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Characterizing Porosity and Diffusive Properties of Monolithic Cement-Based Solidified/Stabilized Materials

ABSTRACT: This paper presents the application of a single reservoir diffusion test to determine the effective porosity of the soil-cement matrix and the diffusivity of tritium through saturated, monolithic, cement solidified/stabilized wasteforms. Testing was performed on a laboratory mixture of cement paste, sand, and kaolinite. The influence of porosity on the proper interpretation of the diffusion tests was examined. Results of tests on three replicate specimens were consistent and indicate effective porosities of 0.26 to 0.28 and effective diffusive coefficients of 2.5×10^{-10} m^2/s to 3.0×10^{-10} m^2/s. The effect of curing time is discussed. Products of the effective diffusion coefficients and porosity (n_eD_e) decreased by 22% from specimens cured for 14 days to specimens cured for 28 days prior to testing while from 70 days to 126 days of curing n_eD_e only changed by 8%. This suggests that curing should be carried out for greater than 70 days prior to conducting these tests.

KEYWORDS: Diffusion, cement, solidification, stabilization, laboratory, monolith, tritiated water

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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 2004).

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 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, 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) suggested 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 (though they 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 pre-design (technology selection) phase and for long-term contaminant migration modelling.

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 the effects of combined treatment methods (e.g. combined cement-based S/S wasteforms with slurry walls) may be analyzed.

The purpose of this paper 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 tritium, 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 evaluate long-term contaminant transport through cement-based S/S materials for hundreds of years, provided the physical integrity of the waste does not change.

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 1 (Rowe *et al.* 2004):

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

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, and λ is the first order decay constant of the contaminant species [-]. 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). This equation states that the increase in contaminant concentration within a small volume (the effective porosity) is equal to the increase in concentration due to diffusive transport, minus the decrease in concentration due to decay.

The n_e in Equation 1 refers to the volume of accessible pores to total volume. Inaccessible pores are excluded from this calculation of porosity. Implicit with the use of the effective porosity, n_e, on the left-hand side of Equation 1is the assumption that a portion of the porosity is entirely inaccessible to the diffusing substance. The n_e used in Equation 1 represents the effective porosity available for transport during the duration of the laboratory test. It is possible that for longer term tests, the 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; 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 Treadway 1982; Luping and Sørensen 1998). Contaminant movement through cementitious materials has been quantified using tests such as ASTM C1556-04, 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 some other authors (e.g. Rowe *et al.* 2004).

To shorten the testing time required, rapid chloride permeability tests have been developed (e.g. ASTM C1202-10; AASHTO T277). These two standards specify the rating of chloride permeability (from negligible to high) based on the electrical charge passed through a specimen subject to a direct current voltage (60V) 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 2004). 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 2004). 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 2004). 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, pre-determined time intervals and the concentration of the contaminant in each removed leachant is measured (Garrabrants and Kosson 2004). 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).

Laboratory Procedure

The basis of design for the diffusion test method presented below is from similar tests which have 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. As the substance is allowed to migrate into the specimen (under zero hydraulic gradient conditions), 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).

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 modelling 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 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, modelling was performed using the assumed diffusion parameters ($D_e = 2.0\times10^{-10}$ m^2/s, and $n_e = 0.20$). Figure 1a presents the theoretical final diffusion profile through the specimen (normalized to the initial concentration, c_0) after test times of 7, 14, 28, 56, and 84 days considering a source reservoir size of 100 mL and 50-µL, twice-weekly, sampling for the assumed diffusion parameters. As can be seen in Figure 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 modelling indicated that the proposed cell geometry and a 28-day test duration were suitable for testing materials for a range of reasonably expected n_e and D_e.

The source reservoir volume of 100 mL was chosen such 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). Modelling showed that larger source reservoir volumes resulted in reductions in concentration of less than 15% and smaller reservoir volumes were not sufficient in size from a practical perspective. 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 1b presents theoretical modelling of the normalized source reservoir concentration with, and without, sampling. Inspection of Figure 1b shows that the source concentration would be reduced to less than 85% of c_0 after 28 days for the assumed parameters. Figure 1b 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 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 during specimen insertion to prevent pressure build up and at the completion of the test when the opening was used to push the specimen out of the cell.

