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A Review of Porous Media Enhanced Vapor-Phase Diffusion Mechanisms, Models, and Data – Does Enhanced Vapor-Phase Diffusion Exist?

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A Review of Porous Media Enhanced Vapor-Phase Diffusion Mechanisms, Models, and Data—Does Enhanced Vapor-Phase Diffusion Exist?

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Abstract

A review of mechanisms, models, and data relevant to the postulated phenomenon of enhanced vapor-phase diffusion in porous media is presented. Information is obtained from literature spanning two different disciplines (soil science and engineering) to gain a diverse perspective on this topic. Findings indicate that while enhanced vapor diffusion tends to correct the discrepancies observed between past theory and experiments, no direct evidence exists to support the postulated processes causing enhanced vapor diffusion. Numerical modeling analyses of experiments representative of the two disciplines are presented in this paper to assess the sensitivity of different systems to enhanced vapor diffusion. Pore-scale modeling is also performed to evaluate the relative significance of enhanced vapor diffusion mechanisms when compared to Fickian diffusion. The results demonstrate the need for additional experiments so that more discerning analyses can be performed.

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Nomenclature

A	Area (m^2)
C	Concentration (kg/m^3)
D	Diffusion coefficient of water vapor in air (m^2/sec)
D_T	Thermal diffusivity ($kg/m-K-sec$)
D_θ	Isothermal diffusivity (kg/m^2-sec)
h_{fg}, H	Latent heat of vaporization ($J/kg-K$)
J	Mass flux(kg/m^2-sec)
k	Permeability (m^2)
k_r	Relative permeability
K_z	Mass flux due to gravity (kg/m^2-sec)
K	Thermal conductivity ($W/m-K$)
m	van Genuchten parameter or mass flow rate (kg/sec)
p, P_v	Vapor pressure (Pa)
P	Pressure (Pa)
R	Universal gas constant ($8300 J/kmol-K$)
S	Saturation
T	Temperature (K)
X	Mass fraction
α	van Genuchten parameter ($1/Pa$)
β	Enhanced vapor diffusion coefficient ($= \tau \phi S_g$)
ϕ	Porosity
μ	Dynamic viscosity ($N-s/m^2$)
λ	Thermal conductivity ($W/m-K$)
ρ	Density (kg/m^3)
τ	Tortuosity coefficient (linear path length divided by actual path length)
θ	Moisture content or material parameter

Subscripts

a	Air
evd	Enhanced vapor diffusion
$Fick$	Denotes Fickian transport
g	Gas
k	Denotes Knudsen diffusion
v	Vapor
l	Liquid
r	Residual
s	Saturated
w	Water

1. Introduction

Gas-phase diffusion in porous media may be significant in the flow of multiphase fluids and the transport of contaminants in the subsurface. Of particular interest is the transport of a vapor in a porous media when its liquid phase is present. Analyses of water vapor movement data in soils under an imposed temperature gradient by Philip and deVries (1959) and by Jury and Letey (1979), among others, have concluded that vapor-phase diffusion in the presence of the liquid phase may be enhanced by up to several orders of magnitude over the standard inert-gas formulation for gas-phase diffusion due to pore-level effects. The two factors postulated to account for this enhancement are an increase in local temperature gradient in the vapor compared to the bulk porous medium, and vapor transport across liquid "islands" at pore throats within the porous media.

In many applications, such as moisture transfer in soils and the removal of nonaqueous phase liquid (NAPL) contaminants from low-permeability layers in the subsurface, vapor-phase diffusion may be the limiting transport mechanism (Ho and Udell, 1992). Vapor-phase diffusion may also be important in the analysis of contaminant migration and drying processes in potential nuclear waste repositories such as the Waste Isolation Pilot Plant and Yucca Mountain (Pruess and Tsang, 1993; Finsterle et al., 1990; Tsang and Pruess, 1990). In addition, recent studies of the postulated geohydrologic evolution of the planet Mars depend on enhanced vapor-phase diffusion mechanisms (Clifford, 1991).

The range of purported enhancement of vapor diffusion compared to the standard inert-gas diffusion model (Fick's law) is typically between factors of 2 and 5 in soil science, which is the discipline the data and models for enhanced vapor diffusion were developed, and up to several orders of magnitude for low permeability rocks at potential nuclear waste repository sites. However, to the authors' knowledge, enhanced vapor-phase diffusion has never been directly observed or quantified. It has always been inferred from various measurements including total moisture movement (including liquid), thermal conductivity, and heat flux. For example, Cary (1965) combined measurements of total moisture movement and heat flux to estimate enhanced vapor diffusion, while Cass et al. (1984) used the change in soil thermal conductivity with moisture content and pressure to evaluate an enhancement factor.

The intent of this paper is not to discredit the previous analyses, but rather to put the previous analyses and conclusions regarding enhanced vapor diffusion into perspective. Early theories by Philip and deVries (1957) and Jury and Letey (1979) have recently been applied to other systems

and models (Pruess, 1991) that include additional transport mechanisms that were not included in the early analyses, which may lead to a possible double-counting of mechanisms. Questions concerning the mechanisms responsible for the postulated enhanced vapor-phase diffusion and its appropriate application in systems ranging from soils to consolidated rock masses need to be addressed. Therefore, this paper provides a summary and analysis of previous studies and data pertaining to enhanced vapor diffusion.

2. Summary of Transport Mechanisms

The present discussion is primarily concerned with vapor-phase diffusion in porous media. However, interpretation of experimental data requires understanding of other relevant transport mechanisms including vapor-phase convection, liquid-phase transport, and unsaturated flow effects in porous media. Many of these transport mechanisms are not thoroughly understood, especially with respect to their temperature dependence. A summary of important gas- and liquid-phase transport mechanisms is included below.

2.1. Gas-Phase Transport

Gas-phase mass transport can occur due to ordinary and Knudsen diffusion and forced and natural convection. Forced convection is simply the flow of the gas phase due to a pressure gradient, while natural convection is flow due to density differences in a gravitational field, often imposed by a temperature gradient. Ordinary and Knudsen diffusion lead to different flow rates of the various components of the gas phase (compared to convection, which transports all components equally) due to concentration differences. Typically, transport by convection and diffusion are analyzed separately by using Darcy's Law for convection (with a Klinkenberg factor to account for Knudsen diffusion) and Fick's Law for ordinary diffusion with a factor to account for the porous media effects. The resulting mass fluxes are then linearly added to yield a total flux, as calculated in the widely-used TOUGH2 computer program (Pruess, 1991).

