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A Model for the Effective Diffusion of Gas or
the Vapor Phase in a Fractured Media
Unsaturated Zone Driven by Periodic
Atmospheric Pressure Fluctuations

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A Model for the Effective Diffusion of Gas or the Vapor Phase in a Fractured Media Unsaturated Zone Driven by Periodic Atmospheric Pressure Fluctuations

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Abstract

There is evidence for migration of tritiated water vapor through the tuff in the unsaturated zone from the buried disposal shafts located on a narrow mesa top at Area G, Los Alamos, NM. Field data are consistent with an effective in-situ vapor phase diffusion coefficient of $1.5 \times 10^{-3} \text{ m}^2/\text{s}$, or a factor of 60 greater than the binary diffusion coefficient for water vapor in air. A model is derived to explain this observation of anomalously large diffusion, which relates an effective vapor or gas phase diffusion coefficient in the fractured porous media to the subsurface propagation of atmospheric pressure fluctuations (barometric pumping). The near surface (unattenuated) diffusion coefficient is independent of mode period under the simplified assumptions of a complete 'mixing mechanism' for the effective diffusion process. The unattenuated effective diffusion driven by this barometric pumping is proportional to an average media permeability times the sum of the square of pressure mode amplitudes, while the attenuation length is proportional to the square root of the product of permeability times mode period. There is evidence that the permeability needed to evaluate the pressure attenuation length is the in-situ value, approximately that of the matrix. The diffusion which results using Area G parameter values is negligible in the matrix but becomes large at the effective permeability of the fractured tuff matrix. The effective diffusion coefficient predicted by this model, due to pressure fluctuations and the observed fracture characteristics, is in good agreement with the observed in-situ diffusion coefficient for tritium field measurements. It is concluded that barometric pumping in combination with the enhanced permeability of the fractured media is a likely candidate to account for the observed in-field migration of vapor in the near surface unsaturated zone at Area G. The model results imply that vapor flux through fracture apertures is potentially an order of magnitude larger than the vapor flux through the matrix.

Introduction

Low level radioactive waste disposal occurs in Los Alamos at Area G, located on the top of a long and narrow finger mesa, with a cross-section width varying in the range from 400 ft to 1000 ft, and an average height of about 100 feet above the adjacent canyon floors. The mesa interior is a complex layered stratigraphy, composed of Bandalier Tuff resulting from volcanic and ash flows [Krier, et.al.95]. The tuff is highly fractured throughout the mesa volume, and much of the tuff matrix has a very low moisture content (<4% volumetric). Vapor phase transport has long been hypothesized as a dominant contributor to the drying of the mesa interior [IT,87]. Recent liquid flux analyses [Vold,96A], vapor flux analyses [Vold,96B] and chloride ion profile analyses [Newman,96] are consistent with this hypothesis and provide estimates of the magnitude of the liquid and vapor flux throughout the mesa. Understanding these fluxes and their magnitudes is essential to the Performance Assessment of the site [Hollis,et.al.,95] as required per U.S. Department of Energy Order 5820.2A.

Field data on the migration of tritiated water vapor from disposal shafts at Area G through the unsaturated zone are consistent with an effective in-situ vapor phase diffusion coefficient of $1.5 \times 10^{-3} \text{ m}^2/\text{s}$ [Vold and Eklund,96], or a factor of 60 greater than the binary diffusion coefficient for water vapor in air. This empirically determined vapor phase diffusion coefficient was used to estimate the vapor flux in the mesa [Vold,96B], although the physical basis for the diffusion of this magnitude was not previously determined. It is important to understand the underlying mechanisms behind the 'enhanced' in-situ diffusion in order to understand the implications for contaminant transport from the disposal facility through the unsaturated zone to the environment. A review of the literature related to enhanced diffusion due to barometric pumping is discussed and included in the references to [Neeper,91].

In this study, a model is proposed for an effective diffusion of vapor or gas phase contaminants in a fractured porous media driven by atmospheric pressure fluctuations. The governing equations are derived and then evaluated for the field parameters appropriate to Area G. The derivation is

intended to briefly outline the model while being sufficiently rigorous so that the results provide a quantitative estimate of the effective diffusion process.

The effective diffusion coefficient resulting in the model is compared to the effective vapor phase diffusion coefficient observed in the tritium field study. It will be seen that there is good agreement between the model result and the field observations when the effective permeability of the fractured media is included. This supports the conclusion that the model may incorporate the essential physics of the observed in-situ diffusion. In the present model, a convective displacement distance is calculated for each mode period of the imposed periodic pressure oscillation and a self-consistent effective diffusion is determined. This is in contrast to a recent investigation [Auer,et.al.95] in which the displacement distance is considered to be a dispersion length, an independent empirically determined value.

Model Derivation

Vapor Flux

The continuity equation for the vapor density, ρ_v , in a porous media with an 'air-filled volumetric fraction', θ_a , is

$$\frac{\partial(\theta_a \rho_v)}{\partial t} + \nabla \cdot \Gamma_v = S_v \quad (1)$$

where the source term, S_v , can be used to characterize changes due to phase exchange (condensation or evaporation) or media exchange (e.g., rock matrix to fracture matrix). The vapor phase flux of moisture in the porous media, Γ_v , can be written

$$\Gamma_v = \theta_a \rho_v u_a - D_v \nabla \rho_v \quad (2)$$

where D_v is a total effective diffusion coefficient which incorporates θ_a and contains contributions from classical diffusion in a porous media and from diffusion driven by fluctuations in gradient force terms. This can include barometric pumping in an environment subject to atmospheric pressure fluctuations, as detailed in this report.

The mean vapor flow is equal to the air flow, u_a , in a porous media driven by the pressure gradient and derived as the solution to the momentum equation for the total gaseous and vapor phase. This is given as

$$u_a = - \frac{K_p}{\mu \varepsilon} \nabla p \quad (3)$$

where K_p is the media permeability [m^2], μ is viscosity for the air phase, ε is the porosity and p is the atmospheric pressure. The pressure gradient and thus the mean velocity are fluctuating quantities and average to zero over time.

The gradient in vapor density, ρ_v in Eqn.2, can be written in terms of vapor pressure, p_v , noting the ideal gas law, $\rho_v = M_v n_v = M_v p_v / RT$. The air and vapor temperatures, T , are the same to a good approximation at a given location within the porous media. It is convenient to express the vapor density in terms of the saturated vapor pressure, p_s , because this is a sensitive function of temperature and dominates the temperature dependence of the vapor density. Assuming the temperature dependence is approximated by that of the saturated vapor pressure (or $1/T$ is approximately constant over the environmental range of T) then one can write

$$\nabla \rho_v \sim \frac{M_v}{RT} \nabla (p_v) = \frac{M_v}{RT} \nabla \left(\left(\frac{p_v}{p_s} \right) p_s \right). \quad (4)$$

A static equilibrium shows $p_v/p_s \sim \exp(h_m/h_c)$, where $h_c = RT/M_v g = 13,300m$ and h_m is the matric potential magnitude expressed as a (water) height. The values indicate that $p_v/p_s \sim 1$ within most porous media under environmental conditions. As detailed previously [Vold,96B], the slight departure from unity is important in determining the dependence upon the gradient in matric potential, h_m . Substituting the static equilibrium into this last equation, the gradient of the vapor flux, $\nabla \rho_v$, can be written approximately as

$$\nabla \rho_v \sim \frac{M_v}{RT} \left(\nabla p_s + \frac{p_s}{h_c} \nabla h_m \right), \quad (5)$$

or expanding in terms of the gradients in the field quantities, T and θ ,

$$\nabla \rho_v \sim \frac{M_v}{RT} \left(\frac{dp_s}{dT} \nabla T + \frac{p_s}{h_c} \frac{dh_m}{d\theta} \nabla \theta \right). \quad (6)$$

The diffusive component of the vapor flux, Γ_{vD} , can then be written

$$\Gamma_{vD} = - D_v \nabla \rho_v \sim - D_v \frac{M_v}{RT} \left(\frac{dp_s}{dT} \nabla T + \frac{p_s dh_m}{h_c d\theta} \nabla \theta \right). \quad (7)$$

A similar expression was derived in [Philips and de Vries,57]. This is combined with the convective air flow to give an expression for the total vapor phase moisture flux in terms of gradients in three state variables for the vapor: pressure, temperature and moisture content,

$$\begin{aligned} \Gamma_v &= \theta_a \rho_v u_a - D_v \nabla \rho_v \\ \Gamma_v &= - \theta_a \rho_v \frac{K_p}{\mu \varepsilon} \nabla p - D_{v(T)} \frac{M_v}{RT} \frac{dp_s}{dT} \nabla T - D_{v(\theta)} \frac{M_v}{RT} \frac{p_s dh_m}{h_c d\theta} \nabla \theta. \end{aligned} \quad (8)$$

The diffusion coefficient, D_v , has been written as two different factors to account for the possibility of different values driving the temperature and moisture gradient terms.

