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Waste Materials in Construction: Putting Theory into Practice

The Influence of Monolith Physical Properties and Integrity on Diffusional Leaching Behavior of Asphaltic Pavements Constructed with MSW Combustion Bottom Ash

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ABSTRACT

The leaching of two municipal solid waste bottom ash constituents (relatively mobile Cl and relatively immobile Ca) was used to evaluate the effects of bituminous pavement physical properties (bottom ash substitution, asphalt cement content, voids, microcracking, bituminous polymer aging) and monolith integrity on diffusional leaching parameters such as cumulative release ($B_{t,Cl}$, $B_{t,Ca}$), tortuosity (τ), chemical retention (R_{Cl}, R_{Ca}), and effective diffusion coefficients ($pD_{e,Cl}$, $pD_{e,Ca}$). For intact laboratory monoliths, mix design parameters such as increasing asphalt cement content and increasing bottom ash substitution both were directly related to increases in $B_{t,Cl}$ and $B_{t,Ca}$, and to increased τ. While increasing the bottom ash loading increased the driving gradient for chloride and calcium, the concomitant increase in asphalt cement content increased τ. For laboratory monoliths subjected to accelerated aging so as to predict future environmental performance, τ was found to be influenced only by monolith microcracking. For pavements subjected to field aging in a test road, no differences could be seen between cores evaluated just after road construction and cores evaluated after 1.25 years of service life. During the 1.25 year study period, some beneficial increases in tortuosity, probably from densification, occurred. For compacted granularized pavements where monolith integrity is lost, the presence of asphalt cement in the bottom ash pore structure and on the particle surface still limited diffusional release. The tortuous, hydrophobic nature of the intact monolith system controls diffusion at the macroscale level. The presence of asphalt cement on the particle surface and in the internal pore structure of the bottom ash particles also controls diffusion at the microscale level, even in compacted granularized specimens.

INTRODUCTION

The life cycle of a waste material used in the construction of a pavement may initially involve a primary use (e.g. as an aggregate substitute in a bituminous wearing or binder course monolithic pavement) as well as a secondary use (e.g. as reclaimed asphalt pavement use in compacted granular base course). Knowledge as to the environmental behavior of the product as well as the leaching of waste constituents is necessary. The physical properties and integrity of the pavement can play an important role in the type of leaching (wash off, dissolution, diffusion) that can occur. These properties also control the magnitude of the fluxes of waste constituents from the pavement. Fluxes are typically small in asphaltic pavement monoliths [1,2,3]. Flux measurements can be useful for source term estimates for health risk assessments, waste utilization application evaluations, and regulatory approval.

Figure 1 shows possible leaching scenarios related to waste utilization in pavement construction [4]. The very low specific surface area, low permeability, and high structural integrity of the monolith or densely compacted granular material results in leaching regimes where diffusion is the dominant mass transfer mechanism. This differs dramatically from loose, uncompacted granular materials where solvent percolation and advection produce contaminant fluxes that are orders of magnitude larger than diffusional fluxes.

Monolith diffusional leaching (Figure 2a) involves diffusion into the pavement of solvents such as H_2O and diffusion out of the pavement of dissolving solutes such as cationic and anionic species. Diffusion occurs by tortuous pathways within the product, frequently at bituminous polymer/waste particle interfaces, within the bituminous polymer, and within the waste particles themselves. However, the integrity of the product provides a macroscale control on diffusional fluxes [2]. At the macroscale level, the pavement bulk density, air voids, waste substitution rate, asphalt cement content, and monolith integrity will all impact monolithic diffusional leaching and contaminant fluxes from the monolith.

For compacted granular diffusional leaching scenarios (Figure 2b), the relatively higher surface area, higher permeability, and lack of structural integrity result in leaching regimes where diffusion is the dominant mass transfer mechanism, but diffusion pathways are much less tortuous. Diffusion occurs by tortuous pathways within the waste particles, and between the waste particles and the residual asphalt cement within the pore structure of the waste particles and coating the particles. However, the particle and asphalt cement coatings provide a more microscale control on diffusional fluxes [1]. At the microscale level, the residual asphalt cement content, waste particle surface area, and waste particle surface chemical speciation will all influence granular diffusion.

For bituminous asphalt pavements constructed as wearing, binder or base course, the in-place hydraulic regime is not well defined. For intact pavements, percolation regimes are unlikely. Rather, contact with water is at monolith exterior surfaces, either by periodic precipitation, localized intermittent groundwater, or periodic condensation of soil water vapor. Assumptions can be made about the types of surfaces that are wetted and the wetting/dying cycles that the surfaces are exposed to [3,5]. The hydrophobic nature of the asphalt cement complicates the interpretation of water uptake during wetting, water absorption, and reaction with the waste particle [6]. Nevertheless, from a conceptual approach, diffusional leaching and cumulative release have been verified for coal fly ash constituents in bituminous shoreline protection monoliths [7], nuclear wastes in bituminous asphalt-stabilized monoliths [6], and pavement material made with MSW bottom ash [3,5].

As part of our efforts to understand the environmental performance of bituminous pavements made with MSW bottom ash, we have examined aspects of monolith properties (e.g. waste substitution, asphalt cement content) and monolith aging (voids, microcracking, bituminous polymer aging, field aging) on monolithic diffusional leaching as well as granular properties (particle size) and asphalt/particle integrity (presence of asphalt cement) on compacted granular diffusional leaching. These scenarios constitute major primary and secondary uses for bottom ash in bituminous pavement. Within each scenario, a continuum between early and later stages of the life history of the product are also provided. Finally, evaluations are provided for both bottom ash (consisting largely of grate ash and small quantities of grate siftings) as well as grate ash; the environmental properties and performance of both these materials being synonymous[3].

MONOLITH DIFFUSIONAL LEACHING FUNDAMENTALS

Figure 2a depicts the fundamental processes involved in leaching from monolithic specimens. The figure depicts the diffusive release of constituents via pathways of varying tortuosity, long term dissolution of solid phase material at the monolith surface, and initial wash-off of material from monolith surface. These phenomena exhibit different cumulative release behaviors, as evidenced by plot slopes, on log-log cumulative release versus time plots.

Diffusion occurs by the random movement of individual molecules or ions. It is driven by the difference in chemical potential between the solid and the leachant[8]. In a slightly porous solid, the ion flux of a soluble contaminant in the pore water system is defined by Fick's Second Law, which relates the concentration of a diffusing substance to both space and time:

$$\frac{dC}{dt} = L\frac{d^2C}{dx^2} \qquad (1)$$

where C is the concentration of the diffusing ion, and L is the leach constant, with units of a diffusion coefficient (m^2/s). In the case of one dimensional diffusion, the leach constant, L, is obtained by applying the following relationship:

$$L = \frac{f^2 \cdot D_o}{R \cdot \tau} \qquad (2)$$

where f is the available leachable fraction of the element in the material, D_o is the mobility of the element in water (m^2/s), R is the chemical retention factor of the element (unitless), and τ is the physical retardation or tortuosity factor (unitless). When the leachable amount of the element equals the total amount of the element present in the material (i.e., f=1), the leach constant L equals the effective diffusion coefficient, which is modified for retention and tortuosity[9].

If Equation 2 is transformed to logarithmic values and using the relationship $pD_o = -\log D_o$, then the new relationship is:

$$pL = pD_o + 2pf - pR - p\tau \qquad (3)$$

Since the available leachable fraction of the element may be obtained from analytical data and remains as a constant, Equation 3 may be simplified to:

$$pD_e = pD_o - pR - p\tau \qquad (4)$$

where D_e is the effective diffusion coefficient (m^2/s)[9]. This equation allows for the determination of the relative contributions of D_o, R, and τ to the magnitude of D_e. As will be seen, the relative contributions of R and τ play the dominant role in the magnitude of D_e as well as in the cumulative flux or extent of the source term leaching from the monolith. The relative magnitude of R and τ, and their change as a function of monolith properties and aging is crucial to understanding long term environmental behavior.