Unfortunately, as shown by Webb (1996a), this approach may not be appropriate, especially if the molecular weights of the components are significantly different from each other. For air and water vapor, where air is treated as a single "dry-air" component, the molecular weights are similar enough that the error involved in this simplistic treatment may be acceptable. However, for other situations, such as for NAPL and air, this approach may not be adequate. The Dusty-Gas Model (DGM) of Evans and Mason, as presented by Mason and Malinkaulas (1983), is preferred for gas-

phase diffusion as shown by Webb (1996a), who modified TOUGH2 to include the DGM for gas-phase diffusion.

2.2. Liquid-Phase Transport

Liquid-phase mass transport can also occur due to forced and natural convection similar to gas-phase flow. Forced convection is simply the flow of the liquid phase due to a pressure gradient, while natural convection is flow due to density differences in a gravitational field, often resulting from a temperature gradient. Liquid-phase mass transport may also be driven by a temperature gradient even for fully saturated flow (Nielsen et al., 1972); Cary (1965) speculated that the flow may be due to unbonded water molecules. Movement of the liquid phase can also arise from capillarity, where surface tension, wetting angle, and material properties play important roles, and from thermo-osmosis due to the heat of wetting (Groenevelt and Kay, 1974b).

Many mechanisms for liquid transfer below liquid residual saturation exist, although they are often ignored. Adsorption of water vapor onto surfaces will occur below relative humidities of approximately 60% (Philip and deVries, 1957; Rose, 1963b; Jackson, 1964c), and little or no movement of liquid occurs. As the saturation increases, however, liquid "islands" begin to form in pore throats between particles, and liquid flows over surfaces in thin films (Rose, 1963b). These liquid "islands" can also move due to surface tension gradients caused by a temperature gradient (Smith, 1943) and due to pressure gradients similar to oil ganglia movement in porous media (Payatakes and Dias, 1984). Further increase in the saturation to values above liquid residual saturation leads to continuous liquid flow paths which are often analyzed by Darcy's Law. However, in contrast to conventional unsaturated flow modeling using Darcy's Law, liquid movement can occur below liquid residual saturation.

2.3. Unsaturated Flow Effects

Two-phase characteristic curves for the capillary pressure and relative permeability are used to describe unsaturated flow (Webb, 1996b). The capillary pressure is the difference between the gas and liquid pressures and is a function of the saturation, so the pressure gradients in the gas and liquid phases are coupled. The permeability of the porous media to each phase is usually expressed as the relative permeability times the intrinsic (fully saturated) permeability, where the relative permeability is also a function of liquid saturation.

In most analyses of unsaturated flow, the gas and liquid phases are analyzed separately with the only coupling occurring through the two-phase characteristic curves (capillary pressure and

relative permeability). Interfacial momentum transfer can affect the phasic mass flow rates as discussed by Bear and Bensabat (1989). Interestingly, they discuss the enhanced vapor diffusion model of Philip and deVries (1957), pointing out that their approach “can represent an alternative, and perhaps more plausible explanation of this phenomena than the ones proposed earlier.”

Additional effects in unsaturated flow include vapor pressure lowering, hysteresis, and phase change. The vapor pressure in a porous medium may be less than the saturation pressure at the local temperature due to interface curvature effects of the wetting liquid. Vapor-phase diffusion may be affected by this behavior due to the resulting difference in the vapor concentration. Hysteresis effects resulting from different wetting contact angles caused by either advancing or receding wetting fronts may also have a significant impact on moisture movement and the moisture content distribution. In experiments similar to many of the soil science investigations, Molenda et al. (1992) showed that it was necessary to use both the wetting and drying curves for capillary pressure as a function of saturation in their model to replicate experimental measurements of moisture content in a closed sand column with an imposed temperature gradient. Use of only the wetting curve or only the drying curve in their model resulted in poor agreement. Evaporation and condensation may also play a large role in the transport of heat and vapor in the presence of a temperature gradient as evidenced by a two-phase heat pipe (Udell and Fitch, 1985). The model of Philip and deVries (1957) and Jury and Letey (1979) propose pore-scale condensation/evaporation which greatly enhances vapor-phase diffusion as discussed in the next section.

2.4. Temperature Dependence

As discussed by Nielsen et al. (1986), the temperature dependence of many transport mechanisms has not been thoroughly investigated. The study by Hopmans and Dane (1986a) indicate that the change in hydraulic conductivity with a change in temperature is generally close to the viscosity variation, except in low water content and high temperature regions where significant thermal vapor movement may occur. Additional temperature effects may also occur through the relative permeability function (Nielsen et al., 1986). For unsaturated properties, the capillary pressure curves including the entrapped air and the magnitude of the capillary pressure curve are a function of temperature as investigated by Hopmans and Dane (1986a,b). In general, as the temperature increases, the surface tension of water decreases, thereby decreasing the capillary pressure. Variation in the capillary pressure curve with temperature has been found to be up to ten times higher than would be predicted by the temperature variation of the surface tension alone.

2.5 Summary

Transport mechanisms for unsaturated flow are often poorly understood as exemplified by the uncertainties in temperature dependence, and modeling approaches often ignore processes such as the flow of liquid below residual saturations. Therefore, gas and liquid flow calculations for unsaturated conditions may have significant uncertainties, especially for non-isothermal conditions.

3. Review of Vapor Diffusion Studies

Vapor diffusion in porous media has been studied in many diverse disciplines ranging from soil science to engineering. The applications that motivated these studies are also diverse, ranging from soil heating problems in agriculture to drying of textiles and foodstuffs in engineering and manufacturing. Unfortunately, the diversity of the applications and disciplines led to a potpourri of analyses and solution techniques that were associated with heat and moisture transport in porous media. Very few cross-references were made in the literature between disciplines, and advances or observations in one field were often not acknowledged in another. Therefore, the purpose of this section is to provide a review of the important studies, drawn from multiple disciplines, associated with moisture transport and vapor diffusion in porous media.

