Aqueous-Phase Diffusion in Unsaturated Geologic Media: A Review

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ABSTRACT: Aqueous-phase diffusion in geologic media is very important in agricultural production, contaminant transport and remediation, risk assessment, and waste disposal. This review was undertaken to investigate (1) the components of effective diffusion coefficients, (2) diffusion as a function of water content and diffusion models, as well as the effects of temperature, compactness, and sorption on diffusion, and (3) diffusion in aggregated media. We focus on the behavior of, and relationship between, nonsorbing diffusion species and water content, particularly in porous aggregates. At low water content, aqueous-phase diffusion occurs in thin liquid films on particle surfaces, and diffusion is very slow. Diffusion is monotonically related to water content, but the relationship is not simple and depends on the range of water contents (e.g., the different forms of relationships at different water-content ranges). Data from the scientific literature further show that such relationship is related to the texture (pore-size distribution) of the geologic medium. In this article, we compile the available models that describe the relationship between diffusion coefficient and water content, with some models incorporating parameters related to medium properties. Temperature dependence of diffusion is related to the viscosity change of water at different temperatures. We note that the effects of water content on interacting sorption and diffusion deserve further investigation. Our investigation showed that, for porous aggregated media such as tuff gravel, the total water content is comprised of surface water (inter-aggregate regions) and internal water (intra-aggregate regions). Surface film water around particles and pendular water between the aggregate contacts serve as the predominant diffusion pathways. Diffusion in tuff gravel could be very slow, because water films on surfaces could be discontinuous or absent. Finally, future directions regarding the testing of aqueous-phase diffusion in complex systems (e.g., unsaturated porous aggregates) are offered.

KEY WORDS: water content, unsaturated, diffusion, porous aggregates, surface water.

I. INTRODUCTION

Aqueous-phase diffusion in geologic media is very important in agricultural production, contaminant transport and remediation, risk assessment, and waste disposal.[1–4] During solute transport, the hydrodynamic dispersion coefficient can be expressed in terms of two components, mechanical dispersion and diffusive

dispersion. At a high flow velocity, mechanical dispersion, which is related to advective flow, is the dominant dispersive process. At a low flow velocity, however, diffusion will be the predominant contributor to dispersion. This could be true for solute transport in either saturated (but low-permeability) media (e.g., a clay liner) or in unsaturated media at low water saturation (e.g., the vadose zone).

Gillham et al.[5] indicated that diffusion would be dominant when seepage velocity (i.e., pore-water velocity) is on the order of 5 mm/yr. For a clay liner, this seepage velocity corresponds to a saturated hydraulic conductivity (K_s) of 8×10^{-11} m/s, with a porosity of 0.5 and a hydraulic gradient of 1. Because U.S. regulations require clay liners to have $K_s \leq 1 \times 10^{-9}$ m/s, diffusion could be a significant transport process in many waste disposal situations involving low-permeability liners.[6] In Canada, for a disposal vault excavated at a depth of 500 to 1000 m in saturated granitic rock, a mixture of bentonite and sand has been proposed to surround containers holding high-level nuclear fuel waste in. For such bentonite-based barriers, K_s is generally less than 10^{-11} m/s.[7] To address diffusion problems in low-permeability media under saturated conditions, some work has been reported for clay-based materials[7,8] and consolidated media.[4,9]

Diffusion testing in unsaturated media requires that the matric suction potential be controlled to prevent advective flow of the diffusing species from the presence of suction gradients. While laboratory diffusion tests in unsaturated media have been performed in a number of instances, the experiments generally are more difficult to perform than those in saturated conditions. Transferring diffusion results from water-saturated samples to water-unsaturated conditions will result in an overestimation of diffusive flux. Shackelford[6] reported that the diffusion coefficient values for both nonreactive and reactive solutes in saturated soils are as much as 10 to 20 times higher than the corresponding values in unsaturated soils. Because the effect of water content on diffusion is not generally linear, the applicability of diffusion results measured in saturated systems within unsaturated media is questionable. This article reviews the current understanding of aqueous-phase diffusion processes in unsaturated media, focusing on the effect of water content on diffusion of nonsorbing species.

The effect of water content on aqueous-phase molecular diffusion in porous media was initially investigated in agricultural science nearly 40 years ago by soil scientists interested in the nutrient supply to plant roots by diffusion processes.[1,10] In 1960, Porter et al.[11] published one of the pioneering works. However, the issue of diffusion as a function of water content in the context of contaminant transport and waste disposal has been largely unexamined. Recently, much interest has arisen in quantifying and harnessing the slow diffusion process to improve the performance of geologic disposal of wastes in unsaturated conditions.[12–15] Crushed tuff has been investigated as a candidate invert material (placed directly underneath the waste-storing packages) to serve as a diffusion barrier in the potential high-level nuclear waste repository at Yucca Mountain, Nevada.[14,15] An analytical

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solution (Equation 1) can be used to calculate the diffusion distance into a homogeneous semiinfinite medium:[16]

$$C(x,t) = C_0 \text{ erfc } \{x/[2(D_e t)^{0.5}]\} \qquad (1)$$

where $C(x,t)$ (M L^{-3}) is the observed concentration based on an initial concentration C_0 (M L^{-3}), x (L) is the distance from the inlet boundary into the medium, t (T) is the time, and D_e (L^2 T^{-1}) is the effective diffusion coefficient of the diffusant in the medium. A nonsorbing diffusant with an effective diffusion coefficient of 2.2×10^{-7} cm^2/s will need about 1000 years for 50% of the diffusant source concentration to travel through a 0.8-m medium distance (the longest distance of the invert material). The diffusion barrier will, in conjunction with other engineered barriers, greatly contribute to the performance assessment of the potential repository for radioactive wastes.

This review is divided into the following sections: (1) components of the effective diffusion coefficient; (2) diffusion as a function of water content, models for unsaturated diffusion, and the effects of temperature, compactness, and sorption on diffusion; and (3) diffusion in aggregated media. At the end of this review, suggested areas for future research in aqueous-phase diffusion in unsaturated media are also discussed.