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% moisture content, corresponding with the standard-proctor optimum water content of the sand-kaolinite blend. The sand-kaolinite blend, classified as SM by the Unified Soil Classification System (ASTM D2487), 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 St. Lawrence 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 listed 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 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 particular combination of soil, cement, and water above were used to ensure consistent mineralogy and grainsize distribution for experimental purposes and to ensure that the materials could be thoroughly mixed with the available laboratory equipment.

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, moisture 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 (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 over 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.

Moisture Content, Porosity, Bulk Density, and Specific Gravity Measurements

As will be discussed in detail below, at the completion of the diffusion test, the specimen was cut into sections and crushed. The water in each 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 moisture content. For moisture 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 moisture 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 dried, crushed (to grainsize < 2 mm) samples of 'dummy' specimens were tested by the Minerals Engineering Centre, Dalhousie University, 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.

Saturation

Just prior to testing, specimens were saturated in the flexible-wall permeameter in general accordance with ASTM D-5084-10. 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:

$$S = \frac{wG_s}{e} \tag{2}$$

where, w [-] is the average moisture content [-], G_s is the specific gravity [-], and e is the average void ratio [-] of the three dummy specimens.

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 hours, as per the manufacturer's recommendations. After application of the epoxy, the final outside 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 applied to where the top of the specimen meets the diffusion cell (as shown in Figure 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 concentration of approximately 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 tritium 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 pieces as this portion contains the largest concentration and concentration gradient. Each section was crushed (to a grainsize 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 hours. After allowing the crushed material to settle for 24 to 48 hours, 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).

Modelling 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 a 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):

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

where c_0 is the initial concentration in the source solution [ML^{-3}], H_r is the 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):

$$f(z = H_b) = 0 \tag{4}$$

where H_b [L] is the depth of the base stratum.

The laboratory diffusion test may be modeled by solving Equations 1, 3, and 4 numerically and the contaminant migration parameters (D_e, n_e) may be inferred by the values which give the best-fit to the measured source and profile concentrations.

Since tritium concentrations of the initial water 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.

Total Porosity Method for Interpreting Laboratory Diffusion Profile

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:

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

where, w [-] (0.22) is the average moisture content determined from the three dummy specimens, and M_T is the total mass of the sample [M] (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 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:

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

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 $0.5\times10^{-10}m^2/s$ to $2.5\times10^{-10}m^2/s$ (in increments of $0.5\times10^{-10}m^2/s$) were analyzed. The theoretical plots corresponding to the combination of n_e and D_e which yielded the lowest root mean squared error (RMSE) for each of the three replicates is plotted on Figure 3 with the laboratory diffusion profiles.

On Figure 3, the solid circles represent the measured values determined from laboratory testing and application of Equations 5 and 6 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_0. 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 $1.5\times10^{-10}m^2/s$ 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 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 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.

Effective Porosity Method for Interpreting Laboratory Diffusion Profile

The laboratory results of the diffusion test were also interpreted assuming that part of the water in the specimen (e.g. hydration waters, waters 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 5, but in this case it was assumed that only a portion of the water in the specimen was accessible to the tritium. The rest of the water in the specimen was assumed to act only 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 7).

$$M_{AW} = M_W \frac{n_e}{n} \tag{7}$$

The mass of the inaccessible water in each sample, M_{IW} [M], is consequently represented by the following equation:

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

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 the following expression:

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

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 measured changes in the observed concentrations profiles, calculated from Equation 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} m^2/s to 4.0×10^{-10} m^2/s (in increments of 0.5×10^{-10} m^2/s). This whole process 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 (Equations 7 to 9). The theoretical plots corresponding to the combination of n_e and D_e which resulted in the best match (by RMSE) for the three replicate specimens are shown with the corresponding observed data on Figure 4.

On Figure 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 modelling. 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 previous 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} m^2/s, 3.0×10^{-10} m^2/s, 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 paper refers to results obtained using this method.

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 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. The figure shows 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.

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 diffusion testing. The results of diffusion testing on these specimens are summarized in Figure 6. Inspection of Figure 6 indicates that the value of n_eD_e changes considerably over the first 28 days of curing (the average value of n_eD_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_eD_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 performing dynamic leaching tests.

Conclusions

The main objective of this work was to apply a single-reservoir type diffusion test to saturated, cured, monolithic, cement-based S/S specimens to determine the effective porosity, n_e, and effective diffusion coefficient, D_e, for a conservative solute diffusing through a soil-cement matrix. 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 from 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 paper.

The method provided in this paper 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 pre-design 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.).