The mobility of an element within the monolithic pore space may be compared to its free mobility in water by determining the physical and chemical retardation factors of the product and the element, respectively. To calculate the physical retardation factor, it is necessary to choose an ion which does not chemically interact with the matrix (i.e., R=1). In most studies, sodium is chosen and the physical retardation is calculated with the formula [9].

$$\tau = D_{Na}/D_{e,Na} \tag{5}$$

where D_{Na} is the diffusion coefficient of sodium in water ($pD_{Na} = 8.88$ m^2/sec at 25°C) and $D_{e,Na}$ is the effective diffusion coefficient of sodium in the monolith (m^2/s). The chemical retardation factor for the element is determined using the following formula:

$$R = D_x/(D_{e,x}\ \tau) \tag{6}$$

where D_x is the diffusion coefficient for the element in water (m^2/s) and $D_{e,x}$ is the effective diffusion coefficient for the element in the monolith (m^2/s).

In monolith leach testing, the material is considered homogeneous and is immersed in a leachant which is renewed at regular intervals. The concentration of the element is uniformly distributed and the surface is maintained at a constant concentration. The solution to Equation 1 under such conditions is presented by Crank [10].

$$\frac{C - C_1}{C_o - C_1} = \operatorname{erf} \frac{x}{2\sqrt{(D \cdot t)}} \tag{7}$$

where C is the element's concentration in the monolithic material as a function of place and time, C_1 is the constant concentration at the surface of the monolith, C_0 is the initial concentration of the element in the material, D is the diffusion coefficient and erf is the standard error function. Since the leachant is regularly renewed during the leaching experiment, the surface concentration, C_1, is assumed to be zero [9], and the solution to Equation 7 under this assumption is:

$$D_e = \frac{\pi \cdot B_t^2}{4t(U_{max} \cdot d)^2} \tag{8}$$

where B_t is the cumulative release of the element at time t (mg/m^2), U_{max} is the maximum leachable quality of the element from the monolith (mg/kg) and d is the bulk density of the monolithic material (kg/m^3).

By plotting the cumulative release of an element leaching from the monolith as a function of time, it can be determined whether matrix diffusion or other leaching mechanisms, such as dissolution or surface wash-off, more common to granular materials, are occurring. The solubility of certain elements within the solid material can be significantly high, such that longer term dissolution of the element at the surface proceeds faster than diffusion through the pores of the solid matrix. Additionally, due to process conditions, a material may be covered with a soluble surface coating that is readily leached with initial leachant contact.

To determine which leaching mechanism is controlling release of the element from the monolith, Equation 8 is rearranged to yield the following [9]:

$$B_t = U_{max}\ d\sqrt{(4D_e/\pi)}\sqrt{t} \qquad (9)$$

After log transformation, Equation 9 becomes:

$$\log(B_t) = 1/2\ \log(t) + \log[U_{max}\ d\sqrt{(4D_e/\pi)}] \qquad (10)$$

From the monolith leach test results, the release of the element per time interval may be calculated using the formula [9]:

$$B_i = \frac{c_i\ V_i}{1000\ A} \qquad (11)$$

where B_i is the release of the element per unit area in period i (mg/m^2), c_i is the concentration of the element in the ith period (µg/L), V_i is the volume of the leachant (L), and A is the surface area of the monolithic material (m^2).

The cumulative release of the element for all N periods (N=8) is calculated from:

$$B_{t,i} = B_i \frac{\sqrt{t}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \quad \text{for } i = 1 \text{ to } N \qquad (12)$$

where $B_{t,i}$ is the cumulative release of the element for all periods (mg/m^2), t_i is the contact time after period i (seconds), and t_{i-1} is the contact time after i-1 periods (seconds) [9]. Eight leaching periods are usually used (0.25, 1, 2, 4, 8, 16, 32, and 64 days). This conforms to a time series relationship (renewal time of the nth period is equal to the square of the period sequence number times the renewal time of the first period) that is based on both leaching behavior and on data distribution in $\log(B_{t,i}) - \log(t_i)$ plots.

If the logarithm of the cumulative release, $B_{t,i}$, is plotted versus the logarithm of time, t_i, for the eight periods, the slope of the resulting graph indicates the mechanism controlling the release of the element. Since the slope may change over different time intervals, the slope is examined over the ranges [9]. The effective diffusion coefficient for the element is then calculated from each period for the release per period (B_i) using the data points where the slope is 0.50 ± 0.15 with a deviation of less than 50% and the slope of the final range is smaller than 0.65 by:

$$D_{e,i,x} = \frac{\pi \; B_i^2}{4(U_{max}d)^2 \cdot (\sqrt{t_i} - \sqrt{t_{i-1}})^2} \tag{13}$$

where $D_{e,i,x}$ is the effective diffusion coefficient of element x calculated from the release in the ith period (m^2/s), and the other terms are as previously described.

COMPACTED GRANULAR DIFFUSIONAL LEACHING

Figure 2b depicts the fundamental processes involved in diffusional leaching from compacted granular specimens. The figure depicts the diffusive release of constituents via pathways of varying tortuosity, long term dissolution of solid phase material at the particle surface, and initial wash-off of material from the particle surface. The same principals for examining release mechanisms, cumulative fluxes, effective diffusion coefficients, tortuosity, and chemical retention in monoliths can be applied to compacted granular specimens provided that they are leached in static, renewal-based leaching tests. This modification to the monolith leaching test was developed by Kosson et al.[11].

MATERIALS AND METHODS

The focus of this paper is on the use of municipal solid waste combustion bottom ash from the Concord, New Hampshire waste-to-energy facility as an aggregate substitute in a primary application in bituminous binder course pavement and in a secondary application as stabilized base course pavement. A great deal of information has already been presented on the use of bottom ash from the Concord facility in asphalt pavements [1,12,13,14], as well as the Laconia, New Hampshire bottom ash utilization demonstration [3,15,16]. The purpose of this research was to identify factors controlling diffusional leaching behavior in monolithic and compacted granular applications, with focus on two elements that exhibit different diffusive leaching behaviors from the MSW bottom ash pavement products; chloride and calcium. The former is considered to be relatively diffusive and mobile because it will not readily sorb or precipitate. The later is less diffusive and more immobile because it can readily sorb or precipitate.

The research was conducted in four parts: (i) the use of laboratory monoliths to evaluate the effects of bottom ash substitution rates and asphalt cement content on monolith diffusional leaching, (ii) the use of laboratory monoliths to study the impacts of air void content, microcracking, and accelerated bituminous polymer aging on monolith diffusional leaching, (iii) the use of field cores from the Laconia, New Hampshire bottom ash utilization field demonstration to examine short term field aging on monolith diffusional leaching, and (iv) the use of laboratory granularized monoliths and granular materials on compacted granular diffusional leaching.

For the first set of experiments, the Dutch monolith leach test (NEN 7345) was used to evaluate the effects of bottom ash substitution and asphalt cement content on monolithic diffusional leaching. Cumulative release ($B_{t,Cl}$, $B_{t,Ca}$), monolith tortuosity (τ), chemical retention

(R_{Ca}, R_{Cl}), and effective diffusion coefficients ($pD_{e,Cl}$, $pD_{e,Ca}$) were used as response variables. Monoliths were made using Marshall mix design procedures [12,13]. Three bottom ash substitution ratios were used (25,50 and 75%). The 50% substitution was made in duplicate. A variety of AC-20 asphalt cement contents were evaluated (e.g. 5 to 12%) as part of the mix design procedure. In all, six monolithic cylinders (10 cm diameter) were made. Monoliths at optimum asphalt cement contents were tested for monolithic leaching properties.