Each diffusion coefficient will be expressed as a sum of two terms, one related to classical diffusion, D_o , and one to a 'fluctuation enhanced' diffusion coefficient, D_{os} , due to temperature or pressure oscillations. The diffusion coefficient for flux with respect to the gradient in either temperature or moisture content, $D_{v(T-\theta)}$, is then written as

$$D_{v(T-\theta)} = \frac{\theta_a}{\phi} D_o + D_{os(T-\theta)}, \quad (9)$$

where ϕ is a tortuosity factor, typically taken to be about 2 [Koorevaar,et.al.,83]. The classical diffusive component is expected to be similar for the gradients in temperature or moisture content. It is the fluctuation enhanced diffusion which will be shown to be different for the temperature and moisture gradient terms, thus, the distinct coefficients, $D_{v(T)}$ and $D_{v(\theta)}$. It is common in the literature to see enhanced diffusion effects incorporated as a multiplying factor times the classical diffusion [Philip and de Vries,57], however, the present analysis indicates these diffusive mechanisms should be treated as separate terms.

Based on field observations at Area G, the moisture gradients (as in Eqn.8) vary slightly or not at all below about 2m from the surface, and so for this study they are considered to be approximately steady state profiles. The pressure and temperature gradients are considered to be periodic functions in time driven by surface fluctuations which propagate down into the subsurface region. Pressure modes are dominated by periods of one year and approximately one week while temperature fluctuations contain predominantly daily and annual modes. These fluctuation spectra were quantified previously [Vold,96C].

Pressure Fluctuations

Pressure fluctuations propagate through the subsurface according to a transient diffusion equation. Assuming isothermal conditions, pressure can be substituted for density in the continuity equation, and combined with the porous media velocity (Eqn.3) to obtain this diffusion equation for the pressure fluctuations, p ,

$$\frac{\partial p}{\partial t} + \nabla \cdot \left(- \frac{K_p p_0}{\mu \varepsilon} \nabla p \right) = 0, \quad (10)$$

where the air pressure has been linearized into a steady and fluctuating term, $p_a = p_0 + p$. This defines the diffusion coefficient for the pressure fluctuations, D_p , as

$$D_p \equiv \frac{K_p p_0}{\mu \varepsilon}. \quad (11)$$

This diffusion coefficient is approximated as a constant in space, and a periodic boundary condition is applied of the form, $p = \Delta p_m \sin(2\pi t/\tau_m)$, where Δp_m and τ_m are, respectively, the amplitude and period for a particular mode of the pressure fluctuations at the ground surface boundary. Surface fluctuations in pressure can be expressed as a Fourier series, a sum over periodic modes. The analytic solution to Eqn.10 in 1-D [Carslaw and Jaeger,59] for these periodic surface variations in pressure which propagate a distance, z , into a semi-infinite medium is

$$p = \sum_{m=1}^{\infty} \left((\Delta p_m / L_m) e^{-z/L_{pm}} \sin(2\pi t/\tau_m - x/L_{pm}) \right), \quad (12)$$

where the attenuation length for each pressure mode, L_{pm} , is

$$L_{pm} = \sqrt{\frac{D_p \tau_m}{\pi}} = \sqrt{\frac{K_p p_o \tau_m}{\mu \varepsilon \pi}}. \quad (13)$$

Propagation into a finite medium, as might be expected for an unsaturated zone bounded at the bottom by a saturated zone which is relatively impermeable to air, is described by a more complex function [Auer,et.al,95]. Quantitatively, the near surface results for that solution are nearly identical to the exponential form in Eqn.12, when the saturated zone is deep relative to the depths of concern and to the mode length of interest. It is the near surface region of interest in this study (<100 ft depths, compared to the depth to the saturated aquifer at Area G of about 900 feet) and so the simpler exponential solution form above is used.

For the periodic surface variations in pressure propagating into a semi-infinite medium, the solution to the pressure diffusion equation (Eqn.12) can be substituted into the expression for air velocity in the porous media (Eqn.3) to obtain the result for the velocity at depth, $u_a(z,t)$, driven by the surface fluctuations in pressure. The result, by analogy to the heat flux problem [Chapman,74], is

$$\begin{aligned} u_a(z,t) &= -\frac{K_p}{\mu \varepsilon} \nabla p \\ &= \sqrt{2} \frac{K_p}{\mu \varepsilon} \sum_{m=1}^{\infty} \left((\Delta p_m / L_m) e^{-z/L_{pm}} \sin(2\pi t/\tau_m - x/L_m + \pi/4) \right) \end{aligned} \quad (14)$$

which applies to the velocity component along the axis of the pressure gradient.

The distance that the air moves through the porous media by the pressure driven convective motion during each period, τ_m , is called the

pressure mode displacement distance, d_{pm} , evaluated as an average magnitude of the displacement over the period. The average half cycle displacement, d_{hm} , is approximately $d_{hm} \sim u_m \tau_m$, and is evaluated more accurately as an integral over time for the convective motion at any depth,

$$d_{hm} = \int_0^{\tau_m/2} u_{om}(z) \sin(2\pi t/\tau_m) dt = \frac{2 u_{om} \tau_m}{\pi}, \quad (15)$$

where $u_{om}(z)$ is a maximum amplitude at a given depth. The phase shift is ignored because we are interested only in the magnitude of the oscillation at some specific depth. Ignoring the phase is a reasonable approximation for a few limited discrete modes, e.g., the one year and one week periods which dominate the observed atmospheric pressure fluctuations [Vold,96C], provided that the power for the displacement in each mode is correctly derived from the spectral distribution of pressure fluctuation data. Ignoring the phase is not accurate for quantitative analysis where many modes with similar periods play a role, such as in reconstructing a particular time series of pressure fluctuation data [Neeper,et.al.,96], however, it is adequate for the present analysis.

During the second half of the convective displacement cycle, the flow direction reverses, and the same displacement occurs in the opposite direction so that the pressure mode displacement distance over the full convective cycle for a particular mode becomes

$$d_{pm} = 2d_{hm} = \frac{4 u_{om}(z) \tau_m}{\pi}. \quad (16)$$

Effective Diffusion

A mass diffusion coefficient, D , can be expressed as a characteristic step size, d , times a mass speed, u , or

$$D \sim d u, \quad (17)$$

which applies under appropriate conditions where a 'mixing mechanism' exists. An effective diffusion process can result when the periodic fluctuating

velocity occurs in the presence of a gradient in the quantity to be diffused. In the pressure driven periodic convective process, the parameters required for a diffusion-like mechanism, a characteristic step size, d , and a mass speed, u , correspond to a mode displacement distance, d_m , and an average mass flow speed related to the magnitude of the fluctuating velocity, $u_a(z)$. The 'mixing mechanism' in the porous media flow is assumed to be generated by classical diffusion across the laminar velocity profile within the pore spaces of the medium, and also by diffusion between pore spaces of varying connectivity. This molecular diffusion is a fast process relative to the pressure driven convective motion given in Eqn.14. Another mechanism possibly contributing to this 'mixing' is the superposition (and relative phase) of harmonic and non-harmonic modes on top of the fundamental mode in the spectral distribution of fluctuations.