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TABLE 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
H_2O	19.5	24.3

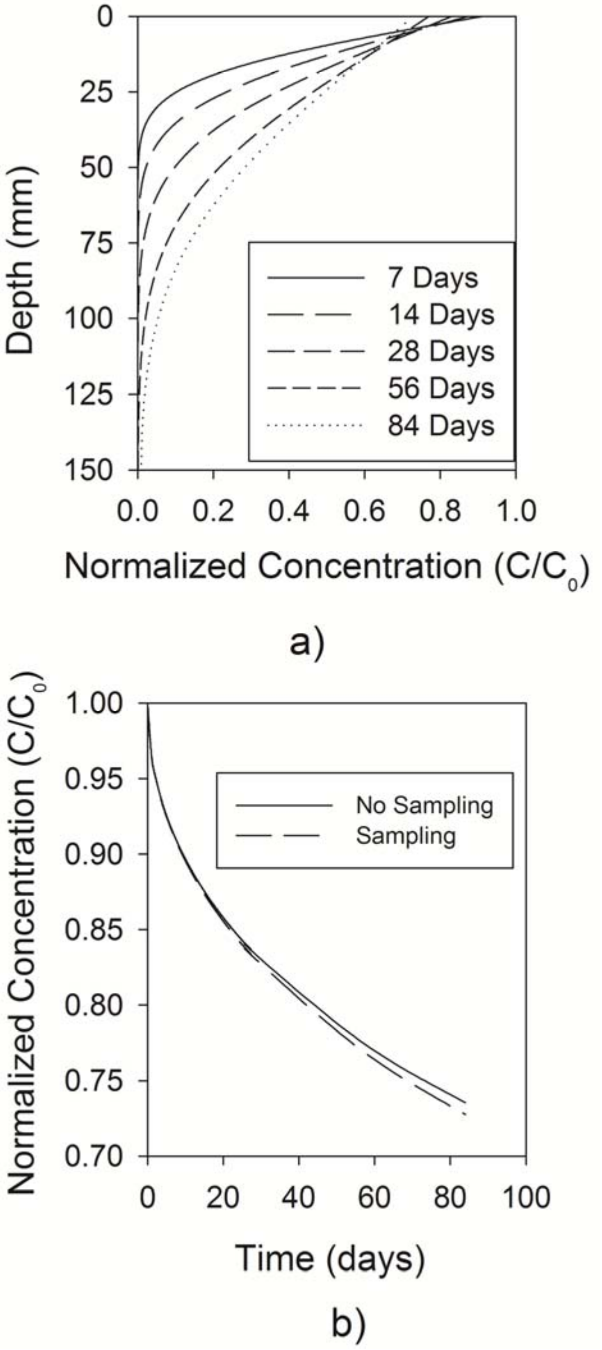

FIG. 1— *Theoretical normalized concentration distribution based on* $D_e = 2.0\times10^{-10} m^2/s$ *and* $n_e = 0.20$. *a) concentration profile changing with time b) reservoir concentration with and without sampling (modified from Goreham et al., 2010).*