For the second set of experiments, the Dutch monolith leach test (NEN 7345) was again used to evaluate the effects of monolith void content, aging, and microcracking on monolithic diffusional leaching [2]. Cumulative release ($B_{t,Cl}$, $B_{t,Ca}$), monolith tortuosity (τ), chemical retention (R_{Ca}, R_{Cl}), and effective diffusion coefficients ($pD_{e,Cl}$, $pD_{e,Ca}$) were used as response variables. A partial $3^3 + 6$ factorial design experiment was conducted. A gyratory test method (GTM) mix design procedure was used [2]. Grate ash was substituted 50% for natural aggregate. An asphalt cement content of 7% AC-20 was used. Three degrees of air voids (low, medium, high), aging (none, medium, high), and microcracking (none, medium, high) were integrated into the experimental design. Air voids (5%, 7.5%, 10%) were created during the compaction of the specimens using the GTM. The 10%, 7.5% and 5% air voids were produced using 60, 110 and 300 cycles, respectively on the GTM. Aging was simulated by heat treatment in the presence of forced hot air (107°C for 5 days for moderate aging, 107°C for 10 days for severe aging). The regimen was based on methods compiled by von Quintus et al. [17]. An Instron machine was utilized to subject some of the samples to cyclical loading parallel to the direction of compaction to produce microcracking (i.e. moderate and high cracking levels). A load of 8.22 MPa at 2 cycles per second was used. Moderate microcracking was produced after 1,250 ± 250 cycles. High microcracking was produced after 1,750 ± 250 cycles. A total of 14 10 cm cylindrical specimens were made.

For the third set of experiments, 10 cm road cores from the test and control sections of the Laconia, New Hampshire bottom ash paving demonstration were collected and subjected to the same Dutch monolith leaching procedure (NEN 7345) to evaluate the effects of short term field aging on monoliths leaching properties [3]. Cores taken just after road construction and after 1.25 years of service were evaluated. The test section binder course was constructed using a GTM mix design procedure. A 50% grate ash substitution was used with an asphalt cement content of 7%. The binder course was subjected to field compaction methods. A total of four cores were collected from each section at each sampling time. After coring, the binder course was manually excised from each core for testing.

For the fourth set of experiments, a compacted granular diffusion leaching test was conducted in an identical manner to the NEN 7345 except that compacted granular specimens were used. The method was developed by Kosson et al. [11]. Specimens were compacted in HDPE beakers to bulk densities of 1,500 to 1,675 kg/m^3 the beakers were then suspended in the leachant at a L/S of 20 to facilitate setup and avoid reverse gradient effects. Three sets of samples were run in duplicate: <300 um ground grate ash, <1.9 cm ground grate ash, and < 1.9 cm ground pavement monoliths made with 50% grate ash and 75 AC-20 asphalt cement. These specimens were designed to mimic the use of granularized binder course in a secondary use as a compacted base course [3]. The measure of surface area available for leaching was the area of the open (but submerged) top of the beaker. A 2 cm thick layer of glass beads (6 mm diameter) was used to minimize agitation.

For the NEN 7345 monolithic and granular procedures, the leachant was Nanopure® ASTM type II (double-deionized) water reduced to pH 4 using Baker Analyzed® Ultrex II® Ultrapure nitric acid. The leachate was filtered and analyzed periodically (0.25, 1, 2, 4, 8, 16, 32, 64 days) to determine specified element concentrations leached per indicated time frame. After each filtration, new contact solution was added to the sample. Samples were analyzed using ion chromatography (IC), graphite furnace atomic absorption spectrophotometry (GF-AAS) and inductively coupled argon plasma atomic emission spectrometry (ICAP-AES). Monolith specimens were also ground to less than 300 μm and subjected to the Dutch total availability leaching procedure (NEN 7341) to determine U_{max}, the fraction available for leaching.

RESULTS AND DISCUSSION

There are approximately 45 elements in the Concord grate or bottom ash [13]. Although 45 elements are present, only 16 consistently leached from specimens ground to < 300 μm when subjected to the total availability leach test: Cl, Ca, Zn, Cd, Mg, Cu, Mn, Pb, Sr, Si, Fe, Al, Na, K, Ba, Cr [13]. Lysimeter leaching data for the granular (< 1.9 cm) bottom ash lysimeter show that the bottom ash leaches Cl, SO_4^{2-}, Ca, K, Mg, Na, Fe, Mn, Si and Sr [1]. Similar constituents leached from a lysimeter containing pavement rubble containing bottom ash, but at much lower levels [1]. Only seven constituents (Na, Cl, SO_4^{2-}, Ca, Si, Mg, and Zn) routinely leached from the grate or bottom ash test specimens during the monolith leach test [3,13].

Influence of Bottom Ash Substitution and Asphalt Cement Content

Marshall mix design procedures were used to identify optimum asphalt cement contents for various levels of bottom ash substitution in binder course. The environmental performance of these monoliths were evaluated. This evaluation is relevant to understanding the possible performance of binder course based on mix design formulation. For instance, increasing the ash substitution percentage may increase the ash surface area available for chemical retention and increase the need for asphalt cement [12,14] which increases tortuosity; both of which are beneficial.

Chloride cumulative release ($B_{t,Cl}$), calcium cumulative release ($B_{t,Ca}$), and tortuosity were influenced by asphalt cement content (Figure 3); though confounding with bottom ash substitution is possible (see below). Generally, as asphalt cement content increased, cumulative fluxes increased even though tortuosity increased.

The observed increases in cumulative release are explained by the higher percent bottom ash substitutions that occurred concomitant with increased asphalt content (Figure 4). This is intuitive given the fact that increased ash loadings increase the driving force promoting diffusion of chloride and calcium. However, these increased fluxes are not considered deleterious given their only modest increase over the range in ash loadings that were used.

Influence of Accelerated Aging: Voids, Microcracking, and Bituminous Polymer Aging

An experimental design was used to study the effects of accelerated aging (decrease in air voids from traffic densification over time, increase in microcracking from cyclical mechanical stress, bituminous polymer aging from oxidation) on the environmental performance of binder course pavement monoliths. Such an evaluation is useful in predicting the long term behavior of the application and in providing source term estimates.

(R_{Ca}, R_{Cl}), and effective diffusion coefficients ($pD_{e,Cl}$, $pD_{e,Ca}$) were used as response variables. Monoliths were made using Marshall mix design procedures [12,13]. Three bottom ash substitution ratios were used (25,50 and 75%). The 50% substitution was made in duplicate. A variety of AC-20 asphalt cement contents were evaluated (e.g. 5 to 12%) as part of the mix design procedure. In all, six monolithic cylinders (10 cm diameter) were made. Monoliths at optimum asphalt cement contents were tested for monolithic leaching properties.

For the second set of experiments, the Dutch monolith leach test (NEN 7345) was again used to evaluate the effects of monolith void content, aging, and microcracking on monolithic diffusional leaching [2]. Cumulative release ($B_{t,Cl}$, $B_{t,Ca}$), monolith tortuosity (τ), chemical retention (R_{Ca}, R_{Cl}), and effective diffusion coefficients ($pD_{e,Cl}$, $pD_{e,Ca}$) were used as response variables. A partial $3^3 + 6$ factorial design experiment was conducted. A gyratory test method (GTM) mix design procedure was used [2]. Grate ash was substituted 50% for natural aggregate. An asphalt cement content of 7% AC-20 was used. Three degrees of air voids (low, medium, high), aging (none, medium, high), and microcracking (none, medium, high) were integrated into the experimental design. Air voids (5%, 7.5%, 10%) were created during the compaction of the specimens using the GTM. The 10%, 7.5% and 5% air voids were produced using 60, 110 and 300 cycles, respectively on the GTM. Aging was simulated by heat treatment in the presence of forced hot air (107°C for 5 days for moderate aging, 107°C for 10 days for severe aging). The regimen was based on methods compiled by von Quintus et al. [17]. An Instron machine was utilized to subject some of the samples to cyclical loading parallel to the direction of compaction to produce microcracking (i.e. moderate and high cracking levels). A load of 8.22 MPa at 2 cycles per second was used. Moderate microcracking was produced after 1,250 ± 250 cycles. High microcracking was produced after 1,750 ± 250 cycles. A total of 14 10 cm cylindrical specimens were made.

For the third set of experiments, 10 cm road cores from the test and control sections of the Laconia, New Hampshire bottom ash paving demonstration were collected and subjected to the same Dutch monolith leaching procedure (NEN 7345) to evaluate the effects of short term field aging on monoliths leaching properties [3]. Cores taken just after road construction and after 1.25 years of service were evaluated. The test section binder course was constructed using a GTM mix design procedure. A 50% grate ash substitution was used with an asphalt cement content of 7%. The binder course was subjected to field compaction methods. A total of four cores were collected from each section at each sampling time. After coring, the binder course was manually excised from each core for testing.