An additional condition for the effective diffusion process to occur is that the mode displacement distance, d_m , should be small compared to the mode attenuation length for the driving force, L_m . Analyses indicate that the ratio, d_m/L_m , is independent of mode period, τ_m , for the pressure gradient driven flux (as seen in the following) and also for the temperature gradient flux (Eqn.8). For the temperature gradient flux, it is always true (work in progress) that $d_{Tm}/L_{Tm} \gg 1$, and so enhanced diffusion due to temperature fluctuations does not occur. On the other hand, the inequality indicates that significant convection over each period cycle can occur throughout the porous region where the temperature fluctuations penetrate. This is restricted to the near surface ($L_T < 2-4m$, typically) and has been discussed in detail [Milly,96].

For pressure fluctuations it is shown here that $d_{pm}/L_{pm} \ll 1$, for the permeability values associated with the Area G subsurface tuff material. Referring to Eqn.14 and 15, the maximum near-surface (unattenuated, or $z = 0$) mass convection speed associated with a particular perturbation velocity mode, $u_{om}(z=0)$ can be approximated as

$$u_{om}(z=0) \sim \sqrt{2} \frac{K_p}{\mu \epsilon} \left(\frac{\Delta p_m}{L_m} \right) \quad (18)$$

Using this with Eqn.16, the ratio of the near surface mode displacement distance to the attenuation length is

$$d_{pm}/L_{pm} \sim \frac{4 u_{om} \tau_m}{\pi L_m} = \frac{4 \tau_m \sqrt{2} K_p}{\pi \mu \varepsilon} \left(\frac{\Delta p_m}{L_m^2} \right). \quad (19)$$

It will become an important issue in matching the model results with field data as discussed later to distinguish two values for the 'in-situ volume average' permeability. One value of K_p is used to evaluate the displacement distance in Eqn.19 which will be denoted as K_{pd} , while the second permeability will be used to evaluate the attenuation length and will be denoted K_{pL} . With this consideration, $K_p = K_{pd}$, in Eqn.19 while $K_p = K_{pL}$ in L_{pm} from Eqn.13. Equation 19 is then rewritten using Eqn.13 as

$$\begin{aligned} d_{pm}/L_{pm} &= \frac{4 \tau_m \sqrt{2} K_p}{\pi \mu \varepsilon} \left(\frac{\Delta p_m}{L_m^2} \right) \\ &= \frac{4 \tau_m \sqrt{2} K_{pd}}{\pi \mu \varepsilon} \left(\frac{\Delta p_m \mu \varepsilon \pi}{K_{pL} p_o \tau_m} \right) = \sqrt{32} \frac{K_{pd} \Delta p_m}{K_{pL} p_o}. \end{aligned} \quad (20)$$

Under the condition that the permeabilities are the same, $K_{pd} = K_{pL}$, then the ratio of lengths is just proportional to the ratio of magnitudes of the pressure fluctuation to the steady ambient pressure. Since these are typically 1 mbar and 800mbar (at LANL 7000 ft elavation) the ratio of lengths is much less than unity, provided the permeabilities do not differ greatly. Under these conditions, enhanced diffusion due to pressure fluctuations could occur.

As discussed, the diffusion coefficient from this pressure driven periodic convective process for a particular mode, D_{pm} , is the displacement step size, d_{pm} , times an average displacement mode speed, $u_m(z)$, corresponding to a single term in the velocity series given in Eqn.14. The diffusion coefficient per mode for this process is then related to average displacement and speed quantities as

$$D_{pm} \sim d_{pm} u_m \sim (u_m \tau_m) u_m \sim u_m^2 \tau_m. \quad (21)$$

Using the integral over the sinusoidal variation as in Eqn.15 to evaluate the average quantities over the displacement oscillation, the diffusion coefficient becomes

$$D_{pm} \sim d_{pm} u_m = \frac{4 u_{om} \tau_m}{\pi} \frac{2 u_{om}}{\pi} = 2 (2/\pi)^2 u_{om}^2 \tau_m, \quad (22)$$

where u_{om} is the mode maximum speed corresponding to the pressure fluctuation mode maximum, Δp_m . A similar expression for this diffusion coefficient, but with a smaller leading coefficient value of 0.1, was previously discussed in comparison to experimental results for flow in porous media [Eqn.7 in Peterson, et.al.,1987].

The diffusion coefficient is the result of periodic convective processes occurring in the presence of a gradient of a quantity dispersed within the convective flow. The diffusion coefficient can be derived in a simplified manner as follows, writing the convective vapor flux from Eqn.2 as

$$\Gamma_v = \theta_a \rho_v(z) u_a(z,t). \quad (23)$$

Variation in the air filled volume fraction, θ_a , is neglected and a linear gradient in the vapor phase density is assumed so that

$$\rho_v(z) = \rho_{v0}(z_0) + \nabla_z(\rho_v) (z-z_0). \quad (24)$$

The time and space dependent velocity, $u_a(z,t)$, is given by Eqn.14. One can ignore the variation with depth here. The phase of the velocity is ignored with the caveats discussed after Eqn.14. For this derivation, it is assumed that each velocity mode looks like $u(z,t) = u_{om}(z) \sin(2\pi t/\tau_m)$, where $u_{om}(z)$ is the maximum convective speed at a given depth independent of the phase. From Eqns.14 and 18, this vapor mass convective speed is equal to

$$u_{om}(z) = \sqrt{2} \frac{K_p}{\mu \varepsilon} \frac{\Delta p_m}{L_m} \exp(-z/L_m). \quad (25)$$

The flux for a single mode is considered first. The average flux per mode over one period is

$$\Gamma_v(z) = \frac{\int_0^{\tau_m} \theta_a \rho_v(z) u(z,t) dt}{\int_0^{\tau_m} dt} = \frac{\theta_a}{\tau_m} \int_0^{\tau_m} [\rho_{v0}(z_0) + \nabla_z(\rho_v)(z-z_0)] u(z,t) dt \quad (26)$$

The convective flux couples the movement in time and space, and the integral depends upon the assumptions made regarding the coupling of the displacement, $z - z_0$, and the convective motion, $u(z,t)$. The crossfield mixing is here assumed to be complete. In this case, the displacement is averaged over each half cycle of the convective flow separately to distinguish the flow in opposite directions. Then for example, $(z - z_0) = d_{hm}$, is the displacement over the half period, $t = 0$ to $t = \tau_m/2$. The flux is integrated separately for the two half periods of the convective flow as

$$\Gamma_v(z) = \frac{\theta_a}{\tau_m} \int_0^{\tau_m/2} [\rho_{v0}(z_0) + \nabla_z(\rho_v)(d_{hm})] u(z,t) dt + \frac{\theta_a}{\tau_m} \int_{\tau_m/2}^{\tau_m} [\rho_{v0}(z_0) + \nabla_z(\rho_v)(-d_{hm})] u(z,t) dt, \quad (27)$$

where the sinusoidal variation of $u(z,t)$ produces a positive half cycle displacement during the first half of the oscillation (when the convective velocity is positive), and a negative displacement ($z < z_0$), during the second half cycle (when the convective velocity is negative). Thus the oscillating flow 'sees' an average concentration during each half cycle of, respectively, $\rho_{0z} + \nabla_z \rho_v(d_{hm})$, and $\rho_{0z} - \nabla_z \rho_v(d_{hm})$. The integral is simplified by assuming an average displacement distance, d_{hm} , over each half period, which was found above to be

$$d_{hm} = \frac{2 u_{0m} \tau_m}{\pi}. \quad (28)$$

Substituting in, the integral takes the form

$$\begin{aligned}
\Gamma_v(z) = & \frac{\theta_a}{\tau_m} \int_0^{\tau_m/2} [\rho_{v0}(z_0) + \nabla_z(\rho_v) \left(\frac{2 u_{om} \tau_m}{\pi} \right)] u_{om} \sin(2\pi t/\tau_m) dt + \\
& \frac{\theta_a}{\tau_m} \int_{\tau_m/2}^{\tau_m} [\rho_{v0}(z_0) + \nabla_z(\rho_v) \left(-\frac{2 u_{om} \tau_m}{\pi} \right)] u_{om} \sin(2\pi t/\tau_m) dt ,
\end{aligned} \tag{29}$$