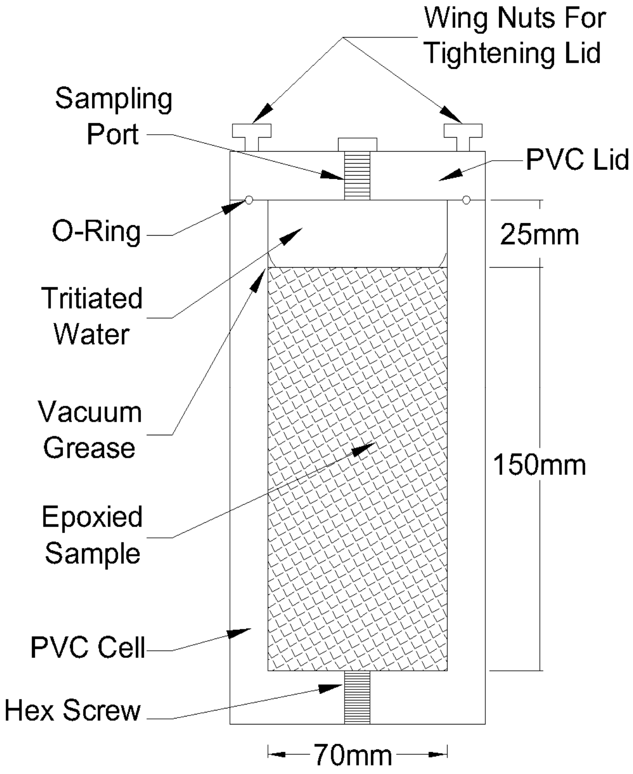

FIG. 2— *Schematic of the diffusion test apparatus used in this study.*

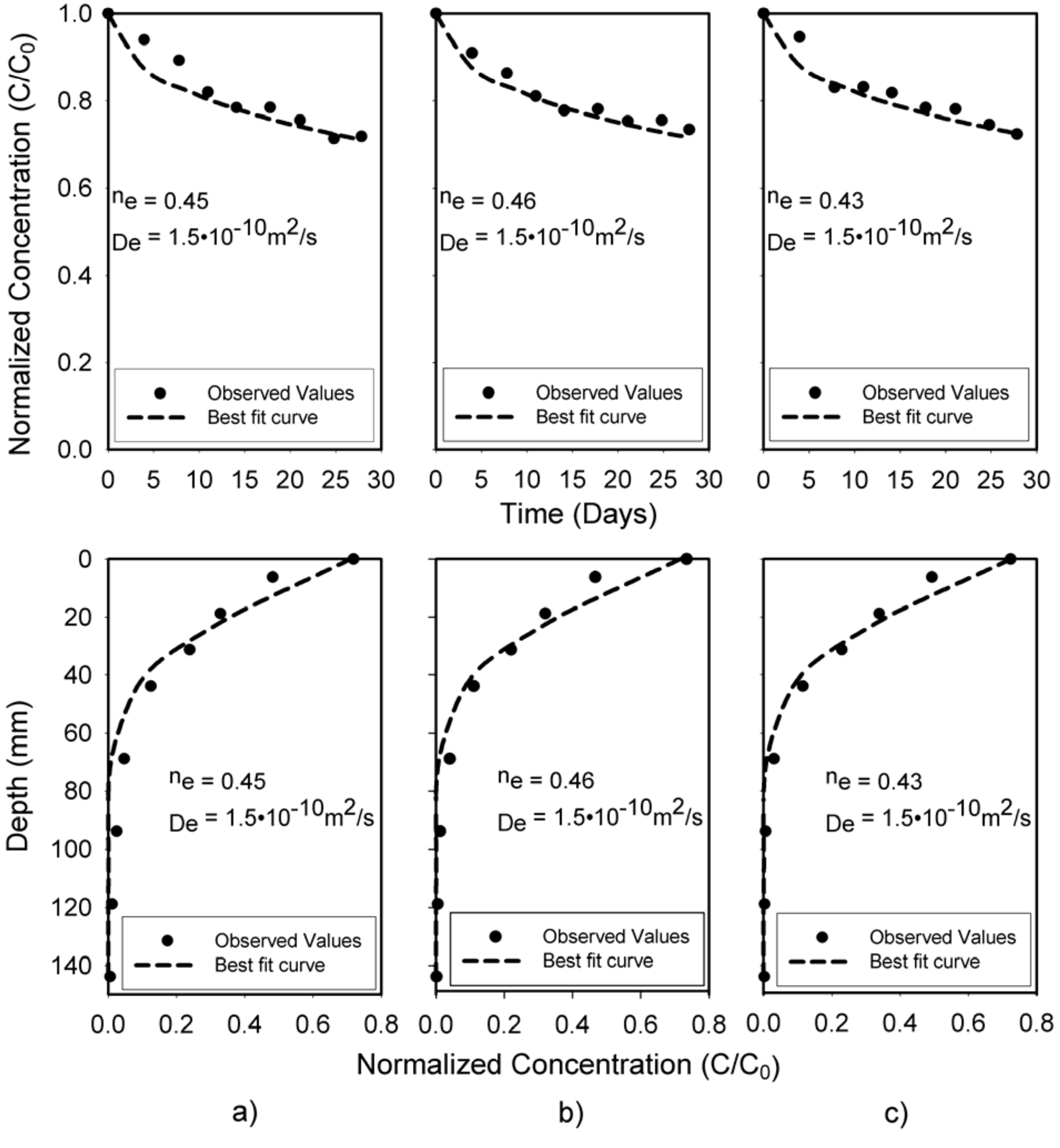

FIG. 3— *Diffusion test results (normalized concentration vs. time in the source reservoir on the top and normalized concentration profiles at the end of the test on bottom) using the "total porosity method" to interpret the laboratory results (solid circles) and best-fit curves determined from modelling (dashed lines) for three replicate specimens.*