3.1 Soil Science Studies

Philip and deVries

Studies of heat and moisture transport in soil science date back to the early 1900's, but the first widely accepted analysis came from Philip and deVries (1957). In their paper, they introduced theory for heat and moisture movement in porous materials. They assume that the moisture is transported in both the gas and liquid phases under moisture and temperature gradients in the soil. Flow due to external pressure gradients is not considered. The total mass flux of water, J_w , is written as follows:

$$J_w = -D_\theta \nabla \theta - D_T \nabla T - K_z \quad (1)$$

where θ is the moisture content, T is temperature, K_z is the flux due to gravity, and D_θ and D_T are isothermal and thermal diffusivities, respectively. The diffusivities contain contributions from both the gas and liquid phases:

$$D_\theta = D_{\theta, l} + D_{\theta, v} \quad (2)$$

$$D_T = D_{T,l} + D_{T,v} \quad (3)$$

where the subscripts l and v denote the liquid and vapor phases, respectively. Equations (1) – (3) acknowledge four basic components of flow in this system: 1) isothermal liquid transport 2) isothermal vapor transport 3) thermal liquid transport and 4) thermal vapor transport. The isothermal liquid transport is due to capillary pressure gradients, while the isothermal vapor transport is a result of vapor concentration gradients established by vapor pressure lowering. The thermal liquid transport is due to surface tension variations with temperature[†], and the thermal vapor transport is due to vapor concentration gradients established by temperature gradients. It is important to note that the transport of both the liquid and gas phases by pressure gradients in the gas phase and condensation/evaporation mechanisms are neglected.

Philip and deVries postulate additional mechanisms that contribute to thermally enhanced vapor transport. The first includes pore-level phase change effects within liquid islands between solid particles. Figure 1 shows the postulated transport of water across liquid islands that results from condensation of water vapor on the “hot” side (A) of the liquid island and subsequent evaporation on the “cool” side (B). The curvature of the liquid decreases at A and increases at B, causing capillary driven transport of the liquid from A to B. The resulting liquid flow through the island equals the rate of evaporation and condensation, and the total flux adjusts itself to equal the vapor flux in the air-filled pores. This mechanism tends to decrease the tortuosity and increase the effective flow area for the vapor phase compared to a gas component. The second mechanism accounts for local temperature gradients in the air-filled pores that may be significantly higher than the average temperature gradient as a result of different thermal conductivities. Both of these postulated mechanisms act to increase the value of the thermal vapor diffusivity, $D_{T,v}$, in equation (3).

Nielsen et al. (1972) summarize a number of problems with the analysis of Philip and deVries, (1957). The temperature coefficient of thermal liquid diffusion was assumed to be proportional to the temperature variation of surface tension, but the variation has been shown to be significantly greater than the temperature variation of surface tension alone as discussed earlier. Also, liquid transport due to the temperature gradient from the unbonded water molecules as discussed earlier was not included. Nevertheless, the theory of Philip and deVries (1957) has delineated possible mechanisms that explain the discrepancies between observations and previous theory.

[†] Cary (1965) and others have suggested additional mechanisms that contribute to thermally driven liquid transport.

Figure 1. Water vapor flux across liquid islands driven by thermal gradients. Condensation occurs on the “hot” side (A) and evaporation occurs on the “cool” side (B).

Cary

From 1962 to 1979, Cary published a number of papers that investigated thermally driven moisture transport in porous media. He derived the expressions for vapor and heat flow based on the thermodynamic theory of irreversible processes (Cary and Taylor, 1962a&b; Cary, 1963; Cary, 1964; Cary, 1965; Cary, 1979). Although a different approach was used, the same fundamental form of equation (1) can be derived from his formulation. In Cary’s work, the coefficients are often treated as phenomenological coefficients that need to be determined through experiments. As a result, most of his work was performed in conjunction with experiments that were designed to measure water movement through a porous material. The phenomenological coefficients in his formulation were then back-calculated (Cary and Taylor, 1962a&b). Figure 2 shows a sketch of the experimental apparatus that produced much of the experimental data that he and others have used to verify formulations of a heat and moisture transport and to demonstrate the existence of enhanced vapor diffusion.

In these experiments, a soil sample is held between two porous ceramic plates. Above and below the ceramic plates are water reservoirs that are heated and cooled, respectively, to yield constant temperatures. The water reservoirs are connected by an external tube that contains an air bubble and is capable of generating a pressure difference across the two reservoirs. The thermal gradient established by the two water baths induced a flow of water (liquid and vapor) through the soil sample and through the external flow tube. The total water flux was measured by the movement of the air bubble through the calibrated flow tube that connected the two water reservoirs. Temperatures were also recorded at several locations within the soil sample. It should

be noted that slight variations to this apparatus were made by Cary between 1962 and 1979, but the general principle remained the same.

The only direct measurement of flow is the propagation of a bubble in a capillary tube to indicate the total flux of water through the system. Issues such as film flow around the bubble and advective gas flow through the sample may have caused inaccurate interpretations of the total water flux. Vapor fluxes were back-calculated from the total observed flux assuming that the flow of liquid due to a temperature gradient could be accurately calculated. In fact, in one of his later papers Cary (1979) states that previous conclusions about the temperature independence of the vapor-phase enhancement factor are incorrect based on his current study, and that “mechanisms causing thermal liquid-phase flow of soil water remain unknown”. As discussed earlier, calculation of gas and liquid flow rates in unsaturated flow can be highly uncertain, especially for non-isothermal conditions.

One last point worth noting of Cary’s work is his derivation for water vapor flow in soil using the thermodynamic theory of irreversible processes (Cary, 1964, 1965):

Figure 2. A cross-section diagram of the experiment used to monitor heat and moisture transport across a soil sample (from Cary, 1979).

$$J_v = - \frac{\beta p D H}{R^2 T^3} \nabla T \quad (4)$$

where J_v is the vapor flux, p , D , H , and T are the average vapor pressure, diffusion coefficient of water vapor in air, latent heat of vaporization, and absolute temperature, respectively, R is the universal gas constant, and β is a dimensionless empirical factor to account for pore scale effects including tortuosity and differences in the pore scale thermal gradients. This equation was used extensively by Cary and others in calculating the enhancement factor, β . Jury and Letey (1979) later showed that equation (4) is analogous to the expression derived by Philip and deVries (1957) for thermal vapor transport if β is defined as the product of the tortuosity coefficient, porosity, and gas saturation ($\beta = \tau \phi S_g$).

Jury and Letey

Perhaps one of the most influential papers in promoting the use of the enhanced vapor diffusion coefficient is from Jury and Letey (1979). In that paper, they interpreted the results of several experiments (many from Cary) and determined an enhancement factor for vapor diffusion. They concluded that the enhancement factor $\beta (= \tau \phi S_g)$ ranged between 1.0 and 3.5 for a number of experiments. They also claimed that a fixed value of β could be used in most circumstances that would predict vapor transport within a factor of 2.