II. COMPONENTS OF EFFECTIVE DIFFUSION COEFFICIENT

In geologic media, the effective diffusion coefficient (D_e) incorporates diffusion in the bulk liquid and factors of medium geometry and liquid content that affect diffusion. The value of D_e is empirically (in Equation 2) related to the tortuosity factor (τ, <1), constrictivity factor (δ, ≤1), volumetric water content (θ), and the aqueous molecular diffusion coefficient (D_0) of the diffusant.[4,17,18] Water content (θ) is the product of the overall porosity (ϕ) and water saturation (S_w). Note that both D_e^* and D_e are called effective diffusion coefficients in the scientific literature, and attention must be given to the definition of diffusion coefficient and the interpretation of results.

$$D_e^* = \tau\delta\theta D_0 \qquad (2a)$$

or

$$D_e = (D_e^* /\theta) = \tau\delta D_0 \qquad (2b)$$

The tortuosity factor, τ, is purely geometric and accounts for a tortuous path around the solid particles in the porous medium. The τ value is usually expressed as follows:

$$\tau = (L/L_e)^2 \qquad (3)$$

where L is the straight-line distance between two points defining the diffusion path, and L_e is the actual distance of diffusion through the porous media between the same two points ($L_e > L$). Some researchers define $(L_e/L)^2$ as the tortuosity factor, and in this case the value of τ is larger than one and is placed in the denominator in Equation 2. The tortuosity (L/L_e) would reduce diffusion in two ways: (1) increasing the travel path length by a factor L_e/L and (2) decreasing concentration gradient along the pathway by a factor L/L_e.[19–21] Therefore, the tortuosity is squared to give the tortuosity factor.

Based on a one-dimensional capillary model of a porous medium that assumes a number of parallel straight pores, the value of τ is calculated to be 0.33 in the case of isotropic random distribution of tubes.[22] In a natural porous medium with nonideal pore-size distributions, τ often serves as a fudge factor. Values of τ are reported to be in the range from 0.01 to 0.84 for saturated soils and from 0.025 to 0.57 for unsaturated soils.[6]

In most cases, only the porosity of geologic media can be easily determined, and τ values are unknown. With this in mind, Boudreau[23] compiled various tortuosity-porosity relations. Aqueous-phase diffusion is analogous to electrical conductivity in porous media,[24] with the concentration gradient that gives rise to the diffusive flux analogous to the electrical field. A relationship similar to Archie's law, an empirical correlation describing electrical conductivity in porous rocks,[25] is used to predict τ (*in the saturated condition*) based solely on ϕ:

$$\tau = \phi^{m-1} \qquad (4)$$

where m denotes the empirical Archie's law exponent. The m value varies between 1.8 and 2.0 in consolidated materials, and is 1.3 in unconsolidated sand.[4] In diffusion experiments with sedimentary rocks, values of m are observed close to 2 (i.e., $\tau = \phi$). In materials of low porosity (e.g., $\phi < 0.2$), however, larger values of m are observed.

Diffusion in some rocks may behave anomalously because of their sparsely connected pore spaces at the percolation threshold, in contrast to diffusion in rocks with denser pore connections. Ewing and Horton[26] found that at the percolation threshold diffusivity drops with sample size, caused both by a decrease in effective porosity and an increase in tortuosity. This anomalous diffusion behavior deserves further attention, considering the importance of matrix diffusion in delaying radionuclide migration in geologic media.

The value of the constrictivity factor (δ) would be one except for diffusion in the narrow pores. In these pores, the value of D_e may be reduced through an increase in drag resulting from a greater water viscosity near the solid. This drag effect is especially applicable in small pores or narrow pore throats (with diameters having the same order of magnitude as the diffusant). The value of δ accounts for

this steric hindrance effect and can be estimated using the empirical equations reported from the chemical engineering literature.[4,27] Most diffusing species of interest have a molecular diameter < 1 nm; a significant steric hindrance effect is expected when pore diameter is < 10 nm.[4]

Using mercury porosimetry, Roberts and Lin[28] reported that the average matrix pore diameters (weighted by increments of pore space filled) are 53.1 nm and 19.7 to 21.4 nm, respectively, for welded and densely welded Topopah Spring tuff samples at Yucca Mountain, Nevada. From the weight-gain measurements for core saturation of densely welded tuff samples inside controlled relative humidity chambers, we found that about 10% of pores were smaller than 10 nm. Therefore, the hindered diffusion effect in the tuff matrix could likely have an impact on the diffusive processes in tuff at Yucca Mountain.

The effective porosity (ϕ_e), the portion of porosity wherein solute transport occurs, can be smaller than the overall porosity of the medium, because of size exclusion or the presence of dead-end pores that do not contribute to the overall solute transport. Values of ϕ_e have been measured to be on the order of 2 to 30% of the total porosities in compacted clay soils.[6] For the Äspö diorite in Sweden, Xu and Worman[29] reported that the pore volume available for matrix diffusion is about 60% of the total porosity. From tracer imbibition tests, Hu et al.[30] found that the ϕ_e value is about 60% of the total porosity, measured from vacuum saturation, in the welded tuff matrix. In most cases, however, there is no knowledge of the effective porosity, and the value of ϕ_e is assumed to be the same as the measured overall porosity.

In this review, D_e (i.e., Equation 2b) is employed (unless stated otherwise) to represent the diffusion coefficient in unsaturated media, and the term tortuosity factor is used to collectively include pore constriction effects (if any) and any other factors associated with pore geometry that could reduce diffusion. We focus here on the diffusion process of nonsorbing species. In this case, the ratio of D_e/D_0 will be related strictly to the tortuosity factor, which will facilitate comparison among results and examination of the water-content effect. In the literature, this ratio is alternatively called the relative diffusivity,[31] transmission factor,[11] or impedance factor.[32]

III. DIFFUSION AS A FUNCTION OF WATER CONTENT

A review of effective diffusion coefficient from the literature suggests that the major physical factor affecting the value of the measured diffusion coefficient is the water content of the medium. As the matric suction increases (as in more unsaturated conditions), water in the larger pores drains. At low content, a greater proportion of water is held closer to the solid surfaces. This means that the pathway for diffusion is likely to be more tortuous and diffusion significantly reduced as the media becomes unsaturated. The small values of D_e reflect the effects of a reduced

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cross-sectional area for diffusion and an increased tortuosity or increased viscosity of the water near the solid surface.

A. Experimental Observations

Klute and Letey[31] investigated the dependence of diffusion on the water content of glass-bead media. Their results indicated a very rapid decrease of D_e as θ was decreased, and the relationship was nonlinear. Porter et al.[11] showed that τ varied from 0.31 to 0.027 in medium- and fine-textured soils as the capillary pressure changed from 0.33 to 15 atm (i.e., a decreasing θ). They reported a straight-line relationship between τ and θ: their tested water contents were all above 0.1.

Romkens and Bruce[33] reported an exponential relationship between the ratio D_e/D_0 with θ for nitrate diffusion, and D_e decreasing with reduced θ. They attributed the results to the partial drainage of large pores through which the bulk of the nitrate ion diffusion takes place. At low water content, a funicular (i.e., continuous) water regime is formed, and ionic movement is restricted to the small pores and water films on the soil particles.