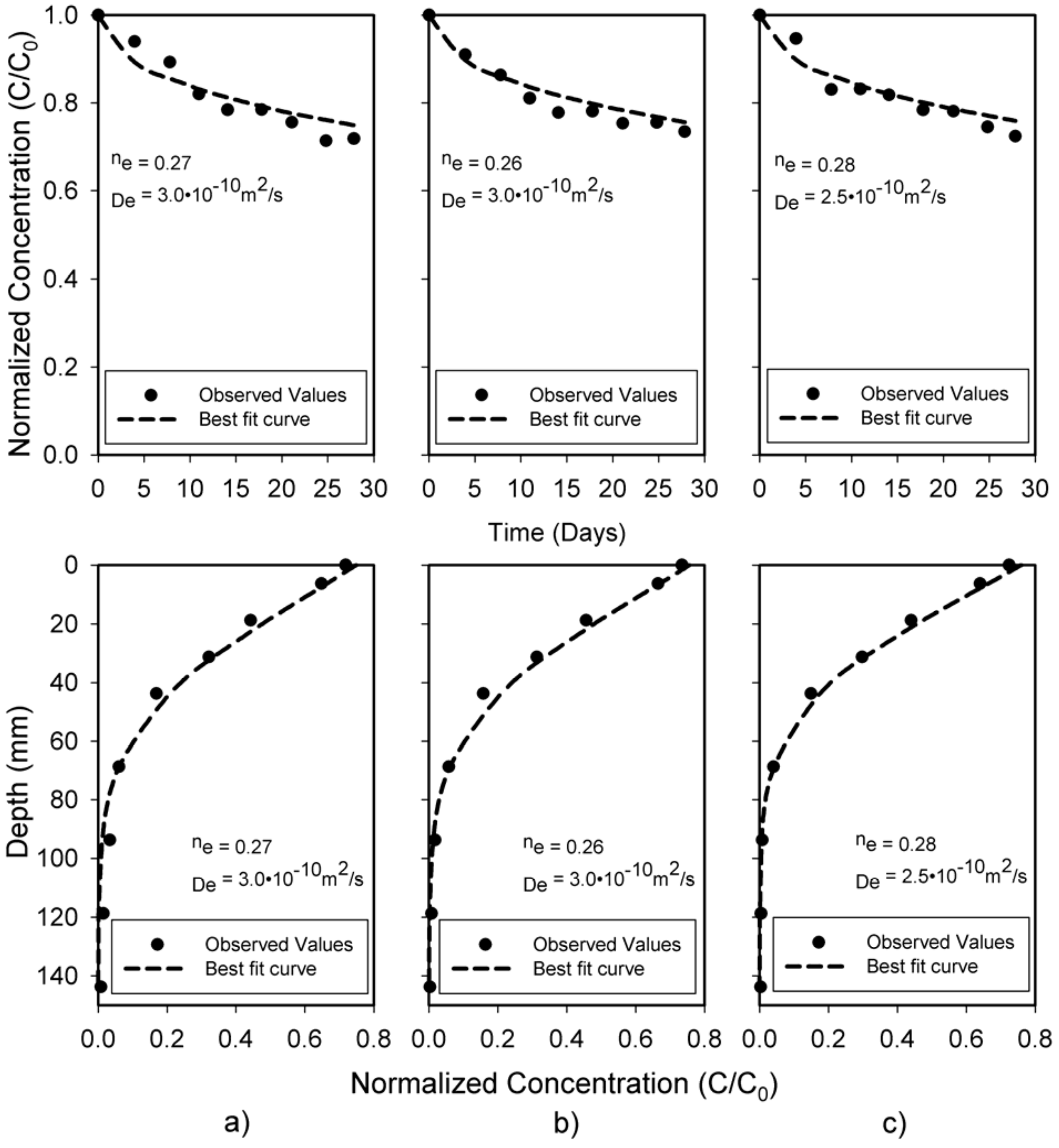

FIG. 4— *Diffusion test results (normalized concentration vs. time in the source reservoir on the top and normalized concentration profiles at the end of the test on bottom) using the "effective porosity method" to interpret the laboratory results (solid circles) and best-fit curves determined from modelling (dashed lines) for three replicate specimens.*

