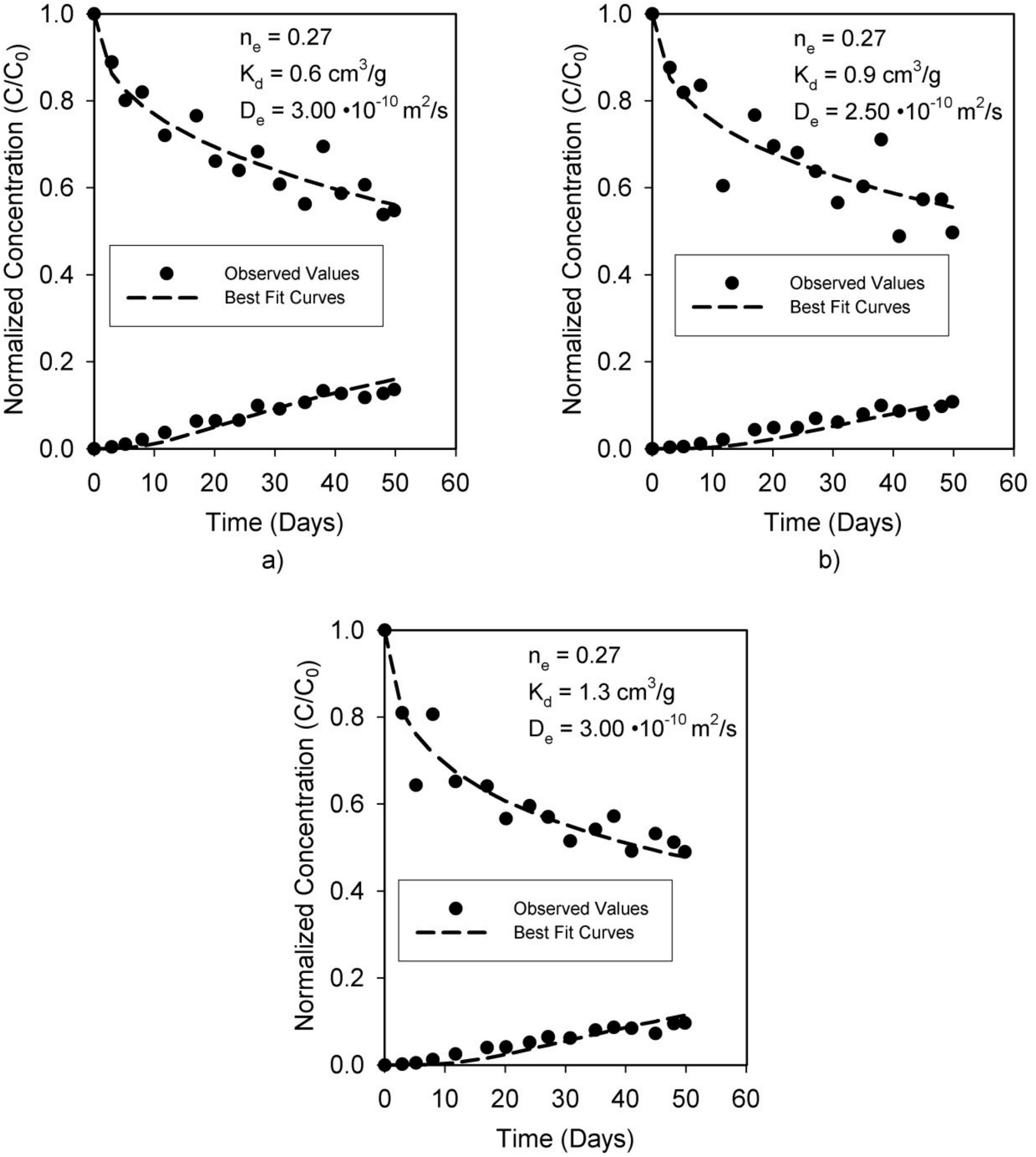


Figure C.28 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen h7.