Such strong claims has prompted the use of this enhancement factor in recent works ranging from geomorphic investigations of the planet Mars (Clifford, 1991) to performance assessments of high-level radioactive waste disposal (Pruess and Tsang, 1993). However, no direct measurements of enhanced vapor diffusion or the responsible mechanisms have been made. For example, Jury and Letey (1979) reference the column experiments of Weeks et al. (1968), who performed heat and moisture transport experiments in horizontal columns of soil. Only temperatures and suctions were measured at several locations in the experiment, which had its ends held at constant hot and cold temperatures. To calculate the value of the enhancement factor, β , they assumed that only vapor-phase flow existed so that Cary's equation could be used. Effects of liquid transport were not considered, even though they acknowledged its existence.

Others

There are numerous other papers in soil science that investigate the combined transport of heat and moisture through soils. Hanks et al. (1967) performed drying experiments on soils using two different modes: 1) a fan was used to blow air over the surface of the soil 2) heat lamps were used to radiate the surface of the soil. Based on temperature and water content profiles and total water evaporation, they back-calculated the enhanced vapor diffusion coefficient using the theory

of Philip and deVries (1957) and Cary (1965). Weeks et al. (1968) performed thermal experiments in a horizontal soil column and back-calculated the enhanced vapor diffusion coefficient using Cary's expression for vapor diffusion (1965). Cass et al. (1984) used thermal conductivity measurements of radial heat transfer in a column of soil to determine enhancement factors to vapor diffusion based on the theory of Philip and deVries (1957). More recently, Globus and Gee (1995) presented a method to estimate the water diffusivity and hydraulic conductivity of moderately dry soils, but they assume a priori that the vapor diffusion coefficient is enhanced by six times over that of ordinary diffusion. In all of these analyses, the estimation of the enhanced vapor diffusion coefficient relied on back-calculating the vapor flux from total water flux data; no direct measurements of vapor flux were performed. In addition, the theoretical formulation that was used in all of the analyses was derived by either Philip and deVries (1957) or Cary (1965), but neither of those analyses included the contribution of advective gas-phase transport due to pressure gradients, and they assumed that liquid water flux could be accurately calculated, which was later questioned by Cary (1979) as mentioned above. Table 1 summarizes these and other selected experiments found in the soil science literature.

3.2 Engineering Studies

Many engineering studies investigating heat and moisture transport in porous materials can be found in the drying literature. Drying of various materials ranging from textiles to foodstuffs encompasses many of the processes that are also investigated by soil science researchers. Unfortunately, very little communication or cross-referencing exists between the two disciplines. This section reviews the significant contributions made in the area of heat and moisture transport in porous media as applied to drying theory in the engineering discipline.

Luikov

Russian researchers have credited Luikov with discovering the phenomenon of moisture thermal diffusion and establishing the importance of temperature gradients on causing moisture transfer in porous materials (Lebedev, 1961; Mikhailov, 1973). In his theory, Luikov employs the theory of irreversible thermodynamics to derive expressions for liquid and vapor flow (Luikov 1975). The resulting flux expressions are similar to the equation derived by Philip and deVries (1957) (equation 1). However, Luikov often neglects the contribution of flux due to gravity so that the driving potentials for moisture flow are moisture content and temperature gradients. It is interesting to note that Cary (1964) uses the same theoretical development as Luikov and references his work (a rare instance of cross-referencing between disciplines). However, Luikov does not

Table 1. Summary of selected soil science experiments.

Reference	Experiment	Data Recorded	Comments
Gurr et al. ¹ (1952)	Loam, Sand, Horizontal Cylinder, 10°C–25°C	MC(x), Pc, Salt Concentration	Used soluble salts to try to distinguish between liquid and vapor flow
Taylor and Cavazza ¹ (1954)	Silt Loam, Horizontal and Vertical Cylinders with Screens, 10°C–30°C	MC(x,t), Pc (wetting and drying), kr, T	Air gaps in soil columns to try to separate liquid and vapor flow greatly complicates analysis (see Philip and deVries, 1957)
Cary and Taylor ² (1962a,b)	Loam, Horizontal Cylinder with Water Flow	Q(ss), q(ss), Pc	Inferred vapor flux from change in total water flow and change in heat flux
Cary (1963, 1964)	Air, Vertical Cylinders with Water Flow, KCl	Q(ss)	Water vapor diffusion across air gap
Jackson (1964a,b,c)	Loam, Silty Clay, Vertical and Horizontal Cylinders, One End Open	MC(x,t)	Low MCs—max 0.08; Estimated liquid flow at 0.50 relative humidity (MC~0.04) for loam
Cary (1965 ² , 1979)	Loam, Vertical Cylinders with Water Flow, Fixed T and P boundaries	Q(ss), q(ss), Pc	Inferred vapor flux from change in total water flow and change in heat flux
Hanks et al. ² (1967)	Sand, Silt Loam, Loamy Sand, Vertical Cylinders, External Fan or Heat Lamps	Average MC(t), T(z)	Boundary conditions not quantified
Weeks et al. ² (1968)	Soil, Horizontal Cylinder, Transient, NaCl Added	MC(x), T(x,t), Pc(x,t)	Used soluble salts to try to separate liquid and vapor flow; Complicated series of transients
Cassel et al. (1969)	Sandy Loam, Horizontal Cylinders, Variable Boundaries	MC(x,t), T(x,t)	Compared net water fluxes to Fick's Law, Philip and deVries; Fick's Law too small by factor of 5; Philip and deVries agreement good; Observed significant radial temperature gradients
Nielsen et al. ² (1973)	Silt Loam, Sandy Loam, Silty Clay, Vertical Profiles	MC(z,t), q(z,t), kr, Pc	Boundaries not quantified
Jury and Miller (1974)	Sand, Vertical Cylinders, Capped and Open-Ends, 26°C–36°C	MC(z), Pc, kr, T	Capped and open column experiments; open column boundaries not quantified
Cass et al. (1984)	Silt Loam, Sand, Cylinders, Transient	T(x,t,P)	Inferred enhancement from thermal conductivity measurements as a function of pressure; Compared to Cary (1979) and Jury and Letey (1979) models
Molenda et al. (1992)	Sand, Horizontal Cylinder, 20°C–54°C	MC(x), Pc (wetting and drying), kr, T(x)	Hysteresis is important; Multidimensional nature of calculated MC
Globus and Gee (1995) (from Globus, 1983; Gee, 1966)	Silt Loam, Soil, Horizontal Cylinders	MC(x), T(x), Pc	No interpretation presented for enhanced vapor diffusion

¹ Used by Philip and deVries (1957), ² Used by Jury and Letey (1979), Legend: MC=Moisture Content, T=Temperature, Pc=Capillary Pressure Curve, kr=Relative Permeability Curve, Q=Total Water Flow Rate, q=Heat flow rate. x,z=denotes function of space, t=denotes function of time

postulate the possibility of enhanced vapor diffusion by any of the mechanisms proposed by Philip and deVries (1957).