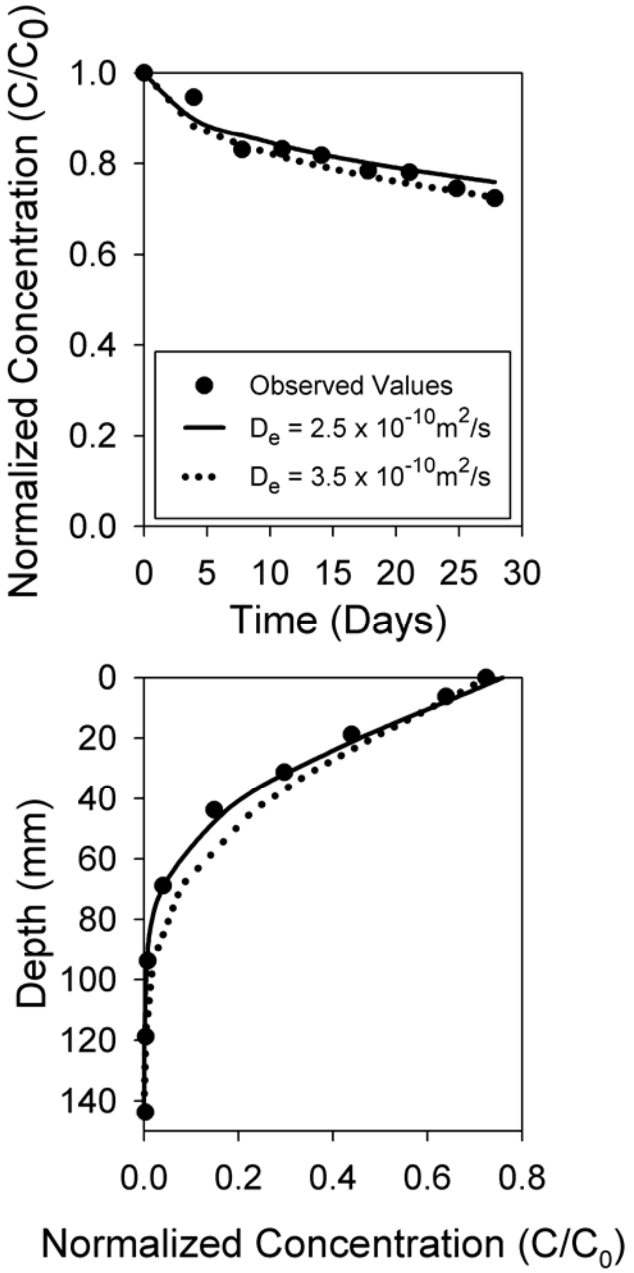

FIG. 5— *Figure illustrating the effect of varying diffusion coefficient in the model. Shown are the normalized observed data (solid circles), concentration profile from the best fit parameters (solid line), and concentration profile from a diffusion coefficient incremented by 1.0* $x10^{-10}m^2/s$ *from the best fit parameter (dotted line) for specimen c.*

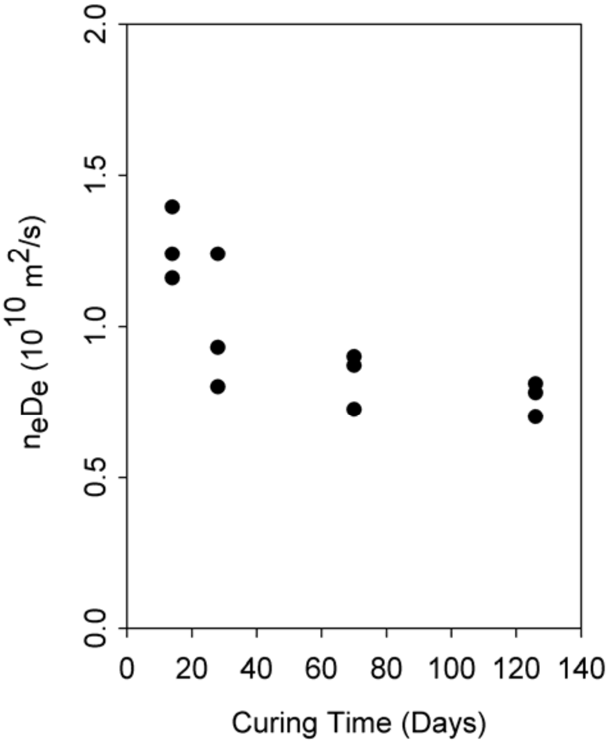

FIG. 6— *The product of n_e and D_e as a function of curing time.*