For the fourth set of experiments, a compacted granular diffusion leaching test was conducted in an identical manner to the NEN 7345 except that compacted granular specimens were used. The method was developed by Kosson et al. [11]. Specimens were compacted in HDPE beakers to bulk densities of 1,500 to 1,675 kg/m^3 the beakers were then suspended in the leachant at a L/S of 20 to facilitate setup and avoid reverse gradient effects. Three sets of samples were run in duplicate: <300 um ground grate ash, <1.9 cm ground grate ash, and < 1.9 cm ground pavement monoliths made with 50% grate ash and 75 AC-20 asphalt cement. These specimens were designed to mimic the use of granularized binder course in a secondary use as a compacted base course [3]. The measure of surface area available for leaching was the area of the open (but submerged) top of the beaker. A 2 cm thick layer of glass beads (6 mm diameter) was used to minimize agitation.

and after 1.25 years of service life (time= 1.25 years). Cores were taken from slabs removed at the pavement margin where traffic loads were light and where any aging would be related to the natural densification or aging. The purpose of this effort was to see if any shorter term aging phenomena could be observed.

The data for chloride leaching is presented in Table 1. Generally the test section monoliths containing the 50% grate ash substitution and the 7.0 % asphalt cement content behaved like intact laboratory monoliths with low cumulative releases, low chemical retentions, high tortuosities, and low diffusivities. Student's t-test (95% confidence level) was used to statistically evaluate aging. No significant differences were seen with respect to short term aging in the field and chloride diffusional behavior. There were differences between the test and control sections; largely because there is no significant level of leachable chloride in the natural aggregates used in the control pavements. Tortuosity in both the test and control sections significantly increased over time (Student's-t, one tail, 95%); probably from natural densification processes.

The data for calcium leaching is presented in Table 2. Calcium leaching in the test section behaved like intact laboratory monoliths. There were significant differences (Student's-t, one tail, 95%) in the effective diffusion coefficient ($pD_{e,Ca}$); calcium becoming less diffusive with time; largely from statistically significant increases in tortuosity. While cumulative fluxes were significantly different between the test and control sections, effective diffusion coefficients ($pD_{e,Ca}$) and chemical retention values (R_{Ca}) were not significantly different.

Overall, there were no deleterious significant changes in the test or control monoliths over the 1.25 year study period. Modest increases in tortuosity from natural densification explain the observed changes.

Influence of Monolith Integrity

The compacted granular leaching test was used to evaluate the effect of loss of monolith integrity (via granularization) on environmental behavior. Three increasing levels of loss of monolith integrity were investigated; low granularization of binder course monoliths (<1.9 cm) so that the resulting coarsely ground ash particles are coated both within the particle pore structure and on the particle exterior with asphalt cement binder, medium granularization using coarsely ground bottom ash particles (<1.9 cm) without asphalt cement, and high granularization using finely ground bottom ash particles (<300 um). This evaluation is useful in better understanding the possible environmental performance of a recycled binder pavement containing ash in a secondary application as a compacted granular base course. Such an evaluation can also provide source term estimates.

As shown in Figure 8, the cumulative release of chloride ($B_{t,Cl}$) and the cumulative release of calcium ($B_{t,Ca}$) both dramatically increased as granularization increased. This would be expected as tortuosity would likely decrease as diffusion path lengths are drastically shortened. Chloride cumulative releases ranged from 70 to 40,000 mg/m^2. Calcium cumulative releases ranged from 10,000 to 50,000 mg/m^2. These cumulative releases from granular diffusional leaching are orders of magnitude larger than monolithic diffusional leaching.

The level of granularization dramatically affected tortuosity (Figure 9a). As granularization increased, tortuosity values decreased from rather low levels (80) down to very low levels (3). These tortuosity values are much less than those seen for intact monoliths. This is expected as granularization would remove macroscale control and shorten diffusion path lengths. Chloride, which is not very reactive chemically with respect to sorption or precipitation, did not exhibit any correlation (Figure 9b) between microcracking and chemical retention (R_{Cl}). The effective diffusion coefficient for chloride ($pD_{e,Cl}$) modestly increased with increasing granularization (Figure 9c); largely because of the decrease in tortuosity (Figure 9a) and the link between tortuosity and diffusivity (see Eq. 4). The diffusivity of the chloride is still higher than those seen in the intact monolith; however, the values are still much less diffusive than a freely mobile anion.

The chemical retention of calcium (R_{Ca}), which is reactive chemically with respect to sorption or precipitation, was correlated with increased granularization (Figure 10b). At high levels of granularization, R_{Ca} values increased from 50 to about 250. These values are significantly higher than those seen for calcium in intact monoliths. This increase from granularization is attributed to either sorption on the ash particle surfaces or precipitation on the ash particles surfaces. Despite significant increases in R_{Ca}, the effective diffusion coefficient for calcium ($pD_{e,Ca}$) increased with increasing granularization (Figure 10c); largely because of the decrease in tortuosity (Figure 7a) and the link between tortuosity and diffusivity (see Eq. 4). Even those these values are low relative to the monolith scenario, they are still significantly less diffusive than a freely mobile cation.

Influence of Ionic Radii and Chemical Reactivity of the Diffusing Constituents

There are some interesting observations that can be made between the relative diffusional behaviors of chloride and calcium in each of the four experiments. Chloride has a larger ionic radius (1.81 Å) and diffusivity or free mobility in water (2.03×10^{-9} m^2/s, $pD_o = 8.69$) than calcium (1.00 Å, 7.93 x 10-10 m^2/s, $pD_o = 9.10$) [19,20]. Chloride is considered to be a conservative constituent; it is highly mobile and does not readily participate in sorption, ion exchange or precipitation reaction [21]. It will form strong complexes with certain metals (e.g. Zn, Cd, Hg, Pb) [21]; however, these are not prevalent in bottom ash leachates [1,3,13]. Calcium is considered to be less conservative and more reactive. It is less mobile and readily participates in sorption, ion exchange, and precipitation reactions though these are pH-dependent [21]. It also forms large complexes such as ion pairs like $CaSO_4^0$, $CaPO_4^-$, and $CaCO_3^0$ [21]. More mobile and less reactive chloride will not be as responsive to τ and have lower R values. Less mobile and more reactive calcium will be more responsive to τ and have higher R values. These differences highlight the contributions of τ and R to the effective diffusion coefficient as shown in Equation 4.

Generally, the chloride anion was more diffusive and less reactive than the calcium cation in the four experiments. This is expected given the properties of the two ions diffusing in a non-reactive, hydrophobic bituminous polymer matrix. However, with increasing loss of monolith integrity via microcracking or granularization, the loss of the tortuosity was made up by increased chemical reactivities within or upon the ash particle surfaces. Chloride did not show this behavior, because it is less reactive than calcium. These data suggest that other more reactive ash constituents (Si, Mg, Zn) would behave similarly to calcium and less reactive constituents (Na, SO_4^{2-}) would behave similarly to chloride. Generally, this has been observed [3].

CONCLUSIONS

In terms of pavement formulation, increased asphalt cement content in the mix design is beneficial with respect to increasing monolith tortuosity at both the macroscale and microscale levels. Higher levels of asphalt substitution, requiring additional asphalt cement content to fill internal bottom ash pore structures, also increase the driving force and therefore the cumulative flux of constituents leaching from monoliths, but not in a deleterious manner. In terms of accelerated monolith aging, microcracking was the only experimental variable influencing diffusional leaching behavior. Increased microcracking decreased diffusional path lengths whereby release occurs and therefore reduced tortuosity. Short term field aging in a bottom ash pavements did not produce any marked changes in the behavior of chloride or calcium in field cores. In fact, some beneficial increases in tortuosity occurred during the 1.25 year study period. If monoliths are granularized, the presence of asphalt cement in the internal pore structure of the bottom ash particles and on the particle surfaces still constitutes an effective control mechanism. The results suggest that MSW bottom ash constituent leaching behavior is controlled by the tortuous hydrophobic nature of the bituminous polymer system in the pavement.