Whitaker

Whitaker developed a comprehensive set of equations governing the simultaneous transport of mass, momentum, and heat in a porous medium (Whitaker, 1977). He derives these equations using volume-averaged quantities in the balance laws for mass, momentum, and energy. By integrating quantities over a representative elementary volume, the local equations of transport can be transformed into macroscopic equations for combined mass, momentum, and energy transport in a porous medium. Ironically, the resulting equations can be written in the same basic form as equation (1) developed by Philip and deVries (1957). In addition, no mention is made to the possible mechanisms causing enhanced vapor diffusion.

Pruess

The multiphase, nonisothermal numerical code TOUGH2 (Pruess, 1991, 1987) has been used extensively in areas including geothermal, environmental remediation, and nuclear waste management (Pruess, 1995). The mathematical formulation for the code is similar to that of Whitaker in that it considers conservation of mass, momentum (via Darcy's law), and energy. The flux of water, J_w , in both the liquid, J_l , and gas, J_v , phases can be written as follows:

$$J_w = J_l + J_v \quad (5)$$

$$\text{where} \quad J_l = -k \frac{k_{r,l}}{\mu_l} \rho_l (\nabla P_l - \rho_l g) \quad (6)$$

$$J_v = -k \frac{k_{r,g}}{\mu_g} \rho_g X_{v,g} (\nabla P_g - \rho_g g) - D_{va} \rho_g \nabla X_{v,g} \quad (7)$$

where k is intrinsic permeability, k_r is relative permeability, μ is viscosity, $X_{v,g}$ is mass fraction of water vapor in the gas phase, P is pressure, ρ is density, g is gravity, D_{va} is the diffusion coefficient for water vapor and air in a porous media, and the subscripts l , v , and g denote liquid, water vapor, and gas, respectively. In equation (6), the liquid pressure is dependent on the capillary pressure, which is a function of saturation. In equation (7), the water vapor mass fraction gradient in the second term on the right-hand side is dependent on temperature gradients as well as

saturation gradients[†]. If these dependencies are considered, the chain rule can be invoked to expand the terms expressed as gradients to yield equations similar in form to equation (1) (Hartley, 1987). Depending on the capillary pressure model, the temperature dependence may or may not be considered by equation (7).

The enhancement to vapor diffusion, as presented by Philip and deVries (1957) and Jury and Letey (1979), can be incorporated into equation (7) by altering the diffusion coefficient. The diffusion coefficient in equation (7) is expressed as follows:

$$D_{va} = \tau \phi S_g \frac{D_{va}^0}{P} \left(\frac{T + 273.15}{273.15} \right)^\theta \quad (8)$$

where τ is the tortuosity coefficient, ϕ is the total porosity, S_g is the gas-phase saturation, D_{va}^0 is the binary diffusion coefficient for vapor in air, P is pressure in bars, T is temperature in °C, and θ is a material parameter. In TOUGH2, a fixed enhancement to the vapor diffusion can be specified by setting the product of $\tau \phi S_g$ to a constant, β . Jury and Letey (1979) have suggested that the value of this constant is on the order of one, which makes the diffusion of vapor in porous media equivalent to diffusion of vapor in free space. Similar methods have also been used in other engineering applications (Baladi et al., 1981) for vapor transport in a porous material. Although Philip and deVries (1957) have postulated the physical mechanisms that would justify this behavior (instantaneous transport across liquid islands via phase change and larger-than-average temperature gradients in the gas phase), the use of the vapor diffusion enhancement factor, β , in equation (7) is speculative. One reason is that gas-phase pressure gradients, which were ignored in the analyses that theorized values for β , are considered in equation (7) and may account for at least some of the observed enhancements to vapor diffusion. Therefore, the approach taken by Pruess (1991) and Baladi et al. (1981) in simply adding an enhancement factor to the diffusion equation may be double-counting mechanisms that are already considered in their general equations.

Experiments

Numerous experiments have been described in the engineering literature pertaining to the movement of moisture in porous media. A large number of these pertain to the drying of porous materials such as soil or foodstuffs. A famous paper by Ceaglske and Hougen (1937) investigated

[†] Although the dominant driving force for vapor diffusion is often vapor pressure gradients induced by temperature gradients, Kelvin's equation can be used to show that vapor pressure decreases with increasing capillary pressure (or decreasing saturation). Therefore, saturation gradients can cause vapor mass fraction gradients if "vapor pressure lowering" is considered.

the one-dimensional drying of wet sand as shown in Figure 3. They described the different regimes associated with the drying of a wet porous material: constant rate period, first falling rate period, and the second falling rate period. The postulated mechanisms that enhance vapor diffusion would be present during the constant rate and first falling rate period when a temperature gradient is established near the evaporating surface. However, liquid-phase transport caused by capillary pressure gradients may dominate the total moisture transport in this system at those times, and evaluation of enhanced vapor diffusion is difficult. Similar experiments have also been performed to evaluate drying processes (Lee et al., 1992; Kaviany, 1991; Kaviany and Rogers, 1990; Chen and Schmidt, 1989; Schadler and Kast, 1986), but no reference is made to the enhanced vapor diffusion mechanisms postulated by Philip and deVries (1957). Perhaps more useful experiments to analyze enhanced vapor diffusion would consist of similar open-ended drying experiments but with appropriate boundaries to establish a well-defined thermal gradient. This would address the role of vapor diffusion under thermal gradients during the drying process, and the experiments could provide useful data to examine the possible existence of enhanced vapor diffusion. Table 2 summarizes selected experiments from the engineering literature.

Figure 3. One-dimensional drying of sand as performed by Ceaglske and Hougen (1937).

Table 2. Summary of selected experiments from the engineering literature.