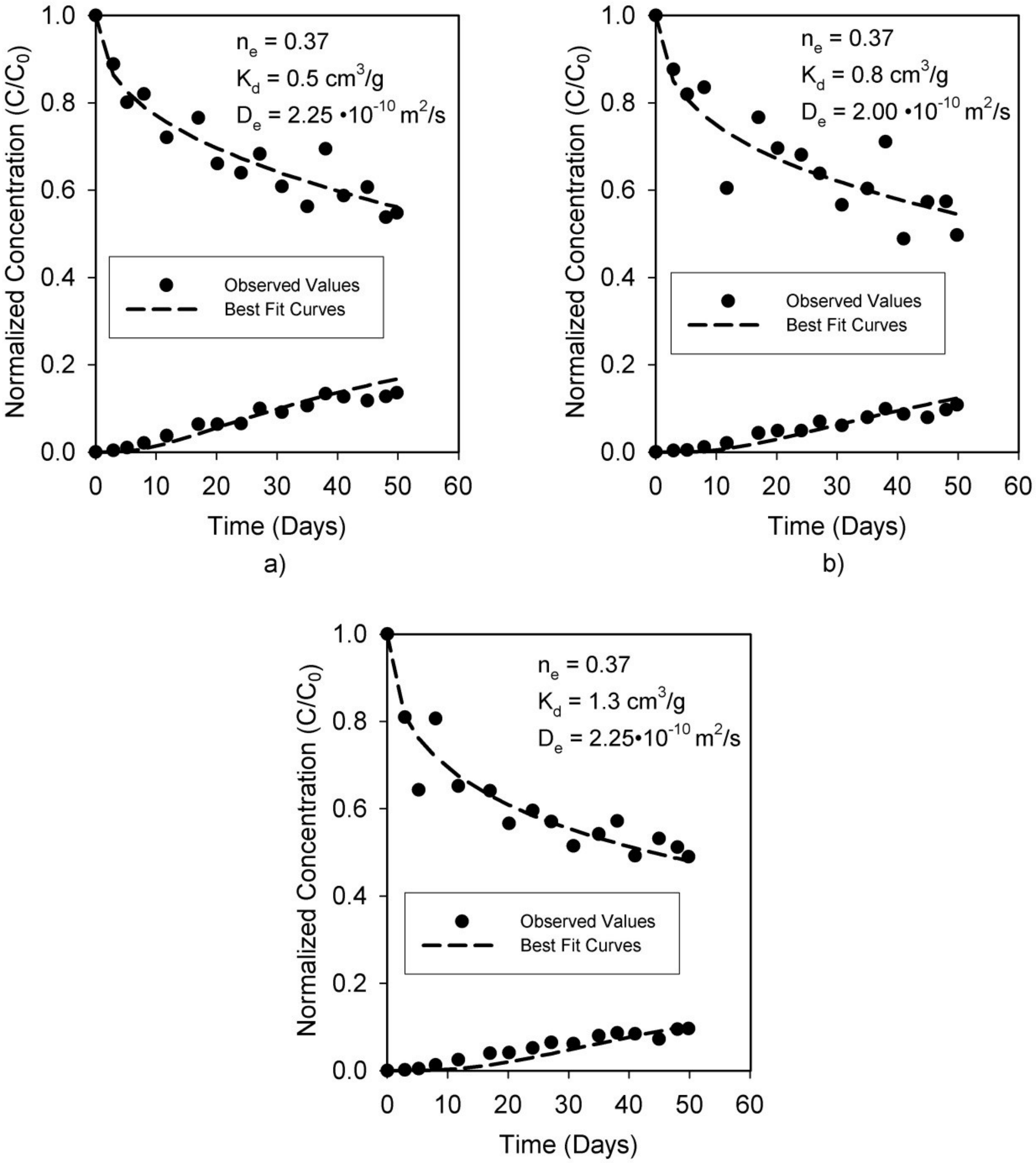


a)

b)

c)

Figure C.29— Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen g4: a)benzene, b)trichloroethylene, c)ethylbenzene.



a)

b)

c)

Figure C.30 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g4: a)benzene, b)trichloroethylene, c)ethylbenzene.

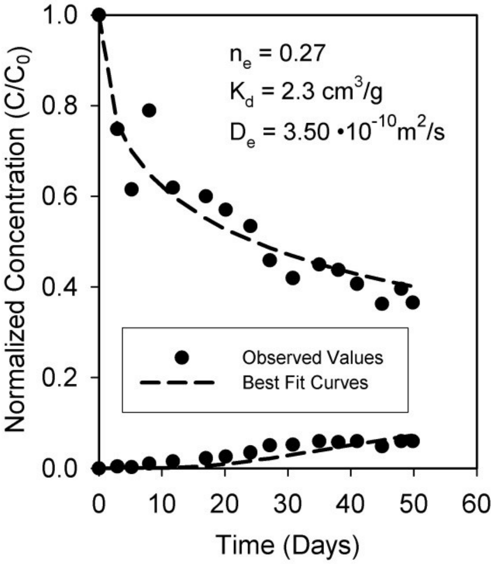


Figure C.31 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen g4.

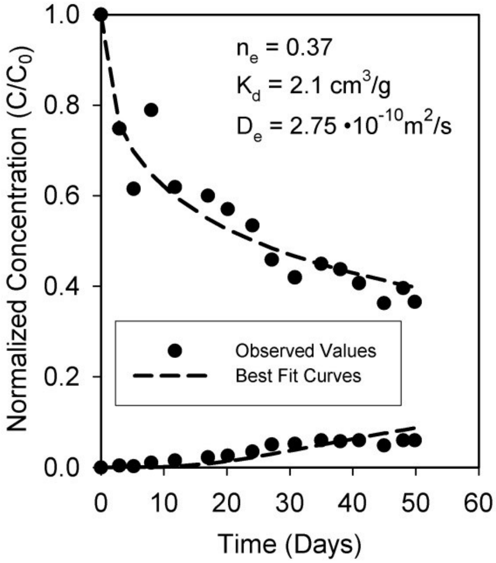
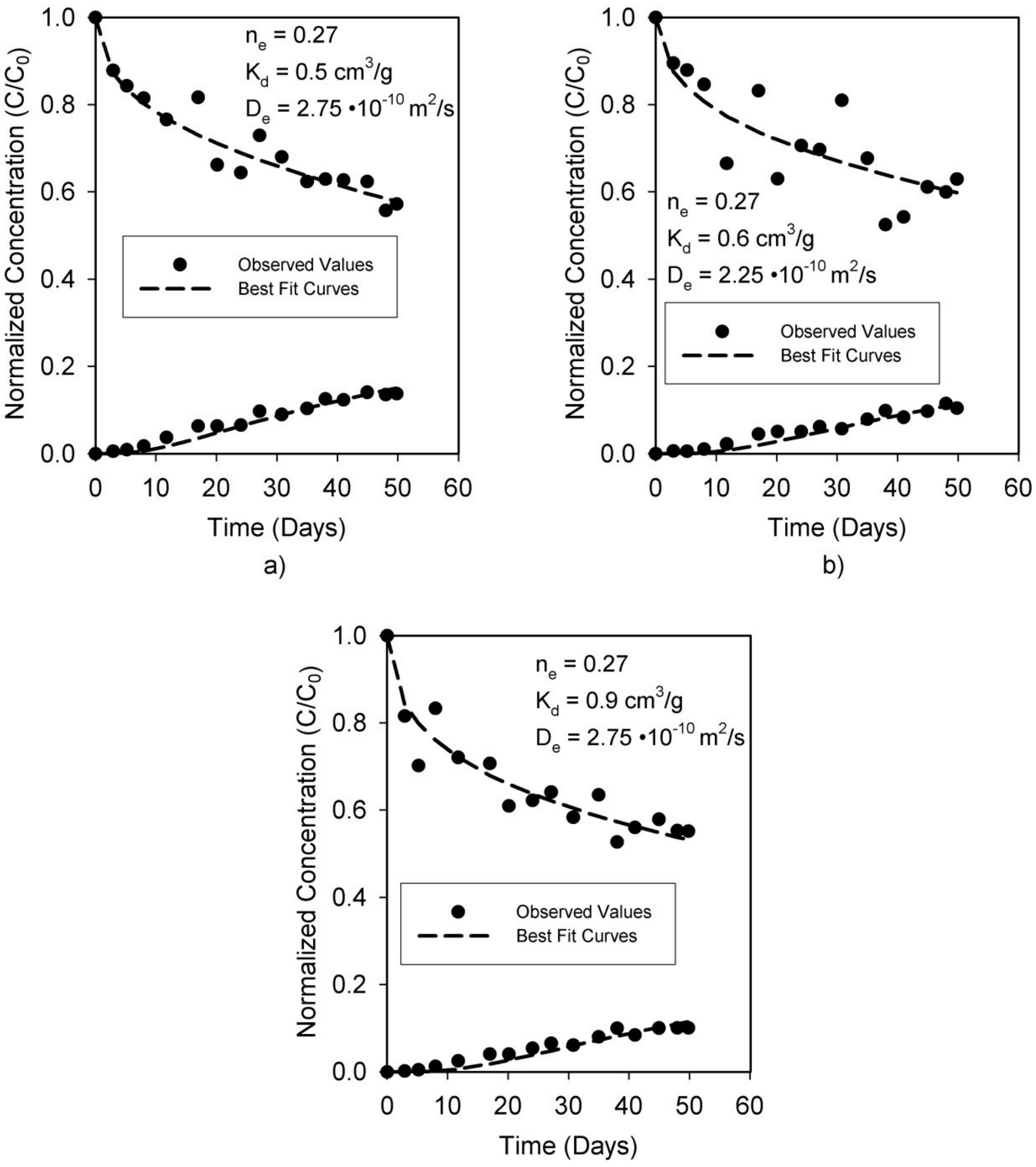