The integral terms are evaluated as

$$\Gamma_v(z) = \frac{\theta_a}{\tau_m} \left(\rho_{v0} + \nabla_z(\rho_v) \left(\frac{2 u_{om}^2 \tau_m}{\pi} \right) \right) \frac{2\tau_m}{\pi} + \frac{\theta_a}{\tau_m} \left(\rho_{v0} - \nabla_z(\rho_v) \left(\frac{2 u_{om}^2 \tau_m}{\pi} \right) \right) \left(-\frac{2\tau_m}{\pi} \right) \tag{30}$$

The ρ_{v0} terms cancel in the two integrals for each half of the cycle, while the $\nabla \rho_v$ terms add together. The solution simplifies as

$$\Gamma_v(z) = - 2 \left(\frac{2}{\pi} \right)^2 \theta_a u_{om}^2 \tau_m \nabla \rho_v . \tag{31}$$

where the minus sign is added to account for the sign of the pressure gradient scale length, L_{pm} , and for the convention that flux is directed away from the gradient, $\nabla \rho_v$. The effective diffusion coefficient per convective oscillatory mode is then,

$$D_m \equiv 2 \left(\frac{2}{\pi} \right)^2 \theta_a u_{om}^2 \tau_m . \tag{32}$$

This agrees with the more heuristic estimate in Eqn.19, except the previous estimate neglected the factor for the air volume fraction, θ_a . Note that u_{om} in Eqn.32 can be interpreted as a speed at depth after correcting for the attenuation as given in Eqn.25. Equation 32 gives the appearance that D_m is mode dependent, however, we still need to substitute the expression for $u_{om}(z)$ from Eqn.25. The mode dependency of D_m will then cancel and the near surface unattenuated D_m value becomes mode independent as detailed in the following..

The coefficient, $2(2/\pi)^2$ which resulted from the integration is considered to be a 'coupling coefficient' between the displacement and the velocity, related to their relative phases. A more detailed 'mixing model' might derive a frequency dependence for this coefficient, but in the simple 'complete mixing model' used here, this coupling is frequency independent.

The total flux due to the effective diffusion is a sum over mode contributions. For practical evaluation, this sum is evaluated over a finite series of Discrete Fourier Transform coefficients as described in the Evaluation section and detailed previously [Vold,96C]. The effective diffusion will only apply to pressure modes with a period shorter than the period of the gradient in the driving force, ∇T or $\nabla \theta$, for the vapor flux. Considering the moisture gradient, it was assumed the moisture profiles are approximately steady state, therefore, all the modes in the pressure driven fluctuations will contribute to this effective diffusion coefficient, $(D_{v(\theta)})$. In this case, the appropriate mode sum is restricted by the minimum number of modes needed in the truncated series to adequately represent the full power spectra of the pressure fluctuations.

For the temperature gradient flux in Eqn.8, only those modes of the pressure fluctuations which are of shorter period than the period of the temperature fluctuation will contribute to $D_{v(T)}$. As discussed further in the Evaluation section, this implies only the short term pressure modes (~ 1 week period) contribute to $D_{v(T)}$ and only to the annual temperature gradient mode. For the present analysis we will indicate the summation over a finite number of modes, $nMax$, and note that it is differences in this value which causes $D_{v(T)}$ and $D_{v(\theta)}$ to differ.

The total flux due to the effective diffusion from the pressure fluctuations is thus written using Eqn.25 as a finite sum over mode contributions,

$$\begin{aligned} \Gamma_v(z) &= - D_{v(p)} \nabla \rho_v, \\ &= - 2 \left(\frac{2}{\pi} \right)^2 \theta_a \sum_{m=1}^{nMax} u_{om}^2 \tau_m \nabla \rho_v, \\ &= - 2 \left(\frac{2}{\pi} \right)^2 \theta_a \left(\frac{K_p}{\mu \epsilon} \right)^2 \sum_{m=1}^{nMax} \left((\Delta p_m / L_{pm}) e^{-z/L_{pm}} \right)^2 \tau_m \nabla \rho_v. \end{aligned}$$

(33)

The expression for L_{pm} , from Eqn.13, is substituted into the denominator and the last equation simplifies as

$$\begin{aligned}
 \Gamma_v(z) &= -\left(\frac{8}{\pi}\right) \theta_a \left(\frac{K_p}{\mu \varepsilon p_0}\right) \sum_{m=1}^{nMax} \left(\Delta p_m e^{-z/L_{pm}}\right)^2 \nabla \rho_v. \\
 &= -\left(\frac{8}{\pi}\right) \theta_a \left(\frac{K_p p_0}{\mu \varepsilon}\right) \sum_{m=1}^{nMax} \left((\Delta p_m/p_0)^2 e^{-2z/L_{pm}}\right) \nabla \rho_v. \\
 &= -\left(\frac{8}{\pi}\right) \theta_a D_p \sum_{m=1}^{nMax} \left((\Delta p_m/p_0)^2 e^{-2z/L_{pm}}\right) \nabla \rho_v.
 \end{aligned}
 \tag{34}$$

Thus, the near surface (unattenuated or $z = 0$) effective diffusion for water vapor (or generally for any contaminant gas entrained in the pressure fluctuation driven convective air flow within the porous media) is reduced from the pressure fluctuation diffusion coefficient, D_p , by the sum of the square of the mode amplitudes normalized to the ambient pressure. This result also shows the near surface diffusion coefficient is independent of mode period, and the subsurface diffusion coefficient depends upon mode period only through the exponential attenuation in $L_{pm}[\tau_m]$. This result is partially a consequence of the simplified 'mixing mechanism' assumed for fully mixed laminar flow in the pore spaces.

Permeability Considerations

The intrinsic air permeability, K_p , has been assumed constant, and thus K_p must be evaluated as an appropriate average value as it applies to the field region of interest. For example, in a fractured region, the fracture and matrix permeabilities should be appropriately averaged. A general formula for the average permeability over a volume, V , is

$$K_p = \frac{1}{V} \int K_p(x) dV. \tag{35}$$

Assuming planar fractures spaced S distance apart, where fracture spacing, S , is large compared to the average fracture aperture, b , an integral along the

perpendicular axis, x , leads to the usual expression for effective permeability in this fractured medium, as

$$K_{pfm} = \frac{1}{S} \int_0^S K_p(x) dx \sim K_{pm} + K_{pf} \frac{b}{S} \sim K_{pf} \frac{b}{S}, \quad (36)$$

where K_{pfm} is an effective or average air permeability of the fractured media, K_{pf} is the permeability of the fracture, and K_{pm} is the permeability of the matrix. An approximate value for K_{pf} for flow between two vertical plates (the fracture walls), neglecting surface roughness, is [Domenico and Schwartz, 1990]

$$K_{pf} \sim b^2/12. \quad (37)$$

The following issue is important in matching all the field data simultaneously and is discussed further in the Evaluation section. The spatial average for the fractured media permeability, K_{pfm} , which is used to evaluate the unattenuated diffusion coefficient may not be the same average value appropriate in evaluating the pressure perturbation attenuation length, L_{pm} , which contributes a dependence upon permeability in the form, $\exp(-z_0/K_p^{1/2})$. Here, one might expect to obtain an appropriate average by weighting different values of K_p proportional to $K_p^{-1/2}$.