Warncke and Barber[34] reported the average D_e/D_0 for chloride in six soils was 0.022, 0.21, and 0.54 at θ of 0.13, 0.36, and 0.39, respectively. Barraclough and Nye[35] reported that the D_e for chloride in a sandy loam soil was reduced from 1.1×10^{-5} cm^2/s (with the corresponding D_e/D_0 value of 0.90) at θ of 0.6 to 7.7×10^{-7} cm^2/s (D_e/D_0 value of 0.27) at θ of 0.14. The relationship between the D_e/D_0 and θ was nonlinear, with a larger change at lower θ.

These observed different relationships (linear or exponential) between τ and θ could be related to the range of water content levels tested, with diffusion studies conducted at high water content or within a narrow range of water contents consistently exhibiting linear relationships.

B. Diffusion in a Medium at Low Water Content

In dry soils, the ratio of D_e/D_0 could be very low. Rowell et al.[32] found that very little movement of chloride in a sandy loam soil occurred at a water content lower than 0.075. The tortuosity factor was 1×10^{-6}, 1.8×10^{-4}, and 9.9×10^{-3} at θ of 0.013, 0.034, and 0.067, respectively. At higher water content, the tortuosity factor increased in an almost linear relationship to water content, similar to the observation of Porter et al.[11] over a small range of water contents. From the water characteristic curve of the soils, Rowell et al.[32] calculated that pores or channels in the soil that remain filled with water had radii less than 100 nm and 10 nm at water content of 0.067 and 0.034, respectively. At these low water contents, thin water

films on the particle surfaces are discontinuous over many empty pores, and diffusion through these pathways is evidently very slow.

Porter et al.[11] extrapolated the diffusion coefficient to zero at finite water content values and indicated that the water phase became practically discontinuous. A monomolecular layer of water (about 2.5 Å in thickness) could account for the major portion of the water content in the investigated soils at this specific wetness on solid surfaces. The high viscosity of the water molecules on the solid surface can explain the slow diffusion, because the diffusivity of ions in water is inversely proportional to the viscosity of the water. Kemper[36] showed that the viscosity of the first three layers of water sorbed on Na-saturated mineral surfaces was about 10, 1.6, and 1.1 times that of bulk water. Kemper et al.[37] also reported the mobility of water adjacent to Na- and Ca-saturated bentonite surfaces from diffusion rates of deuterium hydroxide at several water contents. The relationship between the tortuosity factor and the average number of molecular layers of water on each bentonite surface was not linear. The first molecular layer of adsorbed water on Na and Ca clays only had 30 and 5%, respectively, of the mobility for bulk water molecules.

Mehta et al.[19] reported the D_e/D_0 ratio for NaCl from 0.31 to 2.98×10^{-3} in Shonai dune sand as θ decreased from 0.317 (with the corresponding matrix suction of 2.15 KPa) to 0.0213 (5 MPa). For an aggregated Kanto loam soil (that can hold much water in its aggregate pores), the ratio decreased from 0.17 to 6.25 $\times 10^{-3}$ as θ decreased from 0.609 (2.1 KPa) to 0.202 (3.1 MPa). They reported a linear relationship between D_e and θ on the log-log scale for these two soils (to be discussed further in Equation 10). However, the relationship showed a break point in the water content that corresponds to a matrix suction of about 0.09 MPa for both soils. This suggests that the ratio of D_e/D_0 is related to the matric suction status, rather than the magnitude of the water content, because the water contents in these soils are quite different at this matrix suction (0.0464 for Shonai dune soil and 0.396 for Kanto loam).

Mehta et al.[19] attributed the steep decrease of D_e/D_0 at low water content range to the restricted diffusion of ions through the electrically charged clay particles. At low θ (high matric suction), most of the soil solution exists in the electric double layer on the surface of solid particles, through which ion diffusion is significantly restricted compared with diffusion in bulk solution. Based on the specific surface area of the soils, Mehta et al.[19] calculated the water-film thickness on the soil surface for these two soils, assuming a uniform water-film thickness on the soils. When the steep decrease in D_e/D_0 started (0.09 MPa), the thickness of water film is six layers for Shonai dune sand and 14 layers for Kanto loam. However, water films will not realistically have uniform thickness. Additionally, the diffusing chloride ions are concentrated in portions of thicker water films separated by thinner or discontinuous water films. Consequently, diffusion was significantly restricted at low water content of unsaturated soils.

Conca and Wright[12] determined D_e values for potassium with a variety of water contents and grain sizes in four types of angular-crushed gravel. For volumetric water contents ranging from 0.5 to 6%, the D_e ranged from 10^{-10} cm²/s to 10^{-7} cm²/s, indicating that the dependence was much stronger than that expected from a linear relationship between D_e and water content. Conca and Wright[13] measured diffusion coefficients in unsaturated soil, gravel, bentonite, and whole rock over a wide range of water contents. They found that D_e in all media were primarily a function of volumetric water content and not material characteristics. At high water contents, $D_e(\theta)$ gradually declined as θ decreased, from 10^{-5} cm²/s at a θ of about 50%, to 10^{-7} cm²/s at about 5%, followed by a sharp decline to 10^{-10} cm²/s at a θ of about 0.5%. This sharp decline was caused by thinning and discontinuous surface water films and decreasing pendular water elements. The authors stated that all water-film thickness as in these samples remained greater than 1 μm (while the electric double layers are several to tens of Å in thickness) even at the lowest water contents tested, and the D_e values represented diffusion in the bulk fluid. Conca and Wright[13] also suggested that D_e values associated with diffusion in electric double layers, interlayer water, or other similar thin films in geologic media would be below 10^{-11} cm²/s (the detection limit of their diffusion evaluation from electrical conductivity measurements) because efficient contact of these layers between adjacent grains was extremely improbable.

Conca and his co-workers[12,38] stated that diffusion is primarily a function of the volumetric water content. In other words, a universal relationship between D_e and θ could be generated, irrespective of medium texture. This was more or less true over a D_e value spanning more than five orders of magnitude when we plotted the compiled literature data along with Conca and Wright's data (Figure 1). However, we noticed that the diffusion coefficient in unsaturated media is related to the energy status (e.g., the mobility) of water, as shown, for example, from the work of Mehta et al.[19] Figure 2 presents the relationship between tortuosity factor and the water content for media with different textures (i.e., energy status).[11,19,32,34,39–41] The location of the curve is clearly related to the medium texture, with coarse-textured media to the left and fine-textured media to the right. If these curves are extrapolated to $D_e/D_0 = 0$, the critical (or threshold) water content (θ_c, when the diffusion coefficient approaches zero or the detection limit of the measurement method) decreases as texture becomes more coarse. The finer the texture, the higher the θ_c values, because a larger amount of water exists in fine-textured media than in coarse-textured media at similar water-potential energy.