Figure C.32 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g4.



a)

b)

c)

Figure C.33 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to that determined from tritium diffusion testing) for specimen g5: a)benzene, b)trichloroethylene, c)ethylbenzene.

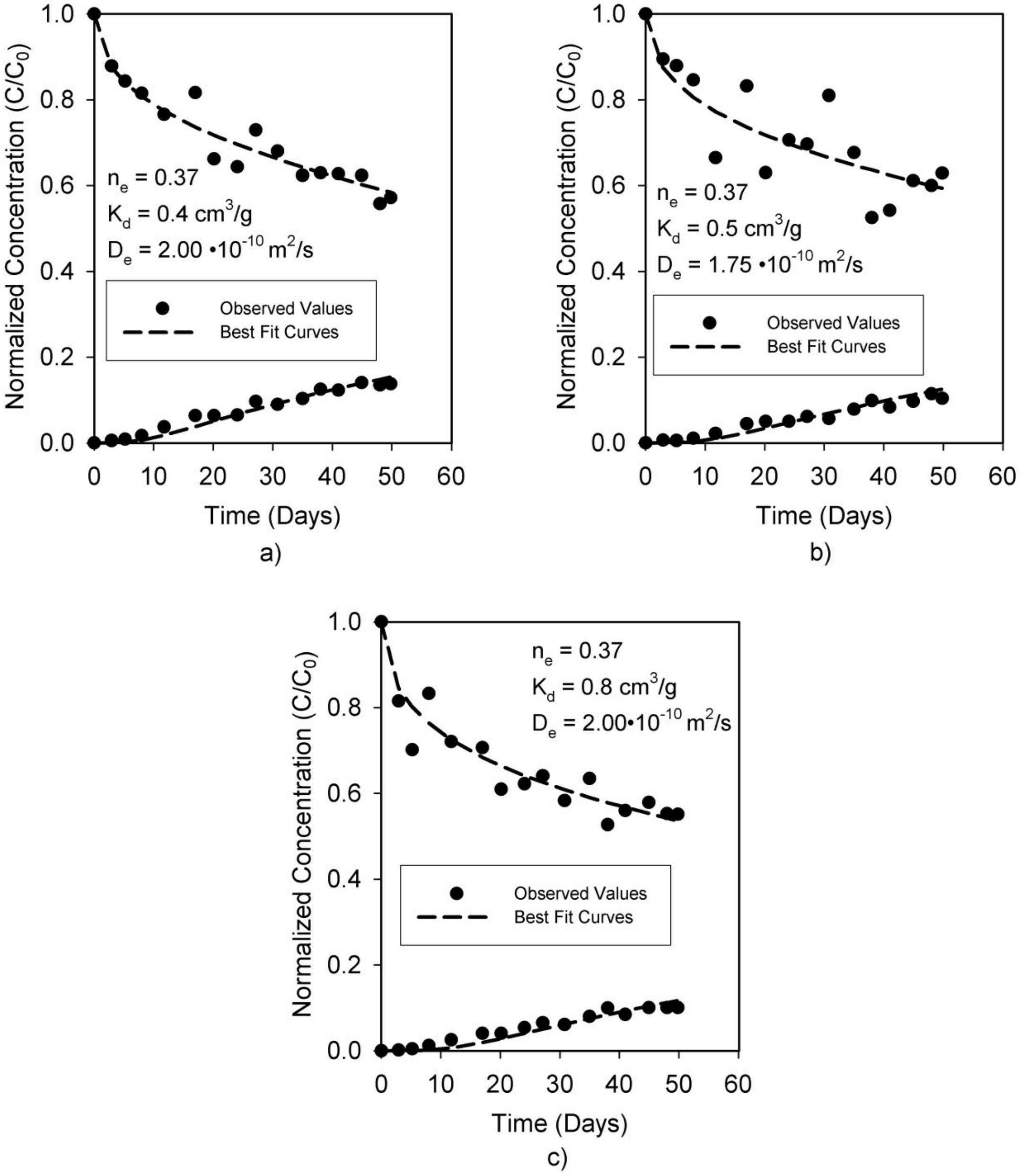


Figure C.34 — Concentration profiles from laboratory diffusion experiments and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g5: a)benzene, b)trichloroethylene, c)ethylbenzene.