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Table 1: **Chloride Leaching From Laconia, New Hampshire Bottom Ash Utilization Demonstration Road Cores**

Pavement Type and Age	$B_{t,Cl}$	R_{Cl}	τ	$pD_{e,Cl}$
	mg/m^2	-	-	m^2/s
Test Section (Time= 0 years)	930-2,540	1.1-7.4	2,200-8,800	12.1-13.4
Test Section (Time= 1.25 years)	230-520	0.66	13,800	12.6
Control Section (Time= 0 years)	no release	-	6,000	-
Control Section (Time= 1.25 years)	30-160	-	13,800	-

Table 2: **Calcium Leaching From Laconia, New Hampshire Bottom Ash Utilization Demonstration Road Cores**

Pavement Type and Age	$B_{t,Ca}$	R_{Ca}	τ	$pD_{e,Ca}$
	mg/m^2	-	-	m^2/s
Test Section (Time= 0 years)	2,900-5,300	6.8-44.6	2,200-8,800	13.8-14.3
Test Section (Time= 1.25 years)	1,200-3,400	6.0-46.4	13,800	14.0-14.9
Control Section (Time= 0 years)	600-730	8.4-15.9	6,000	13.8-14.1
Control Section (Time= 1.25 years)	400-650	4.8-25.9	13,800	13.9-14.6

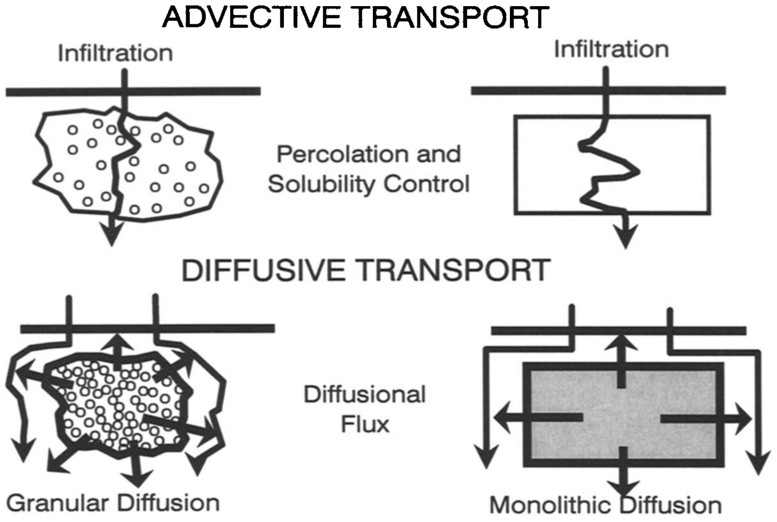

Figure 1: Schematic Depicting Advective Versus Diffusive Transport

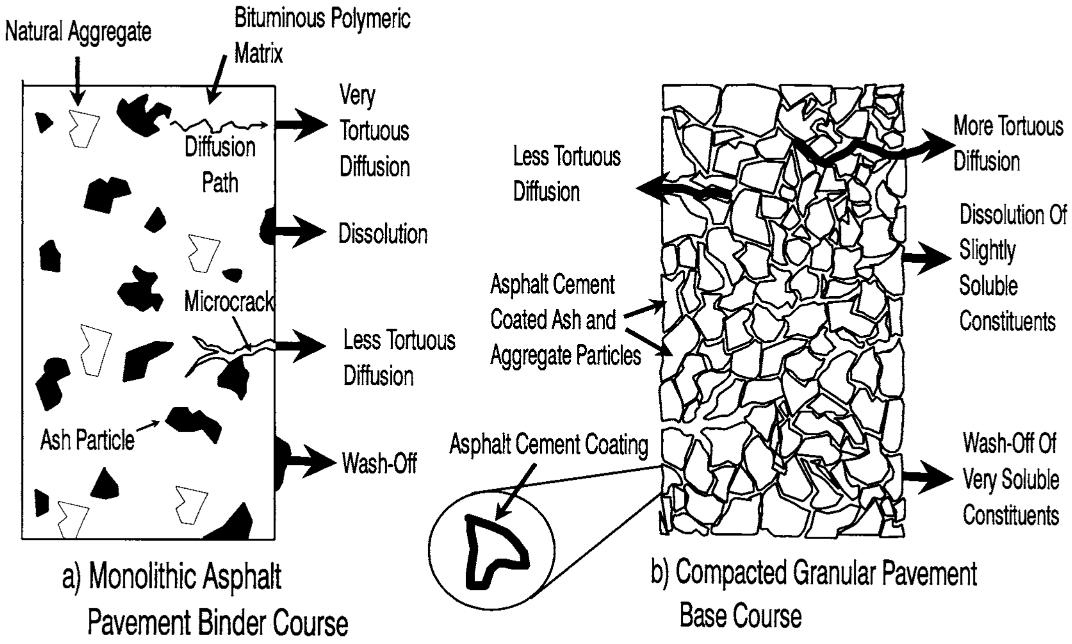

Figure 2: Schematic Depicting Diffusive Transport Processes in Monolithic (a) and Compacted Granular (b) Forms

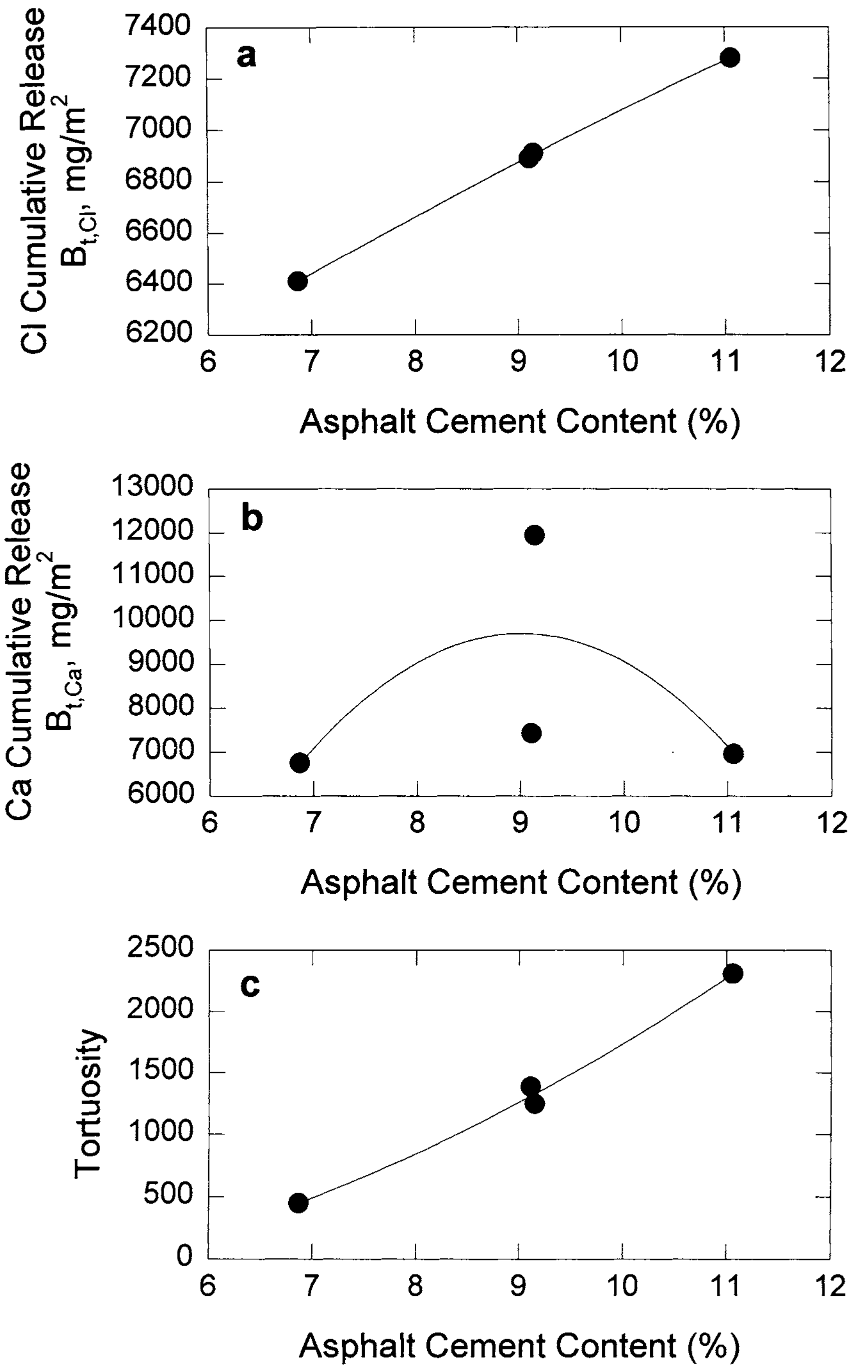

Figure 3: Influence of Asphalt Cement Content (%) on $B_{t,Cl}$ (a), $B_{t,Ca}$ (b), and tortuosity (c)