Different averaging methods for K_p in different contexts might be consistent physically with different paths for propagation through the media. The vapor diffusion flux sees 'parallel' paths as the vapor diffuses through matrix or fractures evaluated with an arithmetic mean weighting over a spatially variable K_p , while the pressure perturbation diffusion propagates in 'series' across the varying permeability of the matrix then fracture and is limited by the permeability of the matrix.

In order to determine the appropriate permeability to use in the diffusion coefficient, it is convenient to evaluate the pressure diffusion at a 'reference value', $D_{p-ref}[K_{ref}]$, based in turn on a reference permeability value, K_{ref} . Thus, one writes

$$D_p = D_{p-ref}[K_{ref}] \frac{K_{pfm}}{K_{ref}}. \quad (38)$$

A site specific evaluation and comparison to field observations provides more insight to appropriate averaging than is possible from a purely theoretical analysis, so this issue is continued and elaborated in the Evaluation section.

Referring to Eqn.34 and incorporating Eqn.38, the total effective diffusion coefficient for vapor flux in the fracture porous media due to pressure fluctuations is finally written as

$$D_{v(p)} = - \left(\frac{8}{\pi} \right) \theta_a D_p [K_{ref}] \frac{K_{pfm}}{K_{ref}} \sum_{m=1}^{nMax} \left((\Delta p_m / p_o)^2 e^{-2z/L_{pm}} \right) \quad (39)$$

where the permeability of the fractured media is evaluated using Eqns.35 to 37. The near surface or unattenuated diffusion coefficient is evaluated at $z = 0$, or with the exponential term equal to one.

Model Evaluation

Reference Matrix Permeability

Field data for the migration of tritiated water vapor through the unsaturated zone from disposal shafts at Area G to the mesa surface are consistent with a vapor phase diffusion coefficient of about $1.5 \times 10^{-3} \text{ m}^2/\text{s}$ [Vold and Eklund,96] which is a factor of 60 greater than the binary diffusion coefficient for water vapor in air. In this section, the model derived above for pressure-driven diffusion in the fractured media is evaluated to provide a comparison to the effective vapor phase diffusion coefficient observed in the field study.

The pressure fluctuation enhanced diffusion coefficient is evaluated at a reference permeability, taken to be $1 \times 10^{-12} \text{ m}^2$, a 'nominal' value observed at Area G, lying between typical (unfractured) core sample measurements (less than 10^{-12} m^2 [D. B. Stephens, et.al.,95]) and in-situ measurement results (1 to a few times 10^{-12} m^2 in the upper most 100 foot depth at Area G [W.E. Lowry, et.al.,96]). In the relatively dry interior of the mesa at Area G a reasonable approximation is that the air volume fraction is equal to the porosity, $\theta_a \sim \varepsilon \sim 0.4$, then the pressure diffusion coefficient reference value is

$$D_{p-ref}[K_{ref}] = \frac{K_{p-ref} p_o}{\mu \varepsilon} = \frac{10^{-12} 0.8 \times 10^5}{2 \times 10^{-5} 0.4} = 1 \times 10^{-2} \text{ m}^2/\text{s}. \quad (40)$$

This is the expected value of the diffusion coefficient for pressure fluctuations in the 'nominal' tuff matrix at Area G.

The spectra of the atmospheric fluctuations have been examined in some detail [Vold,96C]. Spectral power densities were evaluated from the discrete Fourier transform of data collected at 8 intervals per day over a duration of several years to resolve simultaneously the daily and the annual period modes. The spectra indicated that the full power distribution in the atmospheric fluctuations had been included, thus, this data series was adequate to represent the spectrum needed here. It was found for the full spectrum,

$$\sum_{m=1}^{nMax} \left(\frac{\Delta p_m}{p_o} \right)^2 \sim \left(\frac{5 \text{ mbar}}{800 \text{ mbar}} \right)^2 \sim 4 \times 10^{-5}. \quad (41)$$

It was also found that the pressure mode spectrum could be crudely approximated as two modes, one at about a 7 day period and a second at the annual period (with the respective binned mode amplitudes of 3.3 mbar and 3.5 mbar). It is worth evaluating the magnitude of the pressure fluctuations in the shorter period mode as this term will drive the effective diffusion coefficient for the temperature gradient term for any longer period variation (annual) in the temperature. The square root of the sum of the squared amplitudes for the pressure modes contributing to the 7 day period was found to be about 3.3 mbar, or

$$\sum_{m=1}^{7 \text{ days}} \left(\frac{\Delta p_m}{p_o} \right)^2 \sim \left(\frac{3.3 \text{ mbar}}{800 \text{ mbar}} \right)^2 \sim 1.7 \times 10^{-5}. \quad (42)$$

As discussed previously, it is this mode summation which is expected to contribute to the effective diffusion of the annual variation in temperature, thus it is seen that $D_{v(T)} \sim (1.7 \times 10^{-5} / 4 \times 10^{-5}) D_{v(P)} \sim 0.43 D_{v(\theta)}$ or the enhanced diffusion coefficient for the temperature gradient flux is slightly less than half that for the moisture gradient flux.

The pressure fluctuation attenuation length, L_{pm} , can be evaluated for each dominant mode in the spectral analysis using the reference permeability. To simplify we consider the simplest spectral approximation with the two modes, a 7 day period and an annual period. The attenuation length for the 7 day mode and the nominal tuff permeability is

$$\begin{aligned}
 L_{pm}(\tau_m = 7 \text{ days}) &= \sqrt{\frac{K_{p-ref} p_o \tau_m}{\mu \varepsilon \pi}} \\
 &= \sqrt{\frac{10^{-12} 0.8 \times 10^5 3.6 \times 10^3 \times 24 \times 7}{2 \times 10^{-5} \times 0.4 \times 3.14159}} = 44 \text{ m},
 \end{aligned}
 \tag{43}$$

and for the annual mode, $\tau_m = 3.156 \times 10^7 \text{ s}$, the attenuation length is evaluated similarly to obtain,

$$L_{pm}(\tau_m = 1 \text{ yr} = 3.156 \times 10^7 \text{ s}) = 320 \text{ m}. \tag{44}$$

The saturated aquifer is 250-300m beneath Area G, and the mesa height is about 30m above the adjacent canyon floors. For near surface evaluations, or within the interior of the mesa, the attenuation of the pressure fluctuations (Eqn.39), is a small factor and can be neglected. Note that the diffusion coefficient attenuates twice as quickly with depth as does the pressure fluctuation amplitude, or with an attenuation length of only about 22m (half that from Eqn.43) for the 7 day period mode. This will be a significant reduction in the diffusion coefficient near the base of the mesa (on the order of 30%) but will not be a large factor in the present analysis comparing model results to diffusion coefficients derived from measurements of near surface tritium migration. Hence, we will assume the attenuation is small and neglect it from quantitative evaluation in this study. A more detailed study of the diffusion coefficient variation with depth should consider evaluating Eqn.39 using the 5-group or 11-group spectra for atmospheric pressure fluctuations in [Vold,96C].

Combining factors using values appropriate to Los Alamos (e.g., $\varepsilon \sim 0.4$), we obtain an estimate for the near surface effective vapor diffusion

coefficient due to pressure fluctuations at the reference permeability of the tuff matrix, $D_{v(p)}$, as

$$\begin{aligned}
 D_{v(p)}[K_{ref}, z=0] &\sim 2 \left(\frac{4}{\pi} \right) \theta_a D_p[K_{ref}] \sum_{m=1}^{nMax} \left((\Delta p_m / p_o)^2 \right) \\
 &= 2 \left(\frac{4}{\pi} \right) 0.4 \cdot 1 \times 10^{-2} \text{ m}^2/\text{s} [\text{at } K_{ref} = 10^{-12} \text{ m}^2] \cdot 4 \times 10^{-5} \\
 &= 4 \times 10^{-7} \text{ m}^2/\text{s} \\
 &= (4 \times 10^{-7} / 2.5 \times 10^{-5}) D_o \sim (1/60) D_o.
 \end{aligned} \tag{45}$$

This value is 60 times less than the classical diffusion coefficient and shows that diffusion in the matrix (at the reference permeability) driven by pressure fluctuations is negligible.