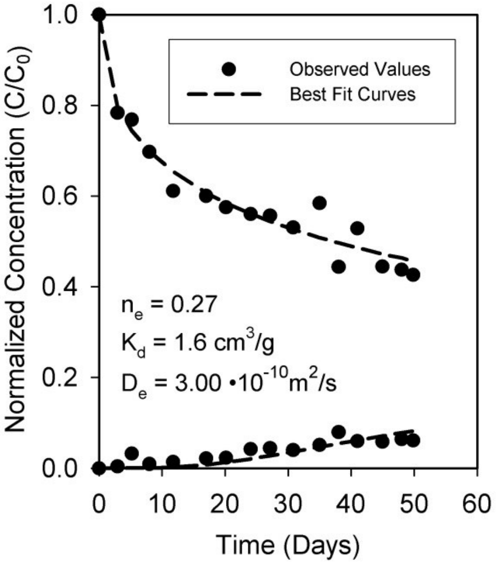


Figure C.35 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen g5.

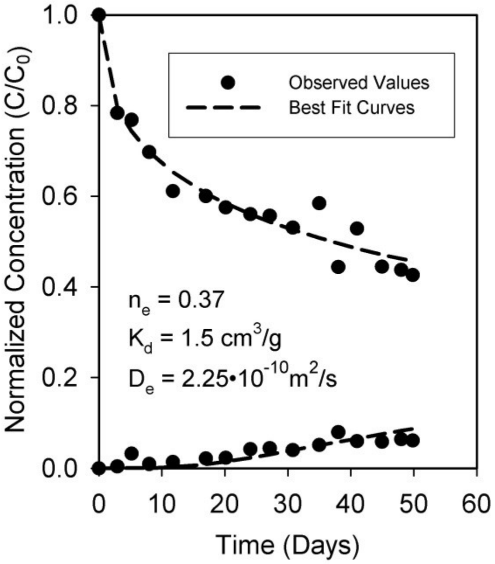


Figure C.36 — Naphthalene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g5.

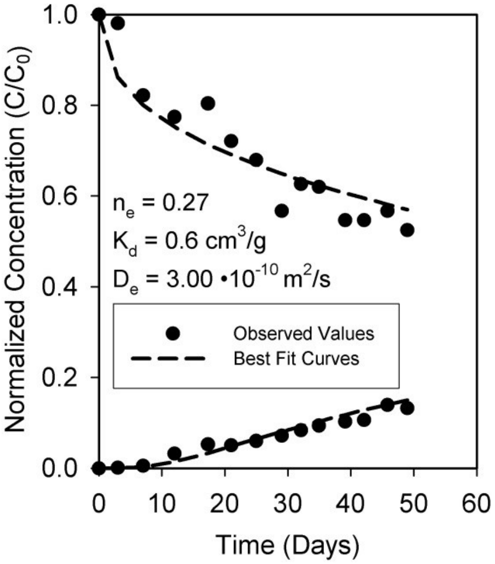


Figure C.37 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen g6.

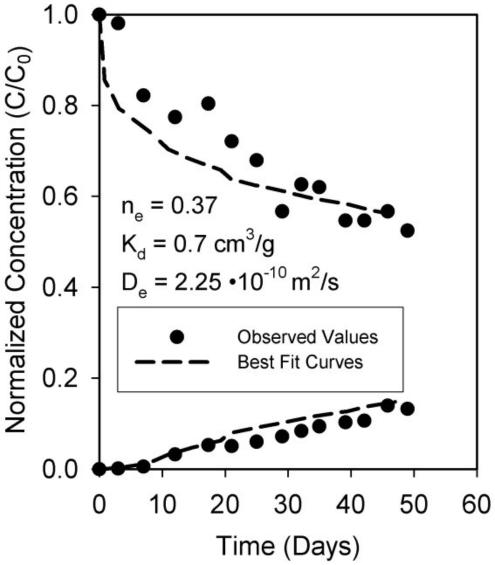


Figure C.38 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g6.

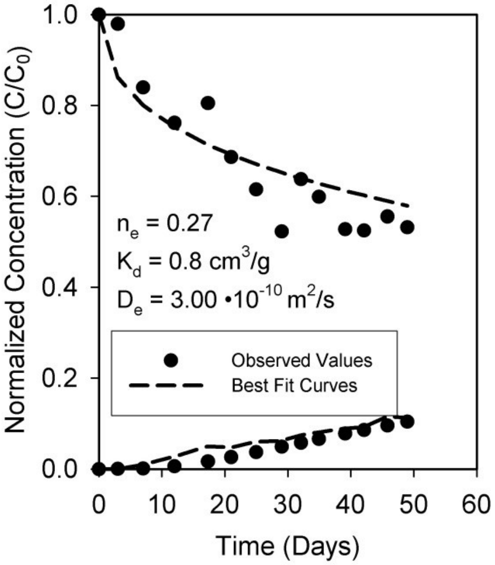


Figure C.39 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (assuming n_e from tritium diffusion testing) for specimen g7.

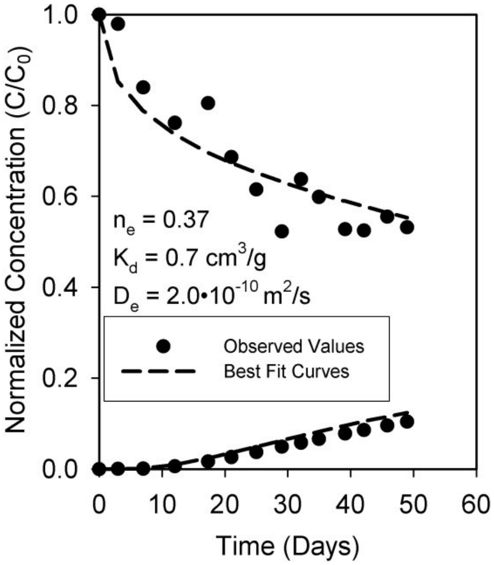


Figure C.40 — Trichloroethylene concentration profiles from laboratory diffusion experiment and best-fit curves (using the assumption that n_e is equal to the total porosity determined from oven-drying) for specimen g7.