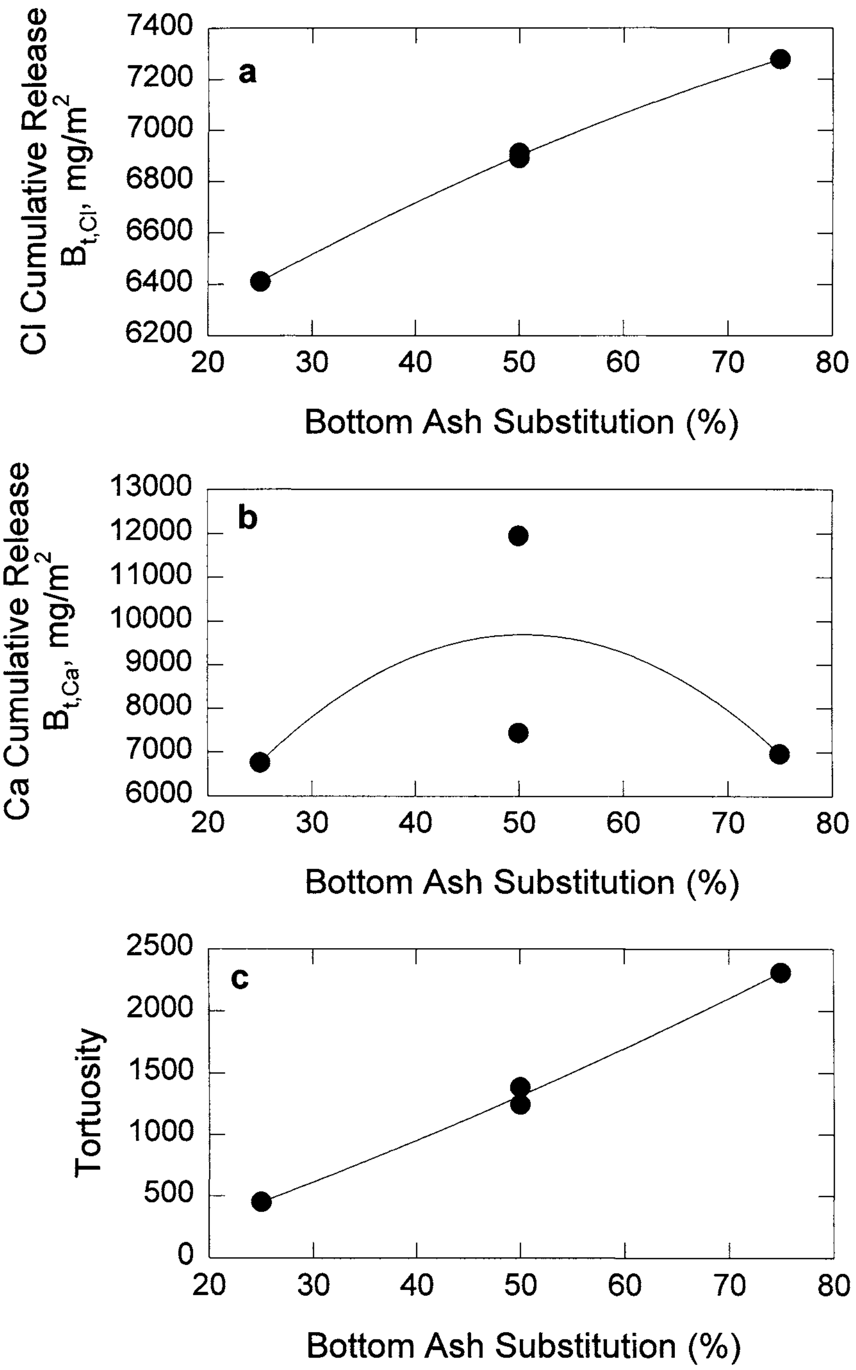

Figure 4: Influence of Bottom Ash Substitution (%) on $B_{t,Cl}$ (a), $B_{t,Ca}$ (b), and tortuosity (c)

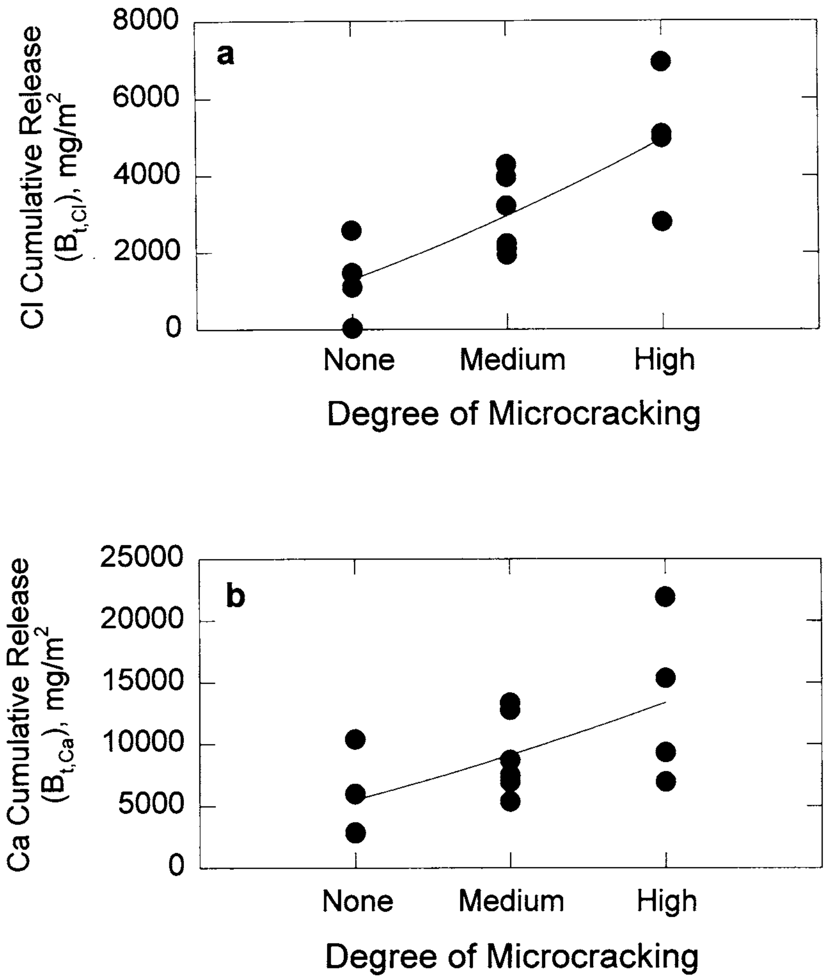

Figure 5: Influence of Microcracking on $B_{t,Cl}$ (a) and $B_{t,Ca}$ (b)