At a given water content, clayey soils have a lower value of D_e/D_0 than sandy soils (as shown by Nye[1]) because of the more tortuous pathways in the fine-textured media. At a given water potential, however, clay soils usually have a higher value of D_e/D_0 than sandy soils because they hold more water and offer more continuous pathways.[1] Rowell et al.[32] reported the θ_c value to be 0.13 for a sandy loam soil. Below this θ_c, the continuity of the liquid phase begins to break down, and the increased viscosity of liquid next to the soil particles becomes very
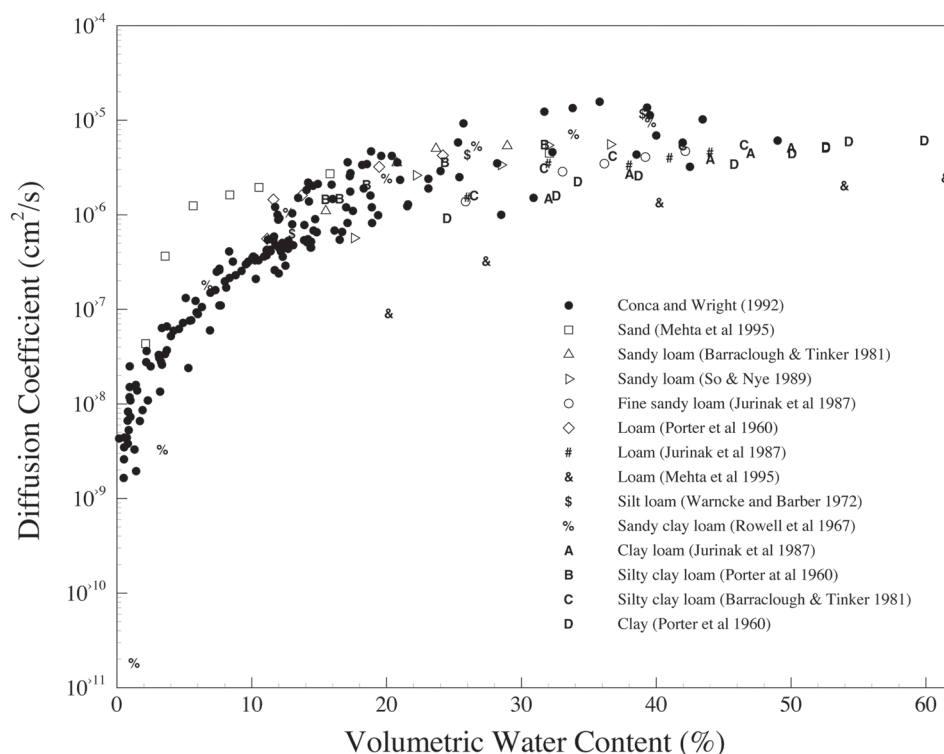
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FIGURE 1. Compilation of literature diffusion data as a function of water content. These data are obtained either from the tabulation or the digitizing (UN-SCAN-IT Automated Digitizing System, Version 5.0, Silk Scientific, Inc., Utah) of figures in the references cited.

significant. Olesen et al.[42] reported that the average threshold water-film thickness was approximately 5 Å (two molecular layers of water) for three soils with clay contents above 25%, and up to approximately 30 Å for the soils with clay contents below 20%. The difference in water-film thickness between the clayey and sandy soils result from the average thickness being only an approximate measure of the water status in the soil. (Water will not only exist as water films around soil particles, but also as capillary water present in menisci.) The average water-film thickness (calculated from water content, bulk density, and specific surface area) therefore could overestimate actual water-film thickness in coarse-textured soils.

Electrical conductivity is analogous to diffusion.[24] From resistivity measurement in the unsaturated tuff (porosity 0.09) of Yucca Mountain, Roberts and Lin[28] reported water existing in three configurations as a function of water saturation. These configurations are adsorbed water on solid surfaces (Region 1, from completely dry to ~15% saturation), isolated pockets of water (Region 2, in the saturation range of ~15 to 35%), and continuous (bulk) water (Region 3, from ~35 to 100% saturation), respectively. Region 1 has the steepest drop in resistivity as
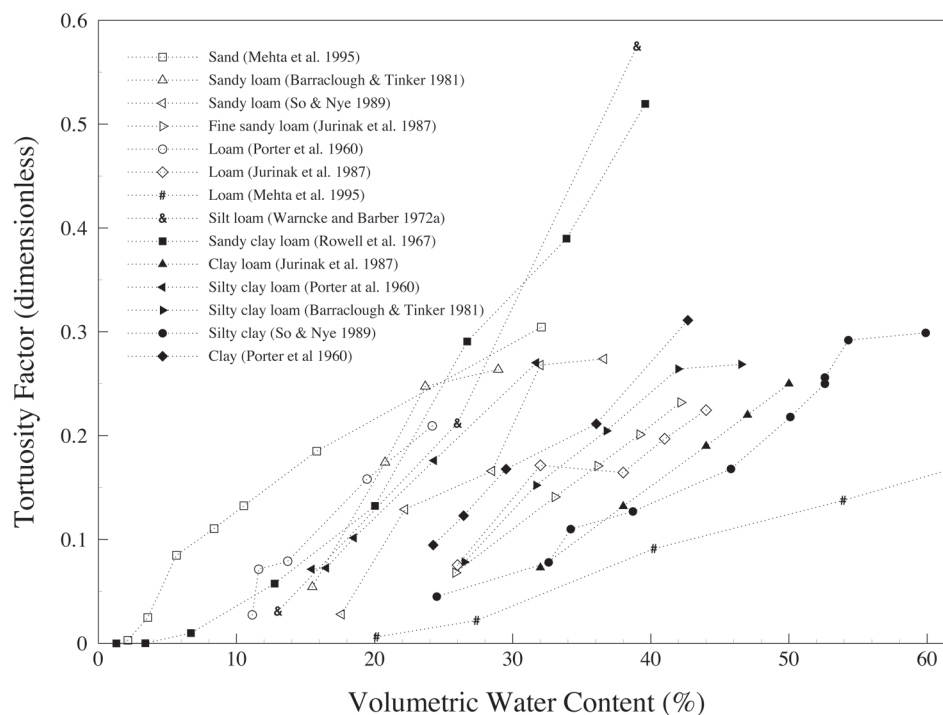
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FIGURE 2. Compilation of literature diffusion data as a function of water content showing the effect of medium texture on the diffusion and critical water content.

saturation increases, and conduction is assumed to be primarily through layers of adsorbed water.[31] From the measured porosity and surface area/volume values reported in Roberts and Lin,[28] we calculate that the average water-film thickness is about 115 Å at a water saturation of 15%. This calculation supports the importance of connected water film on resistivity and diffusion at this range of low water content. Region 2 is comprised of pendular rings at grain contacts and pore-throat constrictions and is physically separated by air. The transition from Region 2 to Region 3 is less abrupt and indicates a gradual displacement of the air in the pore space. This result has a direct bearing on diffusion in the unsaturated tuff at Yucca Mountain.