APPENDIX D: BATCH TESTING RESULTS

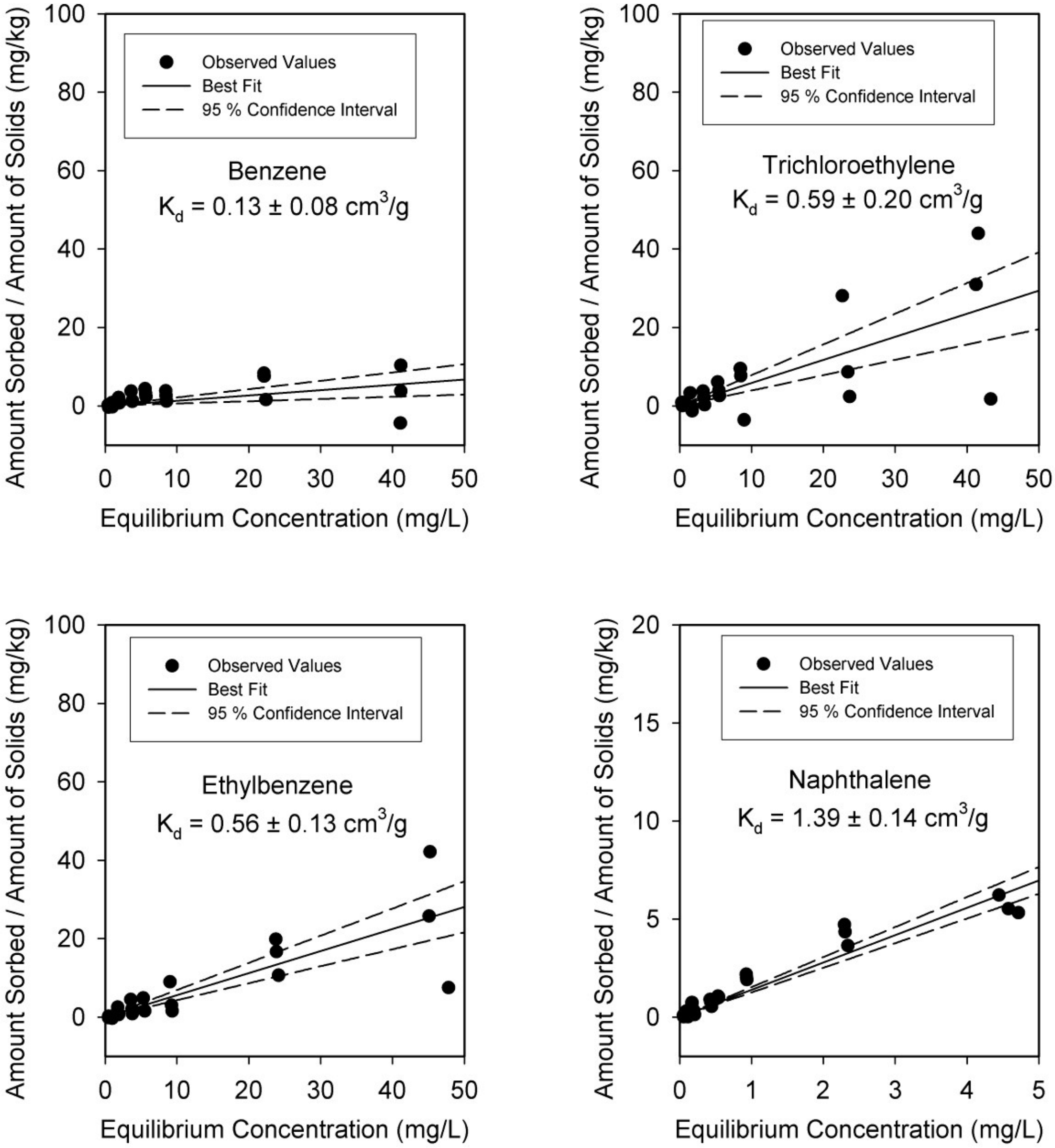


Figure D.1 — Soil-cement mixture c batch test results for benzene, ethylbenzene, naphthalene, and trichloroethylene.

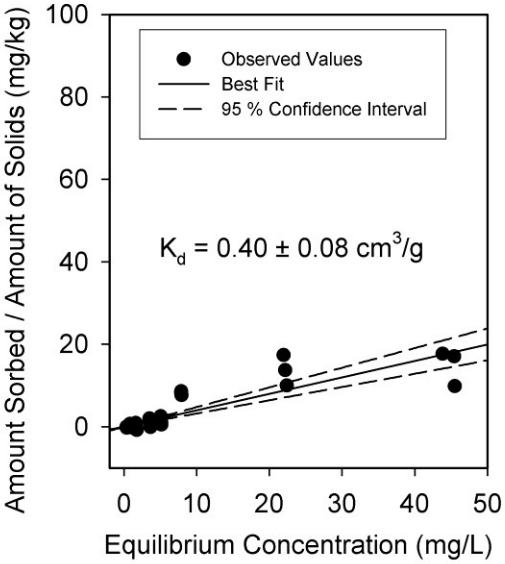


Figure D.2 — Soil-cement mixture c batch test results for trichloroethylene (alone).