Effective Permeability due to Fractures

Consistent with Eqn.9, the classical diffusion coefficient in porous media will not change significantly in a fractured medium because the porosity and tortuosity will not be changed by more than a factor of about two. However, the diffusion due to pressure fluctuations is proportional to an effective permeability of the media and therefore the fracture contribution to permeability can be important. This can increase the diffusion by orders of magnitude for the fracture characteristics at Area G.

Fracture mapping data from Area G in disposal unit #39 to ~ 60 foot depth [Reneau and Vaniman,94] indicates a mean value for the distribution of fracture apertures in the near surface is about 3mm over the upper walls. The average over the lower walls in that disposal unit is about 5mm. The mean value for fracture frequency is about 1 m^{-1} , or the mean fracture spacing is, $S = 1 \text{ m}$. This indicates a fracture permeability in the simple model of

$$K_{pf} = b^2/12 \sim (3 \times 10^{-3})^2/12 = 0.75 \times 10^{-6} \text{ m}^2 \tag{46}$$

and an effective media permeability of about

$$K_{pfm} \sim (b^2/12) (b/S) = ((3 \times 10^{-3})^2/12)(3 \times 10^{-3}/1) = 2.3 \times 10^{-9} \text{ m}^2. \quad (47)$$

Using these mean values from the fracture aperture and spacing distributions, the ratio of the effective permeability of the fractured media to the reference permeability is

$$K_{pfm}/K_{p-ref} = 2.3 \times 10^{-9}/1 \times 10^{-12} = 2.3 \times 10^3. \quad (48)$$

Using this ratio to modify the enhanced diffusion coefficient to a value for the effective fractured media, one obtains

$$\begin{aligned} D_{v(p)} &= D_{v(p)}[K_{ref}, z=0] \frac{K_{pfm}}{K_{ref}} \\ &= (4 \times 10^{-7} \text{ m}^2/\text{s}) \times 2.3 \times 10^3 \sim 1 \times 10^{-3} \text{ m}^2/\text{s}. \end{aligned} \quad (49)$$

This value is 40 times greater than the binary diffusion coefficient and only 50% less than the empirically derived value for tritium diffusion at Area G, $1.5 \times 10^{-3} \text{ m}^2/\text{s}$ [Vold and Eklund,96].

The value of the diffusion coefficient from the pressure fluctuation model is very sensitive to the fracture aperture, proportional to b^3 . As noted above, the mean value of the distribution of fracture apertures, $\langle b \rangle$, is about 5 mm on the lower walls and over the upper face of the disposal unit walls the mean aperture is 3 mm. If a lognormal distribution is assumed for the data from the upper face (the data plots support this, however, the original data was not available to quantify this) then the geometric mean and standard deviations are estimated from the data graphs in [Reneau and Vaniman,94] to be about 2 mm and 2, respectively. These values characterize the distribution in aperture width, while the mean values for higher moments, $\langle b_2 \rangle$ or $\langle b_3 \rangle$, will be larger. In fact, the average for the lognormal distribution of the third moment, $\langle b_3 \rangle$ (we are interested in effective permeability proportional to b^3) can be expressed in terms of the estimated parameters [Seinfeld,86] as

$$\ln \langle b_3 \rangle = \ln \langle b \rangle + 3 \ln^2 \sigma_g.$$

or

$$\langle b_3 \rangle = \exp(\ln 2 + 3 \ln^2 2) = 8 \text{ mm} \quad (50)$$

Where we previously used the arithmetic mean of the aperture distribution equal to 3 mm, it may be more appropriate to use this mean of the higher moment used to evaluate the effective permeability. This corrects the effective diffusion coefficient upward by a factor of 8/3, to give an estimate from the factors considered thus far as

$$D_p \sim (8/3) 1.5 \times 10^{-3} \text{ m}^2/\text{s} = 2.6 \times 10^{-3} \text{ m}^2/\text{s}. \quad (51)$$

This estimate from the model is about 50% greater than the estimate from the field data for the in-field diffusion coefficient for tritium vapor at Area G. The estimate from the model in Eqn.51 and the previous model estimate in Eqn.49, thus bracket the value observed in the field. There are a number of factors associated with the pressure fluctuation model and with the field determination which would indicate the error for either estimate is larger than this difference between the estimates. One possibility to account for the relatively good agreement, is that this pressure fluctuation model accounts for the main physics in determining the in-field vapor phase diffusion.

Another possibility which cannot be entirely discounted is that large errors in two or more factors which are important in this analysis cancel each other leading to an apparent agreement with the field data for erroneous reasons. One possible inconsistency in the analysis is that in deriving the enhanced diffusion coefficient (Eqns.33-34), factors of K_p cancel in the numerator and in the denominator. It is then found in the model evaluation that these two values may be different in order to best match the field data. This leaves the agreement of the field data and the model open to further interpretation and refinement.

Discussion

Effective Permeability

The volume averaged effective permeability used to evaluate the pressure attenuation length, L_{pm} , may not be the same as the effective permeability factor used to evaluate the unattenuated diffusion coefficient (Eqn.49). A second related issue is the difference between permeability seen in recovered core (unfractured samples) and the in-situ measurements.

It has been shown that the attenuation of atmospheric pressure fluctuations with depth agrees with the attenuation length calculated using air permeability values from in-situ field study measurements [Neeper, et.al.,96]. These in-situ measurements are by an isolated packer pressure injection method and permeability values within 100 ft of the mesa surface are typically in the range of $1-2 \times 10^{-12} \text{ m}^2$ [Krier, et.al.95]. This permeability is a factor of 2 to 10 times greater than air permeability measured analytically on small core samples recovered and analyzed in the laboratory [Stephens, et.al.,95]. However, it is orders of magnitude smaller than the effective permeability, K_{pfm} , predicted for the fractured media at Area G using the fracture distribution data, which agrees with the tritium mass diffusion field data as seen in the model above. The propagation of pressure fluctuations appears to be consistent with a permeability close to the matrix or in-situ values.

The response function of the in-situ packer measurement suggests that permeability determined by this method represents a sample volume of characteristic dimension approximately 0.3 to 0.5 m [Lowry,96]. Comparing this effective sample size to the fracture distribution it is reasonable to conclude that the in-situ measurement includes a response to a fraction of the fractures at the low end of the fracture spacing distribution. Thus, the in-situ determination sees an effective permeability which is large compared to the core sample (unfractured) permeability but still small compared to the volume averaged permeability over a larger volume that encompasses and thus effectively averages over the entire distribution of fracture spacing.

A consistent picture requires reconciliation between the large K_{pfm} , as needed in the effective diffusion model to agree with the tritium vapor diffusion observed in the field, and the relatively small K_{pfm} , as seen in the attenuation with depth of the pressure fluctuations. A possible explanation is that the effective diffusion for mass (vapor) sees the matrix and fractures as parallel flow paths and an appropriate average is a simple mean. For pressure fluctuations, their propagation with depth follows a path through varying permeabilities in series, through matrix then fractures. In this case, the effective permeability is 'series weighted' ($1/K_p$) and becomes dominated by the smaller permeability of the matrix.

Some influence of the fracture permeability on this 'series weighted' permeability is suggested by the agreement of the pressure attenuation data

with the in-situ permeability [Neeper,et.al.,96], since the in-situ permeability (presumably representing some fraction of the fractures) is significantly greater than the matrix permeability (represented by the unfractured core sample results). This issue needs additional analysis to determine if the data for pressure fluctuation with depth is sufficiently well resolved that one can discriminate a 'best fit' to the permeability which is closer to the in-situ values than to the core sample (unfractured) values.