Reference	Experiment	Data Recorded	Comments
Ceaglske and Hougen (1937)	Sand, Heated external convective drying; Varied T of the heated air and sand thickness, Initially saturated	T(z), MC(x), drying rates	Described different regimes of drying—constant rate period and falling rate periods
Schadler and Kast (1986)	Crushed glass of various sizes, External convective drying at various T, Different liquids, Initially saturated	Surface T, drying rates	Analyzed receding drying front
Kaviany and Mittal (1987)	Glass beads, External heated convective drying, Initially saturated	T(z), Drying rates	Calculated surface mass transfer coefficient
Chen and Schmidt (1989)	Alumina spheres and polymer pellets, External convective drying at various T, Initially saturated	Surface and bottom T, drying rates	Compared data with integral model
Rogers and Kaviany (1990)	Plexiglass and glass spheres, Heated external drying at constant T, Initially saturated	T(z), air velocity, drying rates	Determined heat and mass transfer coefficient variations during drying
Tao and Kaviany (1991)	Single layer of glass cylinders, Liquid ethanol, Heated external convective drying, Variable saturation	Drying rate, Surface T, Pc, Meniscus location	Emphasized surface conditions
Lee et al. (1992)	Glass beads (varying sizes), Heated external convective drying, Initially saturated	Drying rates, T(z,t), MC(z,t), Pc, kr	Most comprehensive data on system parameters and material properties

Legend: MC=Moisture Content, T=Temperature, Pc=Capillary Pressure Curve, kr=Relative Permeability Curve, x,z=denotes function of space, t=denotes function of time

4. Analyses

Two experiments are modeled in this section to provide a comparison between analyses that are typically reported in the soil science literature and analyses that are presented in the engineering literature. In the first experiment, a capped column of sand similar to the experiments of Cary (1965) is used to compare predicted and measured moisture content profiles during an imposed temperature gradient. The second experiment compares predicted and measured saturation and

temperature profiles for external convective drying of an open-ended column of glass beads, similar to the experiment performed by Ceaglske and Hougen (1937). These two experiments were chosen because of the availability of the material and system parameters that were reported. The analyses are presented to indicate the influence that enhanced vapor diffusion may have on experimentally measured quantities.

An simple pore-scale analysis is also presented in this section to assess the feasibility of enhanced vapor-phase diffusion in porous media. An energy balance is used to determine an order-of-magnitude estimate for the mass flux of vapor that can be transported across a liquid island, and this value is compared to typical mass fluxes based on Fickian diffusion in porous media.

4.1 Analysis of Capped Experiment (Jury and Miller, 1974)

Jury and Miller (1974) conducted column experiments in a medium sand to measure the transport coefficients for heat and moisture flow described by Philip and deVries (1957). The experiments involved capped column and an open column configurations under steady-state conditions. The capped column experiments are similar to tests conducted in soil science by Cary. A simple one-dimensional model of the capped column of Jury and Miller (1974) has been analyzed with a modified version of TOUGH2 (Pruess, 1991); the simulation parameters are summarized in Table 3. Modifications include the Dusty Gas Model for gas-phase diffusion (Webb, 1996a), Millington and Quirk (1961) for the gas-phase tortuosity, and the van-Genuchten/Parker two-phase characteristic curves (Parker et al., 1987) including variation of the capillary pressure with temperature as discussed below. A linear variation of thermal conductivity with saturation was used, which is similar to the variation of the measured values.

The capillary pressure and wetting-phase relative permeability presented by Jury and Miller have been fit with the van Genuchten/Parker characteristic curves (Parker et al., 1987), which provide a reasonable representation of the experimental data as shown in Figures 4 and 5. The parameters for capillary pressures also resulted in a reasonable fit to the relative permeability data. Jury and Miller note that the temperature variation of the capillary pressure curve is greater than the surface tension variation with temperature alone; similar effects have been noted by others as discussed earlier. The data of Jury and Miller indicate an increase in capillary pressure by up to a factor of five for a given moisture content. For simplicity, the current analysis uses a constant factor of four to calculate the capillary pressure dependence on surface tension variations with temperature.

Figure 4. Measured and fitted capillary pressures as a function of moisture content for the capped experiment of Jury and Miller (1974).

Figure 5. Measured and fitted wetting phase relative permeabilities as a function of moisture content for the capped experiment of Jury and Miller (1974).

Table 3. Model parameters used in analysis of capped experiment by Jury and Miller (1974).

Permeability (m ²)	2.1x10 ⁻¹²
Porosity	0.35
K _{dry} (W/m°C)	1.93
K _{wet} (W/m°C)	3.76
D _{air,k} (m ² /sec)	4.5x10 ⁻⁴
D _{wv,k} (m ² /sec)	5.7x10 ⁻⁴
D _{va} (m ² /sec)	2.13x10 ⁻⁵
θ	1.8
van Genuchten Parameters	
S _{lr}	0.15
S _{ls}	1.0
m	0.78
α (Pa ⁻¹)	4.65x10 ⁻⁴
1/α (Pa ⁻¹)	2150

A sketch of the capped experiment is shown in Figure 6 along with the corresponding TOUGH2 model. A 15 cm diameter cylinder (5 cm high) was used to contain sand at prescribed moisture contents. The column was insulated radially with polystyrene foam to minimize radial heat losses. The ends are capped with vinyl “pillows” and are maintained at prescribed temperatures using water baths. The calculated moisture content profiles for various moisture contents is shown in Figure 7 along with the experimental data for which the top boundary is at 36°C and the bottom boundary is at 26°C. For this analysis, the tortuosity parameter in equation (8) was calculated according to Millington and Quirk (1961)[†]. The experimental moisture content profiles are reasonably well matched by the model without enhanced vapor diffusion.

These experiments were also analyzed with enhanced vapor diffusion. Figure 8 shows the effect of enhanced vapor diffusion on the moisture content profiles ($\phi \tau S_g = 1$). For the lowest and highest average moisture content values, the profiles are shifted slightly; for the other two average moisture content values, the change is difficult to detect. Increases in the calculated vapor mass flux and the heat flux across the column due to enhanced vapor diffusion are summarized in

$$^{\dagger} \tau = \frac{\phi_a^{7/3}}{\phi^2} = S_g^{7/3} \phi^{1/3}$$

Figure 6. Sketch of the capped column apparatus used by Jury and Miller (1974) and the corresponding TOUGH2 model.

Figure 7. Predicted and measured steady-state water content profiles of the capped column experiment of Jury and Miller (1974) denoted by lines and symbols, respectively.

Figure 8. Simulated steady-state water content profiles using Millington and Quirk (1961) (solid lines) and enhanced vapor diffusion ($\tau \phi S_g = 1$) (dashed lines).

Table 4. The increased vapor flow rate ranges from 11 for the lowest average moisture content to about 1300 for the highest average moisture content; the corresponding increase in heat flux varies from 4% to 1.6%, respectively. Interestingly, the highest heat flux ratio occurs for the lowest vapor flux ratio. Therefore, moisture content distributions and heat fluxes (and thermal conductivities) seem to be insensitive to the possibility of enhanced vapor diffusion for this capped column experiment, which is typical of soil science experimental configurations.