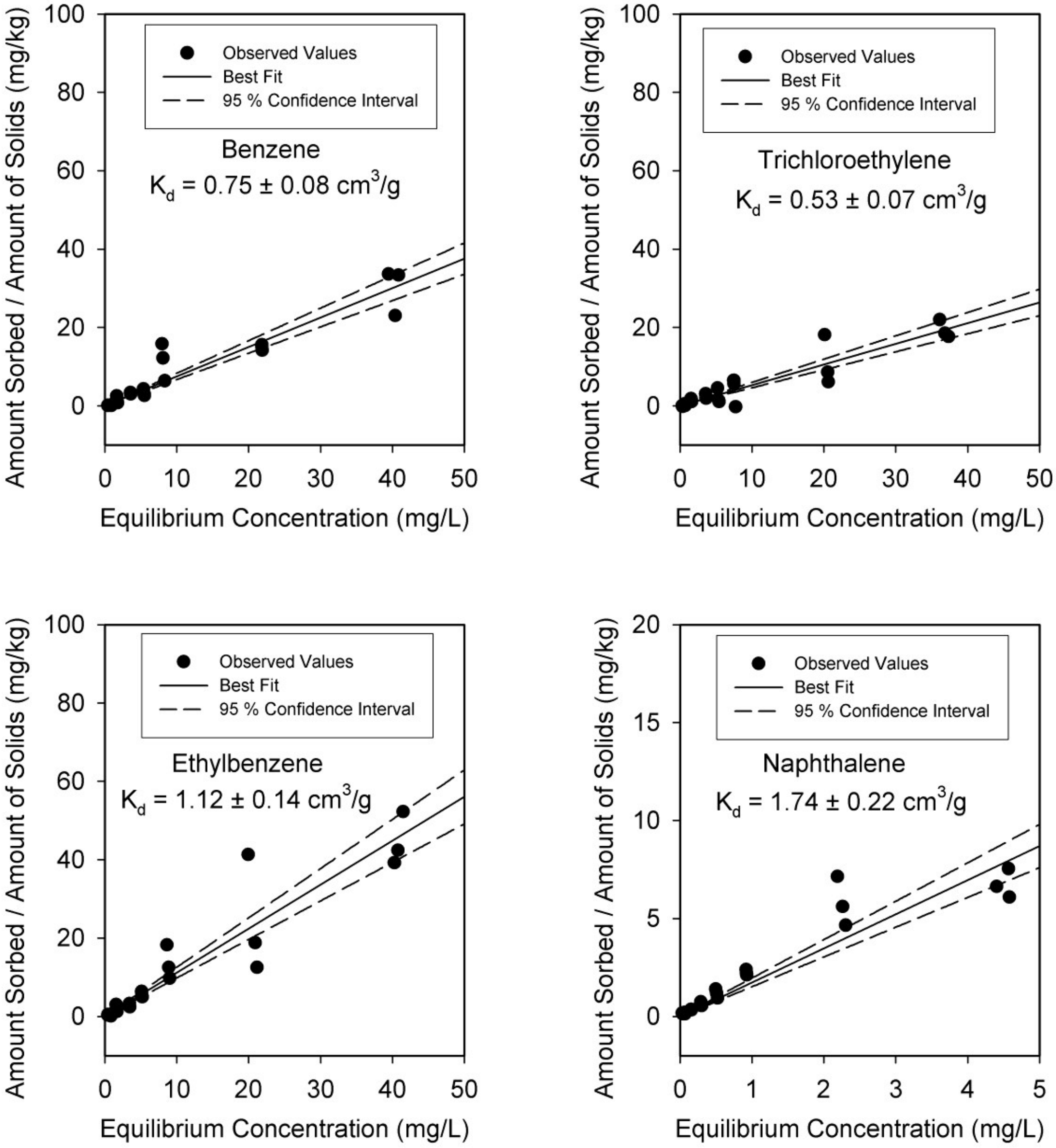


Figure D.3 — Soil-cement mixture h batch test results for benzene, ethylbenzene, naphthalene, and trichloroethylene.

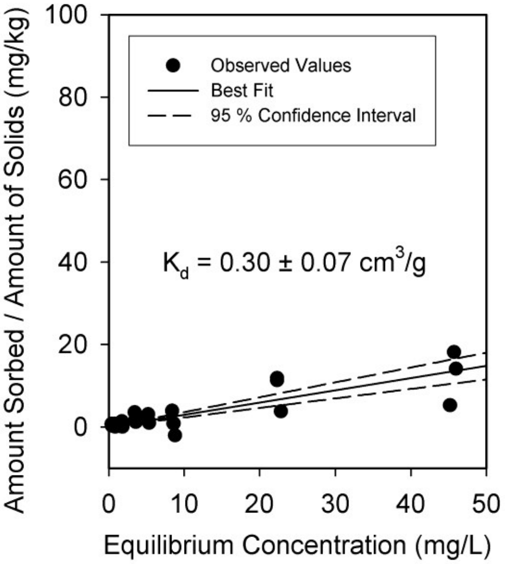


Figure D.4 — Soil-cement mixture h batch test results for trichloroethylene (alone).