Fracture Presence and In-situ Diffusion Observations

The effective diffusion coefficient for tritium vapor observed in the field study, $1.5 \times 10^{-3} \text{ m}^2/\text{s}$, was determined for tritium diffusion in the upper most 60 ft of the mesa subsurface. It was noted in that study by comparison to borehole tritium moisture profiles [Vold and Eklund, 1996] that the diffusion coefficient appeared to be significantly less, by about a factor of four, for tritium diffusing downward from 60 ft. It has also been observed at Area G that along the lower portion of the excavated walls of a currently open disposal unit #38, many of the fractures penetrating towards the bottom, stop abruptly here (at ~ 60 ft). This is estimated to be the interface of Units 2B and 2A, based on borehole profile logs from nearby boreholes. The observations that there is a decrease in effective diffusion below 60' in the tritium diffusion study and that the fracture density decreases near the 2B-2A interface (~60' deep), are qualitatively consistent with the enhanced diffusion model which predicts a dependence of the enhanced diffusion upon fracture permeability.

Diffusion Isotropy

The enhanced diffusion coefficient in this analysis has been evaluated in a simple manner as an isotropic quantity. The diffusion mechanism actually indicates that the diffusion occurs along the axis of the pressure gradients imposed at the surface boundary, implying diffusion along the axis normal to the surface plane. However, the magnitude of the diffusion requires that the permeability of the fractures be invoked so that the mass or vapor diffusion is presumably dominated by flux through fracture apertures, and therefore the directionality of the effective diffusion will be related in a complex unknown manner to the distributions describing fractures and their orientation. Fractures at Area G are observed to be predominantly vertical,

but with a broad distribution as mapped previously [Reneau and Vaniman,94]. The broad distribution introduces some degree of isotropy into this effective diffusion coefficient which is expected to become more isotropic as the volume of interest increases thus averaging over a larger distribution of the fractures. A nearly isotropic diffusion coefficient is consistent with the surface efflux of tritiated water vapor measured from the ground area surrounding the tritium disposal shafts at Area G, which is seen to be reasonably symmetric around the three high level tritium disposal shafts [Eklund and Vold,95].

Enhanced Diffusion with Hydrodynamic Dispersion

A factor contributing to transport is the hydrodynamic dispersion that develops by spreading mass with respect to a specific convective front and to the axis of convective motion in a porous media. This dispersion might typically contribute to a 10% (plume width to length) mass spreading normal to the local axis of convective motion. This axis for the pressure enhanced diffusion is along the axis of the pressure gradient. In unfractured media this would direct the convective oscillations normal to the ground surface and the hydrodynamic dispersion would be dominantly parallel to the ground surface. However, in the densely fractured mesa geometry with a broad distribution in fracture orientations, the dispersivity in the field due to the pressure fluctuation enhanced diffusion is likely to enhance the isotropy of the contaminant plume. Thus, isotropy in the dispersivity should be similar to the isotropy expected for the enhanced diffusion coefficient itself as discussed in the previous paragraph, but is expected to be of secondary significance in the transport.

Diffusion Model Validity

As discussed previously, the diffusion model is valid when the displacement distance is small compared to the attenuation length, or $d_{pm}/L_{pm} \ll 1$. The inequality is always true for the pressure fluctuations when the same permeability value is used in evaluating the displacement distance as in evaluating the attenuation length, since the pressure perturbation amplitude is always small compared to the ambient pressure background (Eqn.20). However, in order to simultaneously match two sets of

field data (the diffusion coefficient for near surface tritium migration and the pressure fluctuation attenuation length) it was necessary to assume that the effective permeability in the displacement distance needed in the diffusion coefficient is K_{pfm} while the effective permeability for the attenuation length is much smaller, $\sim K_{insitu}$.

This K_{pfm} value implies that the convective displacement distance is larger by the ratio of K_{pfm}/K_{p-ref} than previously assumed. This leads to $d_{pm}/L_{pm} \sim 1$, not $d_{pm}/L_{pm} \ll 1$ as assumed for diffusion theory to apply. The large value implied for the displacement distance might physically represent a large convective displacement through a fracture. Under these conditions the constant diffusion coefficient model assumptions are not strictly valid, the diffusion coefficient is varying significantly in space and the diffusion may be non-linear. Nevertheless, the diffusion model still appears to be in agreement with the field data.

The use of different values for K_p to match data sets simultaneously leads to another dilemma. As discussed previously, two factors of K_p cancelled in the derivation of the diffusion coefficient (Eqn.33-34). These factors, which implicate a role of the fractures in defining an appropriate permeability, were later evaluated to be different values to match the field data. The role of the fractures requires additional investigation. The present analysis does not unambiguously resolve these issues.

Application of Result

Having derived an effective diffusion coefficient which appears to be consistent with field data it is appropriate to next consider how this diffusion coefficient can be applied in modeling or analyses. Discussion in this section is speculative and will be reviewed in a subsequent study in comparison to a detailed two phase dual media model formulation.

The component of vapor flux due to the enhanced or effective diffusion coefficient, $D_{v(p)}$, acting on the vapor density gradient can be generally written

$$\Gamma_v = - D_{v(p)} (\nabla \rho_v), \quad (52)$$

where this expression can be applied to fractures or to the matrix depending upon the values used for ρ_v . The derivation indicates that the effective diffusion coefficient is an average over the effective permeability of the combined fracture-matrix system, and therefore a single value for $D_{v(p)}$ applies to the flux within fractures or to the flux within the matrix. The flux difference will be related only to the difference in vapor density gradients in the two media.

The empirically determined effective diffusion value for tritiated water vapor, D_{v-eff} , [Vold and Eklund,96] has been used in combination with observed moisture content profiles in the matrix (as measured in bore holes at Area G) to estimate the magnitude of vapor flux to be about 2 mm/yr water equivalent [Vold,96B]. This analysis is independent of the underlying diffusion mechanisms suggested by this model derivation. This flux within the matrix is driven by the effective diffusion acting on the moisture gradient observed in the matrix. Thus, the vapor flux through the matrix was estimated as

$$\Gamma_v (m) = - D_{v-eff} (\nabla \rho_v)_m \quad (53)$$

using the effective diffusion coefficient with the gradient of the vapor density within the matrix, $(\nabla \rho_v)_m$, inferred from the moisture profile measurements.

The diffusion model evaluation implies that $D_{v(p)} \sim D_{v-eff}$. The model derivation indicates the transport is actually dominated by flow through fractures. A physical picture from these considerations is that the volume averaged transport is dominated by flow through the fractures and this effective diffusion drives a vapor flux within the matrix (presumably towards the nearest fracture where it is lost to evaporation) which is on the order of 2 mm/yr.

The derived diffusion coefficient also applies to the fractures, since the effective permeability (Eqn.36) was a volume weighted average. This implies that the vapor flux within the fractures is given by

$$\Gamma_v (f) = - D_{v-eff} (\nabla \rho_v)_f \quad (54)$$

where the vapor density gradient is evaluated within a fracture along an axis normal to the mesa top or mesa side boundary. If one accepts that the same

effective diffusion coefficient applies to the fracture or to the matrix media, then the ratio of vapor flux in the fracture to that in the matrix is equal to the ratio of their respective vapor density gradients. Referring back to Eqns.4 and 7, the vapor gradients can be approximated under isothermal conditions, giving us

$$\frac{\Gamma_v (f)}{\Gamma_v (m)} = \frac{(\nabla \rho_v)_f}{(\nabla \rho_v)_m} = \frac{p_s \nabla \left(\frac{p_v}{p_s} \right)_f}{\frac{p_s}{h_c} (\nabla h_m)_m} \quad (55)$$

An isothermal condition is a good approximation in the matrix below 1-2m, but it may not be a good assumption within the fracture spaces during convective cycles of atmospheric pumping, so the actual case will be more complex than considered here. With this caveat, the gradient of the relative humidity in the fracture, $\left(\frac{p_v}{p_s} \right)_f$ can be evaluated. Preliminary numerical results are consistent with the following simple approximation.