4.2 Analysis of Open-Ended Experiment (Lee et al., 1992)

An open-ended drying experiment (Lee et al., 1992) is modeled using the same TOUGH2 code described in the previous section. This experiment is typical of many drying experiments described in the engineering literature and is shown in Figure 9 along with the corresponding TOUGH2 model. The unique aspect of this experiment is that a thorough description of the experimental parameters including characteristic curves of the porous medium and system boundary conditions is provided in Lee et al. (1992), which aids in the modeling effort. A square Plexiglass container holding 450 μm glass beads was initially saturated with water. Heated air at a constant temperature flowed over the top of the open container, creating a stagnant flow at the surface. Analysis of the stagnant boundary layer yields a heat transfer coefficient equal to 45 $\text{W/m}^2\text{-K}$. The effective distance assuming a linear temperature gradient between the surface and the constant hot-air boundary used in the TOUGH2 model is calculated by setting the convective heat transfer from the surface equal to the conduction across the surface. The resulting distance is 0.64 mm. Because the Lewis number (ratio of thermal diffusivity to mass diffusivity) is near one, the same distance applies for the mass transfer boundary as well. This distance is used in the model as the distance from the surface to the hot-air boundary element.

For simplicity, the surface areas available for heat and mass transfer are assumed to be equal. Rigorously speaking, as the surface dries and becomes only partially covered by liquid, the heat and mass transfer surface areas will not be equal as discussed by Kaviany and Mittal (1987) and

Table 4. Simulation results of capped column experiment (Jury and Miller, 1974)

Average Moisture Content	0.10	0.16	0.20	0.30
Average β ratio ¹	12	29	67	2300
Heat Flux Ratio ¹	1.040	1.036	1.032	1.016
Vapor Flux Ratio ¹	11	27	59	1280

¹(enhanced vapor diffusion)/(no enhanced vapor diffusion)

Figure 9. Sketch of experimental apparatus used by Lee et al. (1992) and corresponding TOUGH2 model for open-ended convective drying experiments.

Plumb et al. (1985). However, these effects were not included in the present model.

The container was insulated along only two of its four sides as a result of the instrumentation, so heat gain to the system may have occurred as hot air flowed past the sides of the container. Modeling studies in this paper do not consider this potential heat gain. Liquid saturations and temperatures were recorded and are used as a basis for comparison with the numerical predictions using TOUGH2. A summary of important experimental and model parameters is given in Table 5.

Three different simulations were performed with the TOUGH2 model to determine the sensitivity of this system to the diffusion coefficients given in equation (8). In the first simulation, the tortuosity was assumed to be constant at 0.7. Penman (1940) showed experimental results that indicated the tortuosity was near this value and invariant with saturation. The second simulation used the expression given by Millington and Quirk (1961) for the tortuosity as described in the previous section. The third simulation assumes enhanced vapor diffusion exists so that the product of the tortuosity coefficient, porosity, and gas-phase saturation equals one (Jury and Letey, 1979).

Figure 10 shows the predicted and experimentally measured liquid saturations at four times during the drying experiment for the experiment and each of the three simulations. None of the models does an exceptional job of matching the results, but the results of the constant tortuosity factor (Figure 10(b)) appear to match the experimental trends the best. The results from the Millington and Quirk model (1961) show that drying takes much longer than the other two simulations as a result of the initially high saturations of the experiment. According to the Millington and Quirk model (1961), the tortuosity coefficient (and hence diffusion) is significantly reduced when the gas saturation is low. The drying is considerably faster in the other two simulations which use fixed values for the tortuosity. Heat transfer along the bottom or sides of the apparatus that were not considered in the model may contribute to the discrepancies between simulated and observed results in Figure 10. Other possible causes for the observed discrepancies include mechanisms and features such as vapor pressure lowering, sub-residual liquid transport, and heterogeneous saturation distributions that were not considered in the model.

Figure 11 shows the predicted and experimentally measured temperatures as a function of time for three locations in the experiment. All the results show that the temperatures experience a series of “plateaus” corresponding to the drying of particular regions. The experimental data shows that the wet bulb temperature of the surface is around 40°C (Figure 11(a)). The constant tortuosity model (Figure 11(b)) and the Millington and Quirk model (1961) (Figure 11(c)) show similar wet bulb temperatures, while the enhanced vapor diffusion model (Figure 11(d)) shows that the wet

(a)

(b)

(c)

(d)

Figure 10. Predicted and measured values of liquid saturation during the drying experiment of Lee et al. (1992). In addition to the experimental data (a), results from three models of the vapor diffusion coefficient are shown: b) constant tortuosity (Penman, 1940), c) Millington and Quirk (1961), and d) enhanced vapor diffusion (Jury and Letey, 1979).

Table 5. Summary of important experimental and model parameters for the open-ended experiment of Lee et al. (1992).

Bead size (μm)	450	Lee et al. (1992)
Total porosity	0.346	Lee et al. (1992)
Permeability (m^2)	1.31×10^{-10}	Blake-Kozeny (Ergun, 1952)
Air thermal conductivity (W/m-K)	0.03	Incropera & DeWitt (1985)
Water thermal conductivity (W/m-K)	0.63	"
Effective dry thermal conductivity (W/m-K)	0.3	Kaviany (1991), Hadley (1986)
Effective wet thermal conductivity (W/m-K)	1.1	"
Air-vapor diffusion coefficient (m^2/sec)	2.13×10^{-5}	Pruess (1991)
Temperature exponent for diffusion, θ	1.8	"
Specific heat of glass beads (J/kg-K)	750	Incropera & DeWitt (1985)
Density of glass beads (kg/m^3)	2500	Lee et al. (1992)
Air velocity (m/sec)	4.8	"
Air temperature ($^{\circ}\text{C}$)	65	"
Dew point ($^{\circ}\text{C}$)	5	"
Partial vapor pressure (Pa)	872	
Saturated vapor pressure (Pa)	25,000	
Relative humidity (%)	3.5	
Air mass fraction	.99461	
Residual liquid saturation	0.1	Lee et al. (1992)
van Genuchten α (Pa^{-1})	7.518×10^{-4}	"
van Genuchten m	0.9331	"

bulb temperature of the surface is just over 30°C . The trends shown in the constant tortuosity model and the enhanced vapor diffusion model seem to match best with the experimental data, while the Millington and Quirk model (1961) exhibits a considerable amount of heating initially as a result of the minimal diffusion at early times when the experiment is nearly saturated. Additional mechanisms and features not considered in the model such as vapor pressure lowering, sub-residual liquid transport, and heterogeneous saturation distributions may also contribute to the discrepancies between the simulated and observed results.