C. Unsaturated Diffusion Models

Because it is time-consuming to measure the diffusion coefficient of solutes in unsaturated media, empirical models are often used to predict the diffusion coefficient from physical characteristics of the geologic media. Note that the definition

of D_e^* (i.e., Equation 2a) is commonly used to derive the relationship of diffusion coefficient with water content in the diffusion models for unsaturated media. One widely used model, presented by Millington[43] and Millington and Quirk,[44] was originally developed for gas diffusion. It is modified for aqueous-phase diffusion as in Equation 5, relating the diffusivity ratio to θ and total porosity ϕ.[45]

$$D_e^*/D_0 = \theta^{10/3} / \phi^2 \qquad (5)$$

Papendick and Campbell[46] proposed a power law model (Equation 6), in which k is a constant with a suggested value of 2.8, based on the Brooks and Corey[47] model for predicting the unsaturated hydraulic conductivity of soils.

$$D_e^*/D_0 = k\theta^3 \qquad (6)$$

Sadeghi et al.[21] measured urea diffusion coefficients for seven soils of different texture and at two different water contents for each soil. They found that the model of Papendick and Campbell[46] underestimated the urea diffusivity and suggested a modified model (Equation 7), in which the constants were derived from a nonlinear regression of measured diffusivity.

$$D_e/D_0 = 0.73 \, (\theta/\phi)^{1.98} \qquad (7)$$

The reduction in the free water-diffusion coefficient for a partially saturated porous medium can be estimated from Archie's law.[25] This gives the diffusion relationship in the form of Equation 8.[14] Parameters m (cementation factor) and n (saturation exponent) are the Archie's exponents. For unconsolidated sand, m is 1.3 and n is 2. For consolidated rocks, m is 2.[25]

$$D_e^*/D_0 = \phi^m S_w^n \qquad (8)$$

CRWMS M&O[14] reported that a power law dependence on water content (Equation 9), in the form of Archie's law, produced an excellent fit to the data of Conca and Wright.[13] This data set comprises whole tuff cores, basalt, mudstone, and 86 soil and gravel samples. The difference between the power constant of Equation 9 and that of unconsolidated sand is related to the characteristics of the medium:

$$D_e^*/D_0 = \phi^{1.849} S_w^{1.849} = \theta^{1.849} \qquad (9)$$

Interestingly, Equation 5 has the same form as Equation 8 at full saturation, which implies that the exponents in the Millington[43–44] model might be appropriate to unconsolidated sandy materials. Many models of unsaturated systems have the form of the empirical Archie's law, and attempts have been made to explain

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Archie's law from theoretical perspectives (e.g., based on percolation models, effective-medium theories, fractal pore structures, and the statistical physics of sedimentary rocks). [4] However, no universal Archie's law exponent exists.

Mehta et al.[19] reported that the relationship between D_e/D_0 and θ could be represented with two power functions, one for higher θ and the other for lower θ, as shown in Equation 10 (and Table 1):

$$D_e/D_0 = \alpha\theta^n \qquad (10)$$

The break point of the water content corresponds to a matrix suction of about 0.09 MPa for two soils with different texture, as discussed in Section III.B. The slope (i.e., the n value in Equation 10) is significantly larger at the lower q region (shown in Table 1), and the diffusion coefficients measured at higher water contents cannot be extrapolated to lower water contents.

A two-part model relationship to account for the critical water content was also presented by Fityus et al.[48] and Olesen et al.[49] Olesen et al.[49] introduced two new diffusivity models (Equations 11 and 12) that incorporated a soil-water-retention parameter, b:

$$D_e^*/D_0 = 0.45\ \theta\ (\theta - 0.022b) / (\phi - 0.022b), \quad \theta \geq 0.022b \qquad (11a)$$

$$D_e^*/D_0 = 0, \quad \theta < 0.022b \qquad (11b)$$

$$D_e^*/D_0 = 0.45\ \theta\ (\theta/\phi)^{0.3b} \qquad (12)$$

Parameter b (>0) is the Campbell[50] soil-water-retention parameter, corresponding to the slope of the soil-water characteristic curve in a log-log plot. This parameter is a simple and convenient measure of the pore-size distribution of the soil.[49] Equation 11 represents a linear tortuosity factor model, in which $0.022b$ equals the

TABLE 1
Diffusivity Relationship for Two Soils (from Mehta et al.[21])

Soil	Water content range	α	n
Shonai dune sand	$\theta \geq 0.0464$	0.739	0.75
	$\theta < 0.0464$	212	4.10
Kanto loam	$\theta \geq 0.396$	0.338	1.41
	$\theta < 0.396$	3.83	3.99

critical/threshold soil water content of continuous water films. Olesen et al.[42] reported an approximately linear correlation between the critical water content and parameter *b*. It has been found that Equations 11 and 12, which take into account the effect of soil texture, have consistently provided better predictions of diffusion data compared with other existing models.[42,49,51] Olesen et al.[42] also reported empirical expressions to derive the parameter *b* from soil texture and bulk density, in case the soil-water characteristic curve is not available.

D. Effects of Temperature, Compactness, and Sorption on Diffusion

Temperature will indirectly affect the D_0 value of solutes, probably from the fluid-phase viscosity changes owing to changes in temperature. Several studies suggested correcting the temperature-dependent D_0, using the following equation to take account of viscosity change from one temperature to another:[8]

$$(D_0 \mu /T)_{T1} = (D_0 \mu /T)_{T2} \tag{13}$$

where T is the absolute temperature and *m* is the viscosity of water.

From Equation 13, the D_0 value will increase by a factor of 1.3 times for every increase of 10°C. If the low-permeability barrier used to contain waste materials generates heat, such as high-level nuclear waste in the potential emplacement drifts at Yucca Mountain, D_e for a contaminant in the barrier will be larger (from the larger D_0 value at the elevated temperature) than under ambient conditions. For example, Oscarson et al.[7] found that the D_e value for iodide in saturated bentonite increased by about a factor of three, with an increase in temperature from 24 to 80°C. They concluded that this increase resulted primarily from a decrease in the viscosity of the saturating solution.

However, the temperature dependence of diffusion may not be as straightforward as the temperature dependence of fluid viscosity. Sen and Deb[52] reported a 1260-fold decrease in the D_e/D_0 for Cl⁻ diffusion as the temperature decreased from 25 to 0°C. This difference is much larger than can be explained by Equation 13. However, the freezing property is not modeled in Equation 3. Sen and Deb[52] ascribed the small diffusion at low temperature to the decreased film thickness of unfrozen water, reduced solubility of chloride, and delayed attainment of the required activation energy.