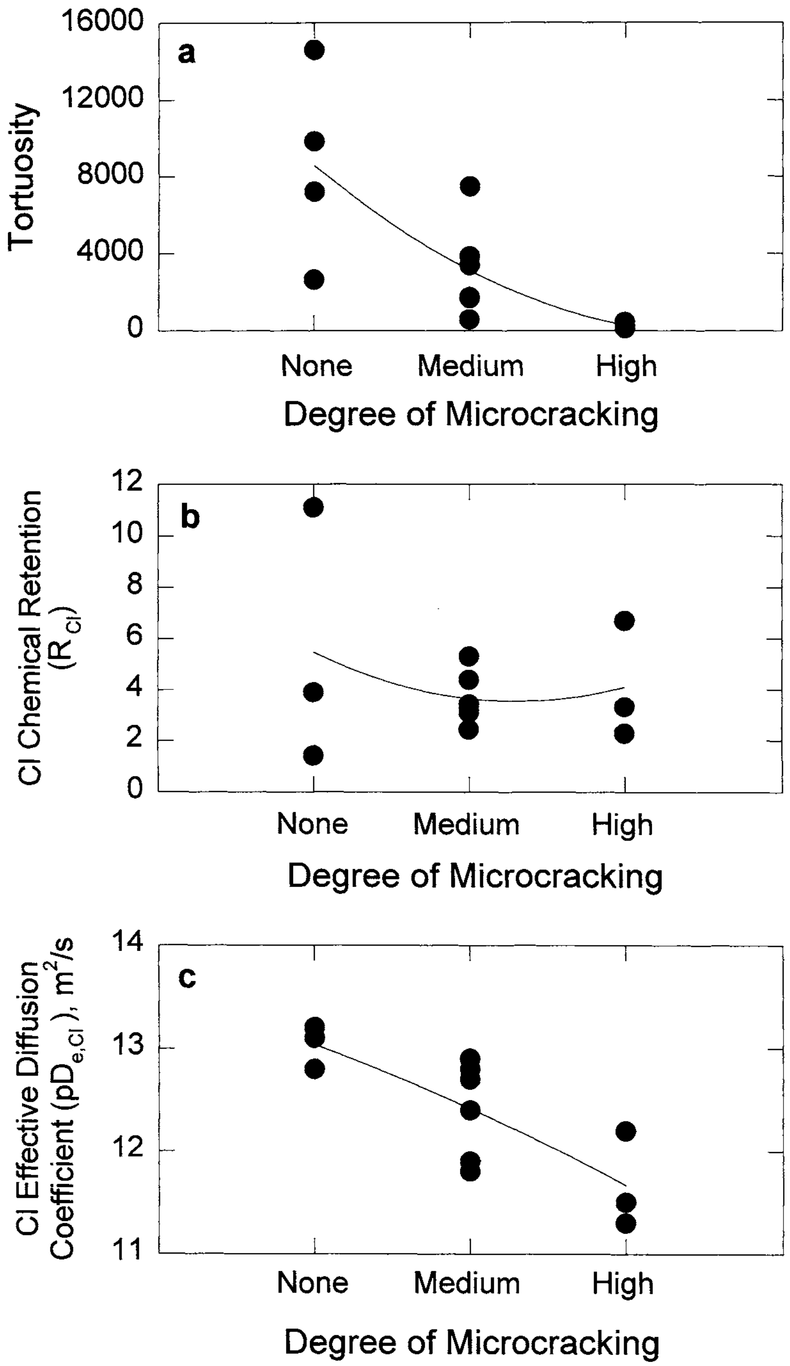

Figure 6: Influence of Microcracking on Tortuosity (a), R_{Cl} (b), and $pD_{e,Cl}$ (c)

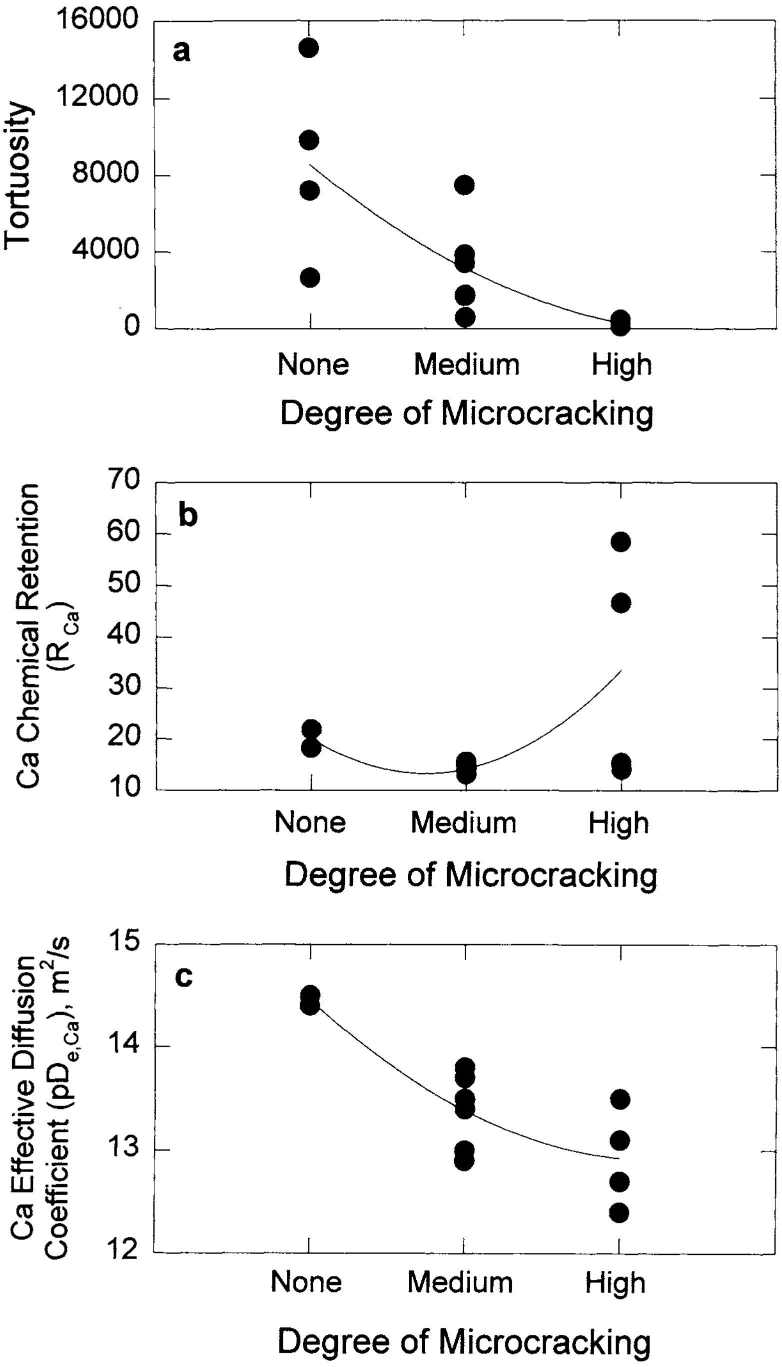

Figure 7: Influence of Microcracking on Tortuosity (a), R_{Ca}(b), and $pD_{e,Ca}$ (c)

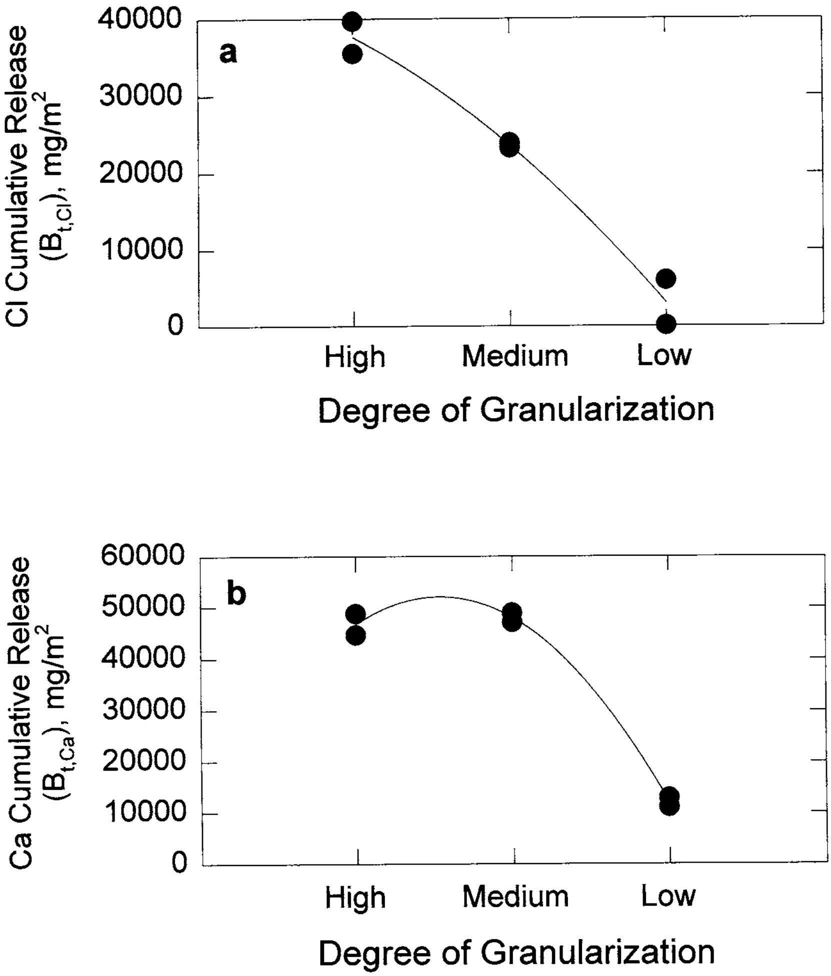

Figure 8: Influence of Granularization on $B_{t,Cl}$ (a) and $B_{t,Ca}$ (b)