These results show that the open-ended drying experiment is very sensitive to the diffusion coefficients. However, the high initial saturation of this experiment and the heating configuration do not allow for rigorous assessment of the enhanced vapor diffusion coefficient. Top- or bottom-heated experiments at lower saturations seem more promising in providing useful data to assess enhanced vapor diffusion based on the simulations and results of this experiment.

(a)

(b)

(c)

(d)

Figure 11. Predicted and measured values of temperatures during the drying experiment of Lee et al. (1992). In addition to the experimental data (a), results from three models of the vapor diffusion coefficient are shown: b) constant tortuosity (Penman, 1940), c) Millington and Quirk (1961), and d) enhanced vapor diffusion (Jury and Letey, 1979).

4.3 Pore-Scale Analysis

A simple pore-scale analysis can be performed to estimate the steady-state mass flow of water across liquid islands due to condensation and evaporation mechanisms (Path A in Figure 12). A comparison of this flux to the flux of water vapor caused by Fickian diffusion (Path B in Figure 12) is made to discern the relative importance of enhanced vapor diffusion mechanisms.

Figure 12. Pore-scale transport paths: A) enhanced vapor diffusion mechanisms and B) Fickian diffusion.

Path A

Consider the space between two solid particles that contains entrapped liquid water as shown in Figure 13. A thermal gradient in the water-wet porous medium induces vapor diffusion from the hot region (left side) to the colder regions (right side). An energy balance is performed on a control volume of the surface of the liquid island exposed to the hotter side (Figure 13). The latent heat of condensation on the upstream side of the liquid island is balanced by conduction through the liquid island:

$$m_{v, evd} h_{fg} = \lambda_l A_t \frac{\Delta T}{L} \quad (9)$$

where $m_{v, evd}$ is the mass flow rate of vapor that condenses on the upstream end of the liquid island, h_{fg} is the latent heat of condensation, λ_l is the liquid thermal conductivity of water, A_t is the cross-sectional area of the surface of the liquid island, ΔT is the temperature difference across the liquid island, and L is the linear distance across the liquid island. Rearranging equation (9) yields an expression for the mass flow of vapor due to the postulated enhanced vapor diffusion mechanisms of condensation/evaporation:

$$m_{v, evd} = A_t \frac{\lambda_l}{h_{fg}} \frac{\Delta T}{L} \quad (10)$$

Figure 13. Sketch of the pore-scale model and a control surface on which the energy balanced is performed.

Path B

Fick's law is now used to determine the mass flow of vapor if vapor diffusion has to occur around (rather than through) the liquid island shown in Figure 12:

$$m_{v, Fick} = -D A_p \nabla C = -D A_p \frac{\partial C}{\partial T} \frac{\partial T}{\partial x} \quad (11)$$

where $m_{v, Fick}$ is the mass flow rate of vapor around the liquid island due to Fickian diffusion, D is the binary diffusion coefficient of air and water vapor in free space, A_p is the cross-sectional area of pore space available for diffusion, and C is the concentration (density) of water vapor. The ideal gas law is used to express the water vapor concentration, and the temperature gradient is expressed in terms of the temperature difference across the liquid island and the tortuosity, τ (actual path length divided by linear path length, L):

$$m_{v, Fick} = D A_p \frac{M_v}{R T} \frac{\partial P_v}{\partial T} \frac{\Delta T}{\tau L} \quad (12)$$

where M_v is the molecular weight of water (18 kg/kmol), R is the ideal gas constant (8300 J/kmol-K), and P_v is the saturated vapor pressure of water.

Ratio

Equation (10) is divided by equation (12) to obtain a ratio of the mass flow rates due to enhanced vapor diffusion mechanisms and Fickian diffusion:

$$\frac{m_{v, evd}}{m_{v, Fick}} = \frac{A_t}{A_p} \frac{\lambda_l}{h_{fg} D} \frac{R T}{M_v} \frac{\tau}{\left(\partial P_v / \partial T \right)} \quad (13)$$

A value of this ratio on the order of one or more indicates that enhanced vapor phase diffusion can be significant relative to Fickian diffusion in transporting water vapor through a water-wet porous medium under a thermal gradient. Table 6 gives values for several parameters in equation (13) at 20°C.

Table 6. Parameter values at 20°C.

λ_l (W/m-K)	0.6
h_{fg} (J/kg)	2.45×10^6
D (m ² /sec)	2×10^{-5}
$\partial P_v / \partial T$ (Pa/K)	146

Plugging the values in Table 6 into equation (13) yields the following expression:

$$\frac{m_{v, evd}}{m_{v, Fick}} = 11.3 \frac{A_t}{A_p} \tau \quad (14)$$

Assuming that the cross-sectional area of the liquid island and the pore space available for vapor diffusion are similar and that the tortuosity is on the order of 1, equation (14) yields the following:

$$\frac{m_{v, evd}}{m_{v, Fick}} \sim 10 \quad (15)$$

This result indicates that the contribution of water vapor transport by condensation and evaporation mechanisms across liquid islands may be significant when compared to Fickian diffusion around liquid islands. Additional pore-scale modeling is currently being performed to more rigorously assess the condensation and evaporation mechanisms across liquid islands. However, the extent, applicability, and existence of enhanced vapor diffusion mechanisms remain to be demonstrated.

5. Conclusions and Recommendations

Although many claims have been made regarding enhanced vapor diffusion, only indirect evidence exists to confirm the enhancement and postulated mechanisms. In experiments performed in soil science, vapor flux was always inferred from other measurements such as moisture content and heat flux; none of the previous experiments measured the vapor flux directly. In addition, the theoretical analyses used in many of the previous models that were used to back-calculate a vapor-diffusion enhancement factor, β , were incomplete, especially in the treatment of gas-phase advection and liquid flow below residual saturation values. Water flow was attributed to vapor diffusion without consideration of the appropriate liquid flow mechanisms. More comprehensive models of moisture transport presented in the engineering literature have been used in drying problems, but the experiments have not focused on systems where vapor-phase diffusion driven by thermal gradients is dominant. The two analyses presented in this paper of a capped column and an open-ended column have demonstrated these points. Does enhanced vapor-phase diffusion exist? Possibly, but existing experimental data and models are not adequate to evaluate the enhancement mechanisms and the degree of enhancement due to vapor diffusion alone. A simple pore scale model has shown that condensation and evaporation mechanisms can be significant relative to Fickian diffusion, but the existence of these mechanisms remains to be demonstrated. A need therefore exists for a comparison between comprehensive theoretical analyses of moisture transport and experiments designed to observe and monitor vapor diffusion. Additional experiments that focus on enhanced vapor-phase diffusion are required to evaluate these models.

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