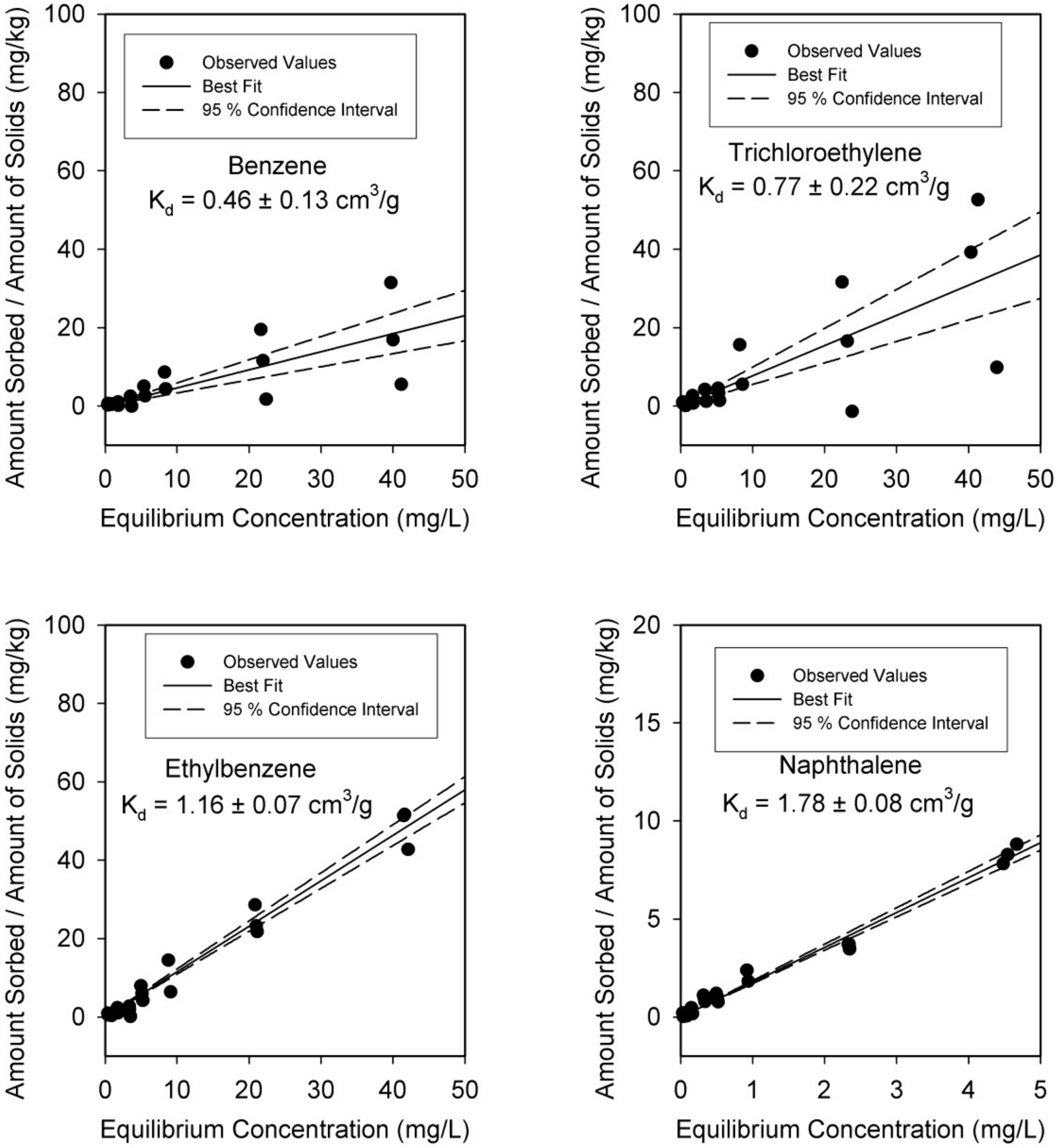


Figure D.5 — Soil-cement mixture g batch test results for benzene, ethylbenzene, naphthalene, and trichloroethylene.

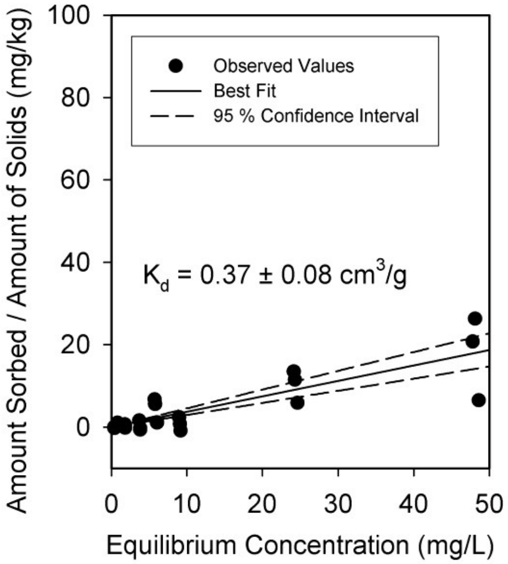


Figure D.6 — Soil-cement mixture g batch test results for trichloroethylene (alone).

APPENDIX E: COPYRIGHT RELEASE FORMS

This appendix contains copyright release forms for previously published papers which constitute Chapters 3 and 4.