The relative humidity at the mesa edge is typically 0.3 and it is ~ 0.99 in the mesa interior with a scale length along the fracture penetrating into the mesa interior about 10m, or

$$\nabla \left(\frac{p_v}{p_s} \right)_f \sim (0.99 - 0.3) / 10m \sim 0.07 m^{-1}. \quad (56)$$

The magnitude of the matrix potential gradient associated with moisture content within the matrix can be approximated from the data for the drier portions of the borehole ER-1123 at depth intervals with the maximum gradients (e.g., Fig. 16A in [Vold,96B]), as

$$(\nabla h_m)_m \sim \Delta h_m / \Delta z \sim 10^4 cm / 1m = 10^2. \quad (57)$$

Combining these approximations in Eqn.55, and canceling the factors of p_s , an estimate for the vapor flux in fractures relative to the flux in the matrix is

$$\frac{\Gamma_v (f)}{\Gamma_v (m)} = \frac{h_c \nabla \left(\frac{p_v}{p_s} \right)_f}{(\nabla h_m)_m} = \frac{13\,300 \times 0.07}{10^2} = 9.1 \sim 10.$$

Though these estimates are crude, they predict that an order of magnitude greater vapor phase flux within the fractures than within the matrix itself can occur for assumed realistic conditions. Where the previous analysis result [Vold,96B] found a vapor flux magnitude of 2mm/yr equivalent in the dry portions of the mesa tuff matrix, there may be ten times this value or 2 cm/yr liquid-equivalent vapor phase flux through the fractures. If the same net moisture flux moves through each media, say, from the matrix to the fractures to be evaporated subsequently from the surface connected fractures, then the flux through the matrix must equal the flux through the fractures by mass conservation. However, a moisture source within the fractures could be evaporated at higher flux rates up to 2 cm/yr under the assumed conditions. Transient events could deposit significant moisture directly into the fractures as hypothesized previously [Turin,95] and thus act as a moisture source term which evaporates before it is wicked into the matrix.

This result may help to explain an unresolved discrepancy in field data [Vold,et.al.,96]. Data from precipitation, evaporation, evapotranspiration and surface run-off indicate that several cm/yr are unaccounted for [Vold and Eklund,96B]. One possibility is that the unaccounted water goes to deep percolation, however, there are geophysical and geochemical analyses that strongly suggest a deep percolation rate of only a few mm/yr or less [Vold,et.al.,96]. If a moisture flux on the order of (cm/yr) is evaporating through the fractures to the mesa walls, this might account for the discrepancy. Another possibility is that the apparent discrepancy is attributable to uncertainties in field data.

Summary

Field data for the migration of tritiated water vapor through the unsaturated zone from the buried disposal shafts at Area G are consistent with a vapor phase diffusion coefficient of $1.5 \times 10^{-3} \text{ m}^2/\text{s}$, or a factor of 60 greater than the binary diffusion coefficient for water vapor in air. A model is derived which relates an effective vapor phase diffusion coefficient in the

fractured porous media to the subsurface propagation of atmospheric pressure fluctuations.

The pressure fluctuation enhanced diffusion mechanism does not relate to the specific transport properties of water vapor and thus is assumed to apply equally well to any gas species entrained in the pore air spaces. The temperature gradient moisture flux was seen to be dominated by the temperature dependence of the saturated water vapor pressure. The temperature gradient driven flux for other gaseous species could be similarly related to the temperature dependence of the vapor pressure for that species, and could be important or not depending upon this temperature dependence.

The near surface (unattenuated) diffusion coefficient is independent of fluctuation period under the simplified assumptions of a complete 'mixing mechanism' for the effective diffusion process. The unattenuated effective diffusion driven by this barometric pumping is linearly proportional to the average permeability of the fractured porous media, while the attenuation length is inversely proportional to the square root of the product of permeability times mode period. The resulting diffusion using Area G parameter values is negligible in the matrix but becomes large at the effective permeability of the fractured media. This finding is in agreement with previous work [Peterson, et.al., 1987]. Using observed fracture characteristics at Area G, the effective diffusion coefficient due to pressure fluctuations predicted by this model is in good agreement with the observed in-situ diffusion coefficient for tritium field measurements.

It is concluded that barometric pumping in combination with the enhanced permeability of the fractured media is a likely candidate to account for the observed in-field migration of vapor in the near surface unsaturated zone. This enhanced migration occurs in the upper most fractured stratigraphic layers beneath Area G to at least 60 ft depth, but does not apply within the disposal units themselves which are unfractured and highly compacted during disposal operations. The implied vapor flux within the fracture volume may be greater than through the tuff matrix by an order of magnitude, if transient infiltration or some other mechanism provides a source of moisture directly to the fracture network.

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Nomenclature Table

b	fracture aperture
$\langle b \rangle$	average of distribution of fracture apertures
D	mass diffusion coefficient
D_m	diffusion coefficient contribution from a single mode
D_o	classical diffusion coefficient (water vapor in air)
D_{os}	fluctuation enhanced diffusion coefficient
D_{pm}	diffusion coefficient from one pressure mode
D_p	pressure fluctuation diffusion coefficient
$D_{p-ref}[K_{ref}]$	pressure fluctuation diffusion coefficient reference value
$D_v(T-\theta)$	diffusion coefficient for vapor flux by either temperature or moisture content gradient
$D_v(T)$	vapor diffusion coefficient for temperature gradient flux
$D_v(\theta)$	vapor diffusion coefficient for moisture content gradient flux
D_v	total effective diffusion coefficient for vapor
D_{v-eff}	effective vapor diffusion coefficient from field data
$D_v(p)$	effective vapor diffusion coefficient from pressure fluctuation model
d	characteristic step size
d_{hm}	average displacement distance over a half period
d_m	average mode displacement distance
d_{pm}	pressure mode displacement distance
d_{Tm}	temperature mode displacement distance
h_c	static equilibrium constant = $RT/M_v g$.
h_m	matric potential expressed as a positive water column height
K_p	air permeability for a porous media
K_{pd}	air permeability used to evaluate the displacement distance
K_{pL}	air permeability used to evaluate the attenuation length
K_{pfm}	effective or average air permeability of the fractured media
K_{pf}	air permeability of the fracture
K_{pm}	air permeability of the matrix
K_{ref}	air permeability reference value
L_m	mode attenuation length
L_{pm}	attenuation length for each pressure mode

L_{Tm}	attenuation length for each temperature mode
$nMax$	finite number of modes
p	air pressure (fluctuation)
p_a	air pressure (total)
p_o	atmospheric pressure (average)
p_v	vapor pressure
p_s	saturated vapor pressure
S_v	source term for vapor phase
T	air and vapor temperatures
u	mass speed
$u(z,t)$, or	convective air motion speed, or
$u_a(z,t)$	time and space dependent air velocity (in context) at depth
u_a	air flow speed (or velocity in context)
$u_a(z)$	time averaged magnitude of the fluctuating air velocity
$u_m(z)$	average displacement mode speed at a given depth
$u_{om}(z)$, or	mode maximum speed amplitude at a given depth,
u_{om}	corresponding to the pressure fluctuation maximum, Δp_m
$u_{om}(z=0)$	unattenuated mass convection speed for a particular mode
V	volume
x	an axis parallel to ground surface
z	distance (height) along axis normal to ground surface
z_o	reference height
Γ_v	vapor phase flux of moisture in the porous media
Γ_{vD}	diffusive component of the vapor flux
Δp_m	amplitude for a particular mode of the pressure fluctuations
ε	porosity
θ	liquid phase volumetric fraction
θ_a	air-filled volumetric fraction
μ	viscosity
ρ_v	vapor density
$(\rho_v)_m$	vapor density within the matrix
$(\rho_v)_f$	vapor density within a fracture
$\rho_{v o}$	vapor density at the reference height, z_o
τ_m	period for a particular mode (of the pressure fluctuations)
φ	tortuosity factor

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