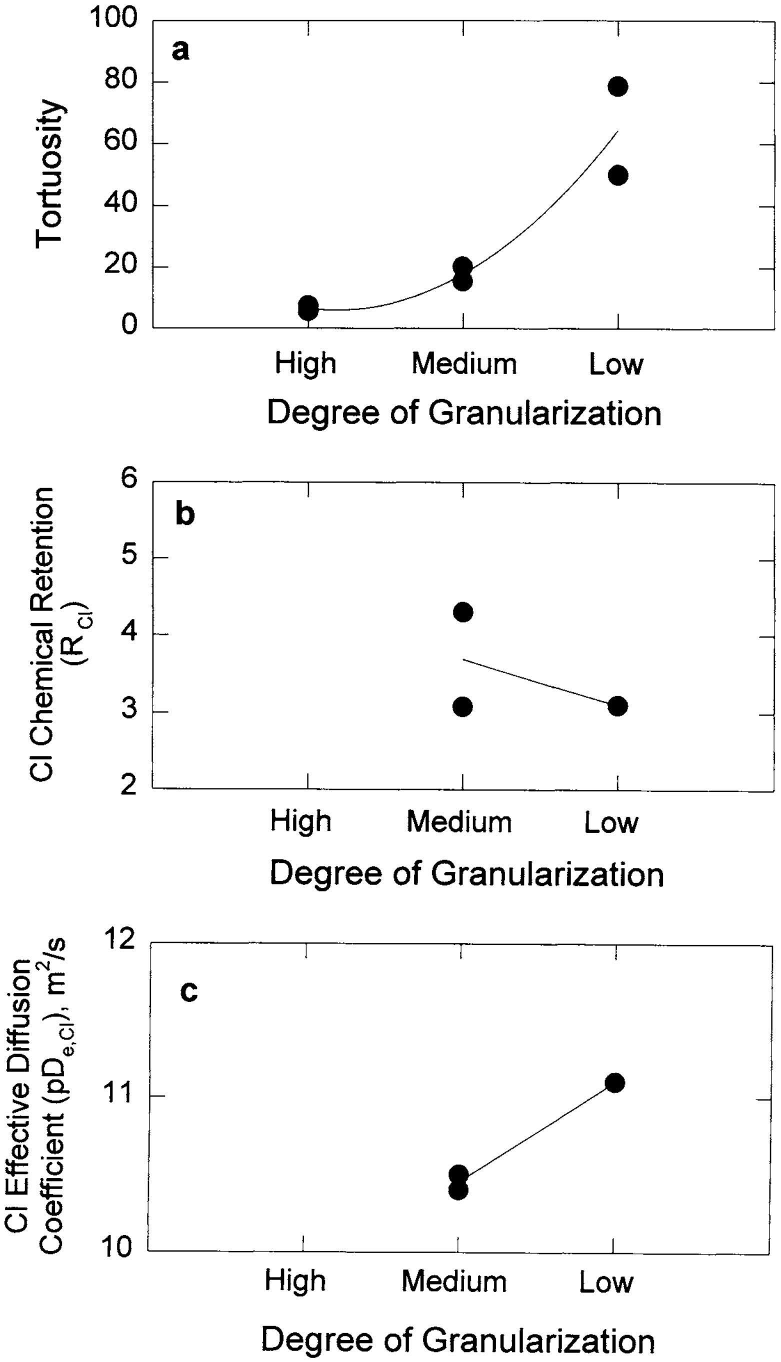

Figure 9: Influence of Granularization on Tortuosity (a), R_{Cl} (b), and $pD_{e,Cl}$ (c)

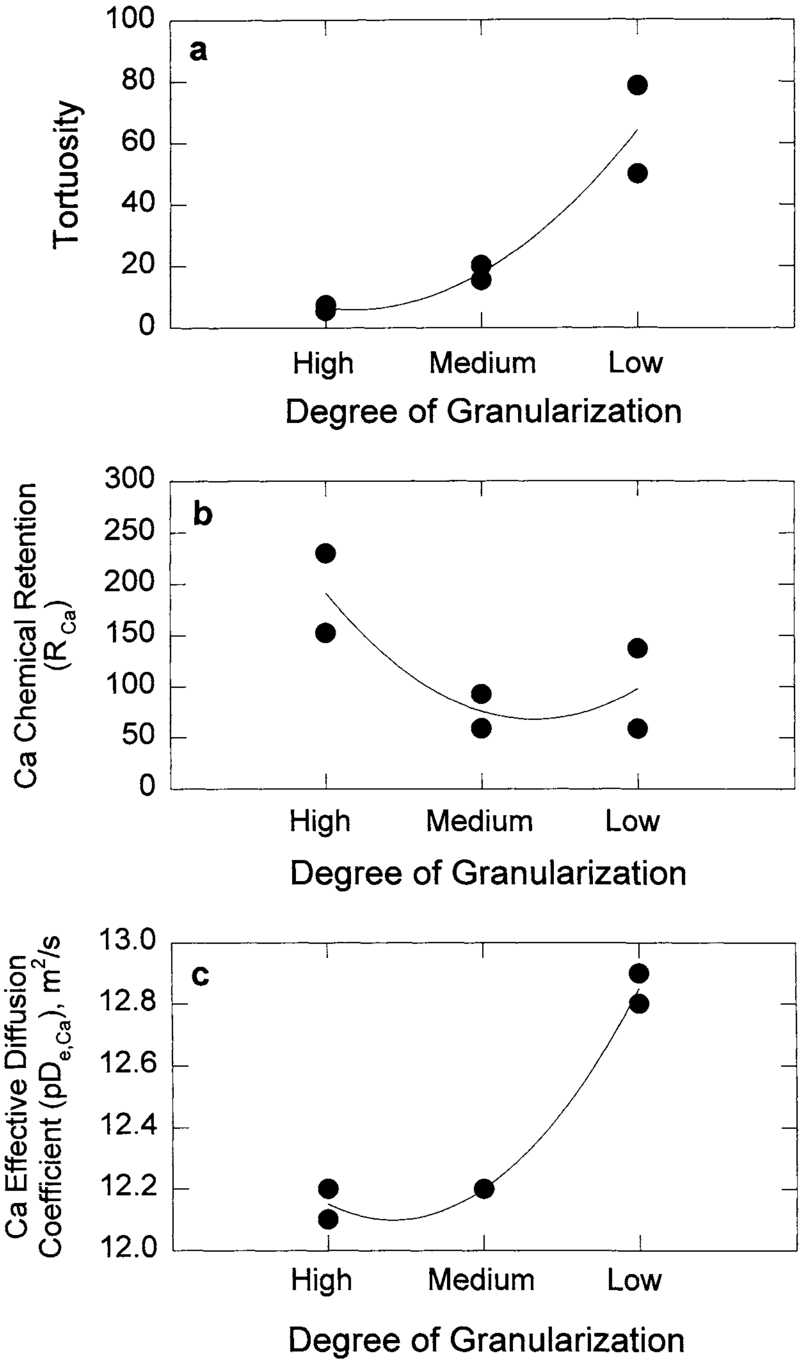

Figure 10: Influence of Granularization on Tortuosity (a), R_{Ca}(b), and $pD_{e,Ca}$ (c)