Chapter 3

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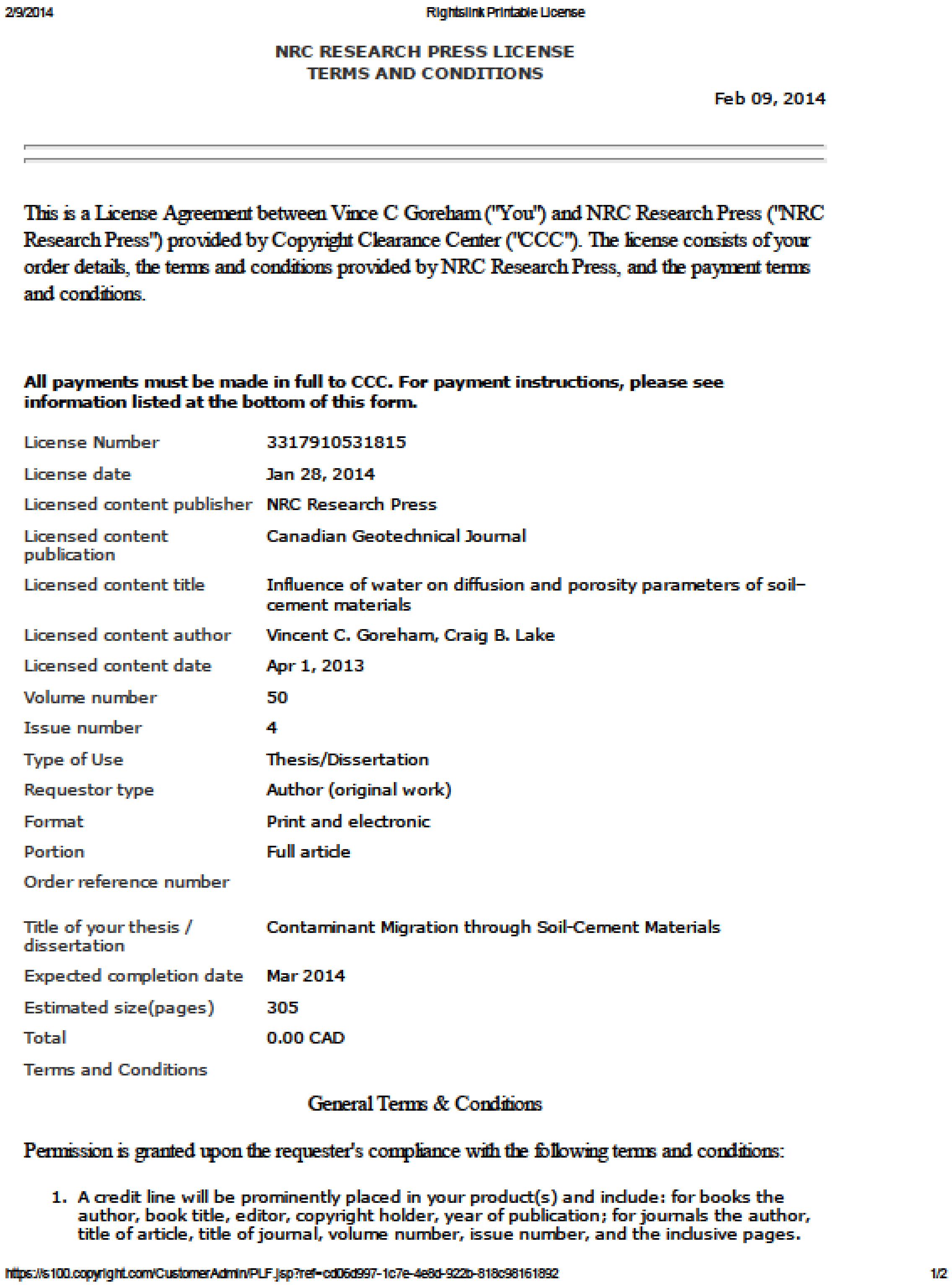

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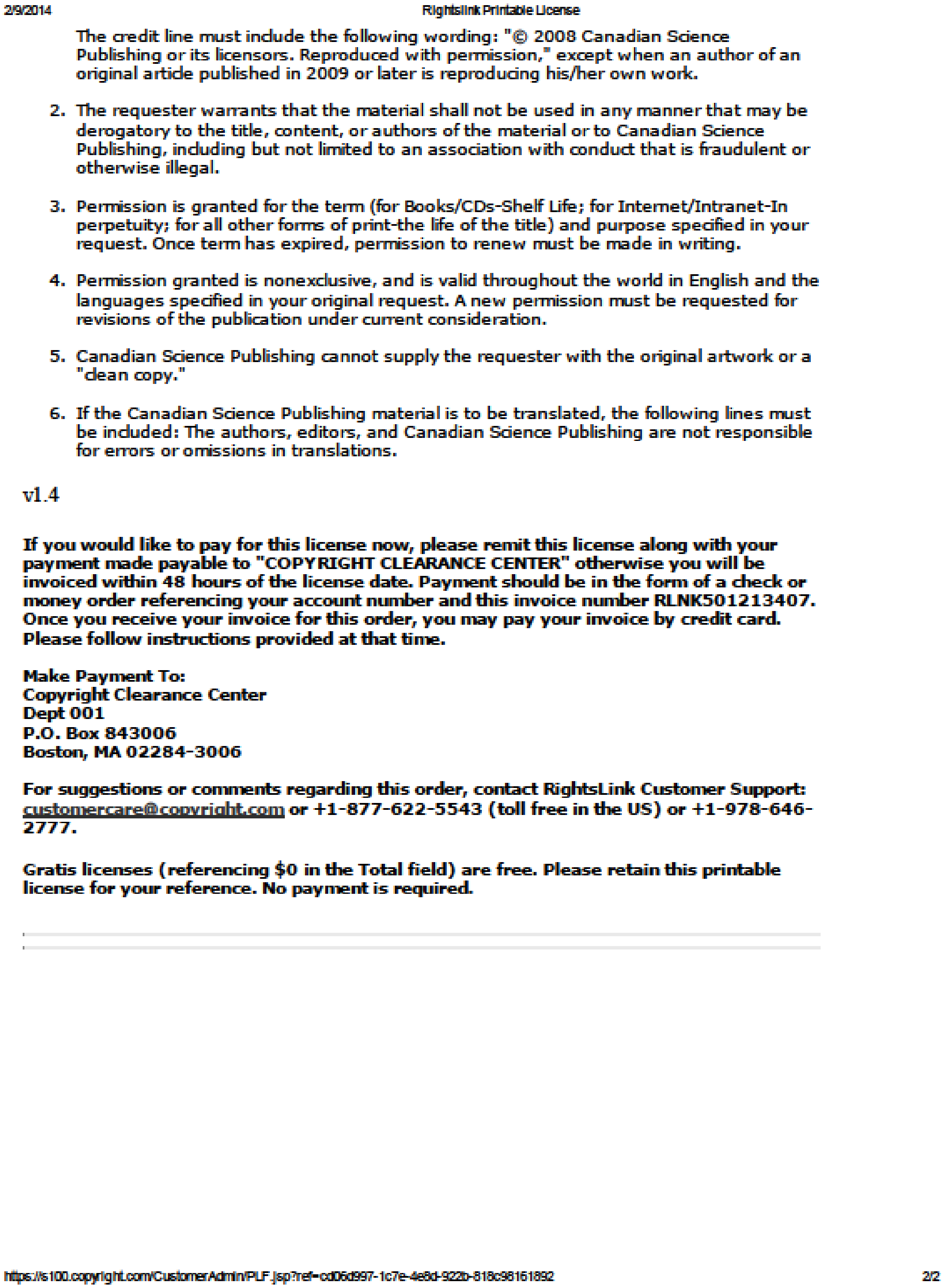

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