Compactness with respect to bulk density (ρ_b) of the media also affects the diffusive flux, because both porosity and pore-size distribution are altered by changing bulk density. There appears to be a critical ρ_b value at which the maximum D_e/D_0 ratio occurs.[7,53] Oscarson et al.[7] found that the critical ρ_b value for a bentonite-sand mixture was about 1.4 Mg/m³, and the D_e value decreased by approximately an order of magnitude when the density was increased beyond this

value. They suggested that this critical value might be a function of the specific surface area of the bentonite.

So and Nye[41] showed that θ_c increases with an increase in bulk density ρ. They stated that it is the water in excess of the critical value that mainly determines the ease of transmission. The value of θ_c is probably associated with water in poorly connected pores, and it seems reasonable that this volume should be greater in the more compact and finer-textured soil.

In the transport equation, the effective diffusion coefficient for a sorbing solute, D_s, is commonly expressed as follows:

$$D_s = D_e/R \qquad (14)$$

where R is the dimensionless retardation factor that accounts for the interaction of the solute with the porous medium. For a linear sorption isotherm and fast sorption (compared with diffusion), $R = 1+(K_d\rho_b)/\theta$ and K_d is the equilibrium distribution coefficient. D_s is also called the apparent diffusion coefficient D_a.[4]

In evaluating diffusion of sorbing solutes, the tortuosity factor obtained for nonreactive solutes is commonly used for sorbing solutes.[8] The R value for sorbing solutes in an unsaturated medium (especially at low water content) could be much higher than in a saturated medium, both because of the smaller θ value and because the close proximity of the diffusant to the soil particle surface increases sorption interaction. As a result, the apparent diffusive transport of sorbing solutes can be reduced significantly relative to that of the nonsorbing solutes in unsaturated media. The diffusive transport rates of sorbing solutes subject to reversible sorption reactions can be as much as 5000 times lower than those of nonsorbing solutes in saturated soils and from 20 to 630,000 times lower in unsaturated soils.[6]

Figure 3 presents the compilation of literature diffusion data for sorbing solutes as well as a nonsorbing solute (chloride) for comparison.[33–35,39,53–57] As expected, the apparent diffusion coefficients for sorbing species can be much lower than chloride, with the magnitude depending on the characteristics of solute-solid-fluid interactions in unsaturated systems. For example, diffusion of zinc (Zn) is as much as five orders of magnitude lower than that of chloride in soils.[34] In a similar trend to that for the nonsorbing species, the smaller the water content, the lower the diffusion coefficient for the sorbing species. Warncke and Barber[34] reported that the relation between D_s for Zn and θ was hyperbolic. Because the sorption evaluation is not readily available from literature, we cannot use D_e/R as the y-axis of Figure 3 to correct for sorption effect. However, the measured data for R-value at a certain water content are seldom available, and R-value under unsaturated conditions is not a constant, but rather related to water content. Furthermore, we speculate that such plotting will not work out because experimental sorption evaluation is conducted mostly under saturated conditions; the effect of water content on solute sorption in unsaturated media is not fully elucidated. Hu et al.[30] proposed an unsaturated transport-sorption approach to realistically quantify retar-
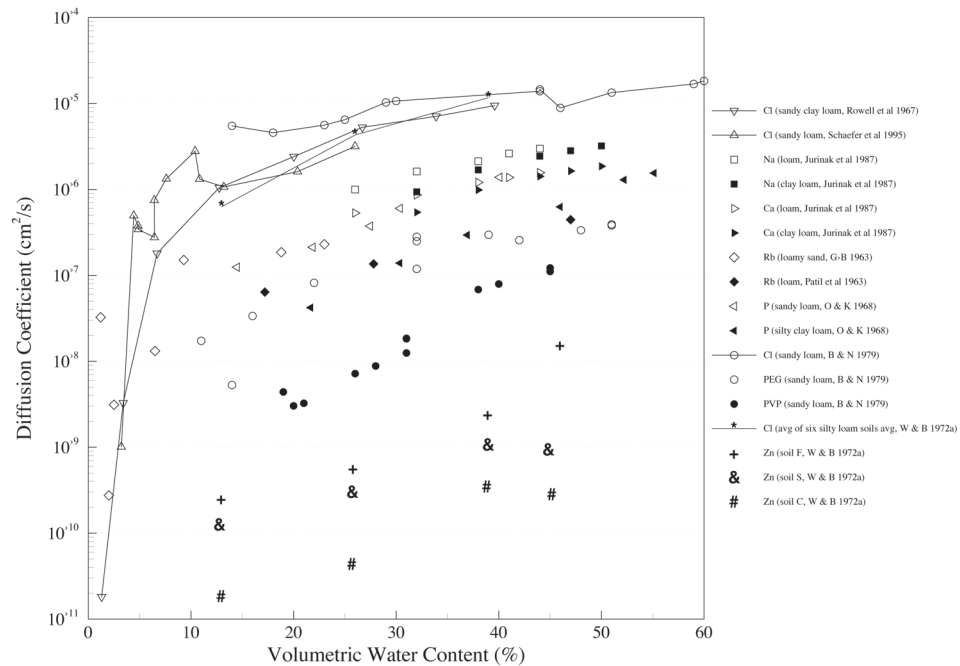
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FIGURE 3. Effect of sorption on apparent diffusion coefficients. Chloride is essentially a nonsorbing diffusant. Soil texture, which is related to the extent of sorption, is indicated in the figure legend. G-B: Graham-Bryce.[19] O & K: Olsen and Kemper.[61] B & N: Barraclough and Nye.[20] W & B: Warncke and Barber.[37] PEG: poly(ethylene glycol). PVP: poly(vinyl pyrrolidones).

dation under unsaturated conditions. The interacting sorption and diffusion processes in the vadose zone deserve much attention.

IV. DIFFUSION IN AGGREGATED MEDIA

Rock surfaces in partially saturated environments generally will be wetted by liquid films held either by adsorptive forces on the flat surfaces of minerals or by capillary forces in surface indentations. For aggregated media with appreciable intragranular porosity (e.g., tuff gravel and aggregated soil), the total water content is comprised of surface water (including surface water film around particles and pendular water between the aggregate contacts) and internal water (water contained within the aggregate pores). Water distribution in the unsaturated porous gravel and diffusion associated with the different water components are schematically illustrated in Figure 4, wherein advection is not important at low water content.
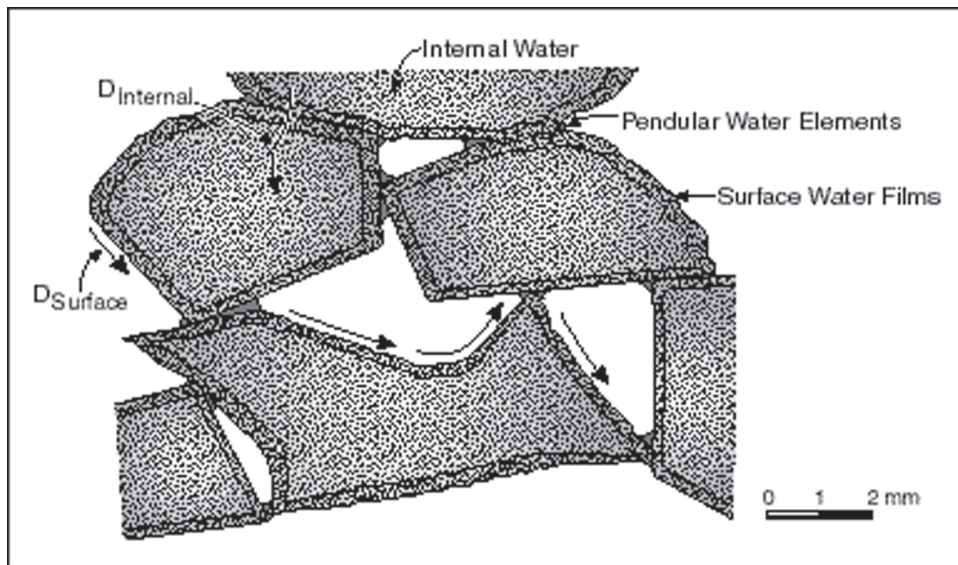
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FIGURE 4. Schematic of different components of water present in the aggregated medium and their effects on diffusion. $D_{Internal}$ and $D_{Surface}$ denote internal and surface diffusion, respectively. (Adapted from Conca and Wright.[13])

Internal water is not expected to contribute significantly to water flow and diffusion in the unsaturated gravel system,[2] because internal diffusion through the rock matrix could be extremely slow. Millington and Shearer[58] noted that liquid-phase diffusion does not occur (or in other words is very slow and difficult to measure) once the inter-aggregate pores are drained. Pendular water elements serve as the bridging pathways between aggregate grains and control the efficiency of the system in attaining the upper limit of diffusion determined by surface films.

Conca[2] conducted 12 consecutive measurements of electrical conductivity for tuff gravel of a single-sized fraction. The resulting diffusion coefficient calculated using the Nernst-Einstein equation was approximately constant at 9×10^{-9} cm^2/s, with total water content varying from 3.6 to 5.9%. Analysis indicated that the surface water content across this range remained at about 3.2%, leading to the conclusion that internal water content plays little role in determining the diffusion coefficient of crushed tuff at these low values. Figure 5 illustrates, for experiments using crushed tuff of two different sizes (2 to 4 mm and 6.3 to 9.5 mm), the contribution of surface water to effective diffusion. The relationship between D_e and θ for *total water* is located to the right side of that for *surface water*. In other words, a higher amount of total water yields a similar D_e value with smaller surface water. Also shown in Figure 5 for comparison is part of the data set compiled by Conca and Wright.[13] These diffusion coefficients were obtained on samples that possessed a definite water film, resulting from the continuous introduction of
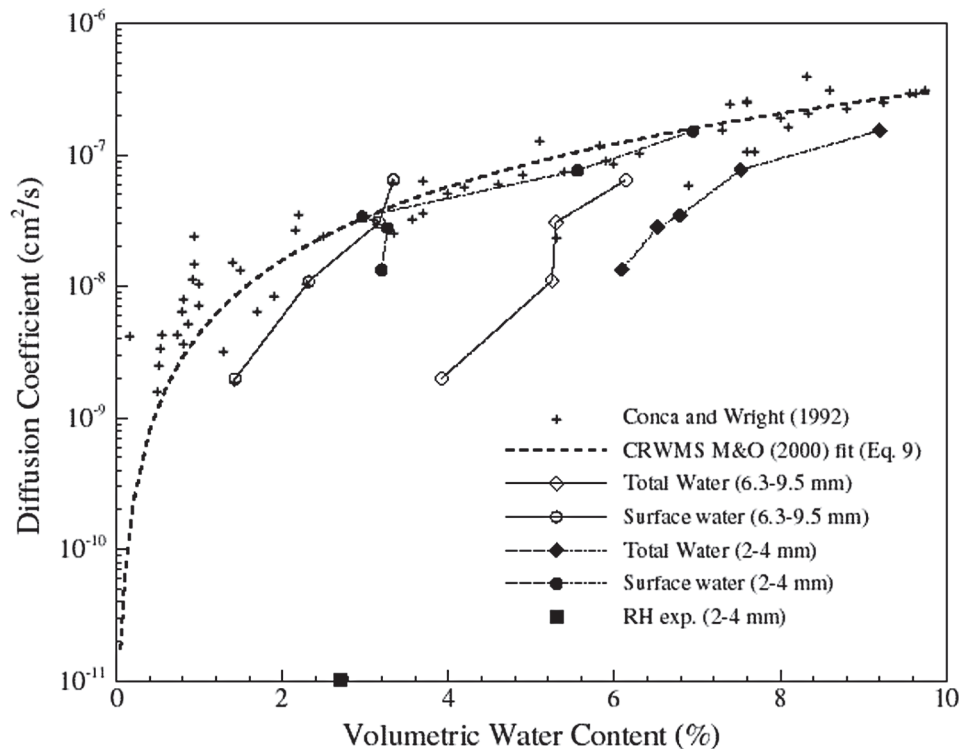
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FIGURE 5. Effect of total and surface water on diffusion measurements. Symbol +: data from Conca and Wright,[13] while other data are from Conca.[2] The diffusion coefficient at relative humidity (RH) experiment is a suggested, rather than measured, value.

liquid water (during sample preparation) into the unsaturated flow apparatus (as described in Conca and Wright[12]).

In another sample preparation test, four different-sized fractions of gravel samples (2 to 4 mm, 4 to 6.3 mm, 6.3 to 9.5 mm, and 15 to 25.4 mm) were in equilibrium with a nearly 100% humidity atmosphere.[2] The sample surface was visually observed to become air dry. The electrical conductivity was not detectable using the given equipment and operating conditions, and the D_e value of 10^{-11} cm^2/s under the experimental condition was suggested. Furthermore, humidity chamber experiments at nearly 100% humidity, using both initially wet and dry tuff gravel (2 to 4 mm size fraction), showed that the water content for both treatments converged to a steady value of 2.7% after about 70 days. The suggested diffusion value of 10^{-11} cm^2/s exhibits a significant deviation from the rest of the data obtained with continuous fluid introduction (Figure 5). In other words, at a similar total water content, diffusion in samples prepared within the high humidity experiment is at least three orders of magnitude lower than the samples prepared with

liquid water introduction. Small pores and relatively large porosity of the crushed tuff could play an important role in retaining water in the internal pores, reducing the surface water content of the particles to levels where diffusion becomes very low, to the level of detection limits of conventional methods. However, Conca[2] noted the difficulty in measuring surface water contents in gravels, and that the determination of surface air-dryness was subjective.

In summary, the finding of extremely low diffusion in tuff gravel within a humid environment has important implications for the performance of a potential high-level waste repository at Yucca Mountain. Following the heating phase and the return to ambient conditions (water content of the near-field environment returning to the prewaste-emplacement level of about 80% saturation, and pore space in the near field and drifts at nearly 100% humidity), water films on surfaces could be discontinuous or completely removed. Therefore, diffusive transport of radionuclides in such a system will be greatly reduced. However, the porous aggregates may still hold a considerable amount of internal water because of their strong capillary force. Given these characteristics of water distribution in porous aggregates, tuff gravel exhibits a unique diffusion behavior. This unique diffusion capacity of crushed tuff can be harnessed to maximize the performance of the potential repository. On the other hand, verification of Conca's result, specifically by measuring low diffusion in a high humidity environment, is necessary.

From diffusion studies in soils with intraparticle porosity (i.e., aggregates), Schaefer et al.[57] observed that the overall diffusive liquid-phase resistance (or the inverse of the tortuosity factor) was extremely large (more than 10^4) when the water content was less than the intraparticle porosity. As the interparticle film thickness went to zero, there were no interparticle "bridges" through which the diffusing molecules could travel.

When no continuous intergranular free fluid exists, grain-boundary diffusion (i.e., internal diffusion in Figure 4) through relatively small pore spaces would be the dominant diffusion mechanism. Such diffusion through thin intragranular water films in well-consolidated rock is often much slower than pore-water diffusion, because the structure of thin water film may be more constrained (from interaction with solids) than "free" water in pores.[59,60] From compiled literature data, Nakashima[59] reported that grain-boundary diffusion is on the order of 10^{-11} cm^2/s.

V. SUMMARY AND FUTURE DIRECTIONS

In this study, we have reviewed aqueous-phase diffusion behavior and examined the processes and factors affecting diffusion in unsaturated geologic media. We especially focus on the relationship between diffusion and the water content and diffusion in porous aggregates. At low water content, water exists as thin films on surfaces of the particles surrounding empty pores. Diffusion through such thin

film is very slow. Diffusion is monotonically related to water content, but the relationship is not simple and is dependent on the range of water contents (i.e., a different relationship for each distinct range of water content). The relationship is also related to the texture of geologic media. Under nonsteady-state conditions, sorbing species can have very low apparent diffusivities in the unsaturated medium. The interacting processes of diffusion and sorption in the vadose zone deserve further investigation. For unsaturated aggregated media with appreciable intra-granular porosity, such as tuff gravel, the total water content is comprised of surface water and internal water. Surface film water around particles and pendular water between the aggregate contacts serve as the predominant diffusion pathways. Water films on surfaces can be discontinuous or completely absent for tuff gravel in a humid environment. Diffusion in aggregated media could be very slow, even though a considerable amount of internal water could be present.

To further explore the low diffusion in materials such as unsaturated tuff gravel, investigations need to refine available testing methods or develop innovative approaches. Shackelford[6] has provided a thorough review of experimental and analytical methods for determining the aqueous diffusion coefficient. However, these conventional measurement methods for unconsolidated media (e.g., steady-state method and half-cell transient method) will not be applicable for systems with extremely low diffusion coefficients (unrealistically long experimental duration) or large grain sizes (difficult for experimental design and sampling). Conca and Wright[12] reported an experimental method to determine diffusion coefficients (using the Nernst-Einstein equation) by using an unsaturated flow apparatus in combination with electrical conductivity (EC) measurements. However, experimental limitations may exist with this approach, such as the contact resistance at low water contact, the use of a two-electrode method for EC measurement (as in Conca and Wright[12]), and the applicability of the Nernst-Einstein equation in geologic media at very low water content. Moreover, the electrical measurements on crushed tuff cannot discern intragranular from intergranular conduction/diffusion. Additional work is needed to refine the EC measurement that infers diffusion—the EC approach offers an advantage because of its short test duration.

For low diffusion coefficients (e.g., $< 10^{-11}$ cm^2/s), microscale profiling is necessary for the measurements to be made within a reasonable time frame. Farver and Yund[60,61] used an ion microprobe with a submicron spatial resolution to measure the grain-boundary diffusion, over a range of temperatures and pressures, from profiles of tracer concentration vs. distance on the sample surface.

We have been exploring the feasibility of using a laser ablation-inductively coupled plasma-mass spectrometry technique to micro-profile tracer diffusion in the porous tuff gravel (both on the sample surface and depth-wise into the sample). Diffusion measurements of contact treatments involving different tuff grain geometries (cube-cube, cube-sphere, and cube-tetrahedron) inside several relative humidity chambers (43, 76, 93, 98, and nearly 100%) were conducted for nonsorbing and sorbing tracers. These treatments investigated the influence of contact points

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and the presence of surface water films on unsaturated diffusion. Results show the critical role of both water-film continuity and pendular water elements in controlling pathways and the magnitude of diffusion.

To further investigate the effect of pendular element-surface film geometry on diffusive transport, scientists need to develop innovative methods to help illustrate water distribution in the unsaturated systems possessing both inter- and intra-granular porosity. Furthermore, modeling approaches need to take into account the dual-porosity system by separating the effects of surface water from the total water.

NOTATION

α	empirical parameter in a power-law function relating diffusivity to water content
δ	constrictivity factor
θ	volumetric water content [$m^3\,m^{-3}$]
θ_c	threshold water content when the diffusion coefficient approaches zero [$m^3\,m^{-3}$]
μ	water viscosity [Pa s]
ρ_b	bulk density of a medium [$kg\,m^{-3}$]
τ	tortuosity factor of the pore system
ϕ	porosity of a porous medium [$m^3\,m^{-3}$]
ϕ_e	effective porosity; the portion of porosity wherein solute transport occurs [$m^3\,m^{-3}$]
b	slope of soil-water characteristic curve in a log-log plot
D_0	aqueous molecular diffusion coefficient [$m^2\,s^{-1}$]
D_e, D_e^*	effective diffusion coefficient of the diffusant in a medium [$m^2\,s^{-1}$]
D_s, D_a	effective diffusion coefficient for a sorbing solute [$m^2\,s^{-1}$]
K_d	equilibrium distribution coefficient [$L\,kg^{-1}$]
K_s	saturated hydraulic conductivity of a porous medium [$m\,s^{-1}$]
L	straight-line distance between two points defining the diffusion path [m]
L_e	actual distance of diffusion through the porous media between the same two points [m]
m	empirical Archie's law exponent, also called cementation factor
n	saturation exponent in Archie's law
R	retardation factor that accounts for the interaction of a solute with the porous medium
S_w	water saturation
T	absolute temperature [K]

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