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DIFFUSION WITH CONDENSATION AND EVAPORATION IN POROUS MEDIA

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ABSTRACT

The diffusion of water vapor in a packed bed containing residual liquid is examined experimentally. The objective is to quantify the effect of enhanced vapor diffusion resulting from evaporation/condensation in porous media subjected to a temperature gradient. Isothermal diffusion experiments in free-space were conducted to qualify the experimental apparatus and techniques. For these experiments measured diffusion coefficients are within 3.6% of those reported in the literature for the temperature range from 25 °C to 40 °C. Isothermal experiments in packed beds of glass beads were used to determine the tortuosity coefficient resulting in $\tau = 0.78 \pm 0.028$, which is also consistent with previously reported results. Nonisothermal experiments in packed beds in which condensation occurs were conducted to examine enhanced vapor diffusion. The interpretation of the results for these experiments is complicated by a gradual, but continuous, build up of condensate in the packed bed during the course of the experiment. Results indicate diffusion coefficients which increase as a function of saturation resulting in enhancement of the vapor-phase transport by a factor of approximately four compared to a dry porous medium.

NOMENCLATURE

j	mass flux	(kg/m^2-s)
D_C	isothermal diffusion coefficient	(m^2/s)
D^o_C	isothermal diffusion coefficient at reference conditions	(m^2/s)
D_T	thermal diffusion coefficient	(kg/m-s-K)
D^c_{eff}	effective diffusion coefficient	(m^2/s)
D^t_{eff}	effective thermal diffusion coefficient	(kg/m-s-K)
T	temperature	(K)
S	saturation	
P	pressure	(Pa)
RH	relative humidity	
Z	diffusion path length	(m)
R	gas constant	(462 J/kg-K)

Greek symbols

τ	tortuosity coefficient	
ϕ	porosity	
ρ	density	(kg/m^3)
ω	vapor mass fraction	
β	enhancement factor	(see Eq.(10))
η	enhancement factor	(see Eq.(9))

Subscripts

g	gas phase
sat	saturated
v	vapor

INTRODUTION

Vapor phase transport in porous media is important in a number of environmental and industrial processes. These include soil moisture transport, vapor phase transport in the vadose zone, transport in the vicinity of buried nuclear waste, and industrial processes such as drying. In some of the above applications a warm moist zone overlays a cooler dryer zone. This is common during the summer near the earth's surface, near heated structures in the winter or perhaps below a repository for buried heat generating waste.

Enhanced vapor diffusion driven by temperature gradients and resulting from condensation and evaporation at the liquid vapor interfaces has been the topic of considerable study since

the mechanism was first proposed and discussed by Philip and deVries [1]. Jackson [2,3,4,5] in a series of papers discusses both theoretical considerations and experimental results. Steady state and transient measurements in different soils resulted in diffusion coefficients ranging up to ten times those for dry soil in the presence of the liquid phase. Diffusion coefficients were shown to increase up to gravimetric water contents around 0.01 to 0.02 and then decrease as the water content was further increased. Jackson's experimental results [3] indicate that the process exhibits hysteresis in that the dependence of the diffusion coefficient on saturation is different depending on whether the transient experiments are conducted with increasing or decreasing water content. Cass, et al. [6] present experimental results for lysimeter sand and Portneuf silt loam which indicate enhancement factors of 2 to 3 relative to free space with a dependence on moisture content similar to that observed by Jackson. Theoretical models which have been presented by Cary [7] and Jury and Letey [8] are not in good agreement with the Cass et al. measurements. Bories [9] reports measurements of the vapor-phase diffusion coefficient that are nearly an order of magnitude higher than those expected for a dry porous medium. More recently Ho and Webb [10] use a simple pore scale model to illustrate that, given a specific geometry, enhanced vapor diffusion can be predicted to occur.

The objective of the work to be presented is to quantify enhanced vapor diffusion using an experimental approach different from that used by the previous investigators mentioned above. Some theoretical background will first be presented followed by a description of the experiment. Experimental results will then be presented and discussed.

BACKGROUND

Fick's law of diffusion, corrected to account for the presence of the solid phase and, if necessary, a liquid phase is the standard model for predicting diffusion in porous media. Fick's law for isothermal diffusion in porous media is commonly expressed as

$$j = -\tau\phi S_g D_C \rho_g \nabla\omega \qquad (1)$$

where D_C is the free-space diffusion coefficient at a given temperature and pressure and ω is the water vapor mass fraction. The product of the tortuosity coefficient, τ, the porosity, ϕ, and the gas saturation, S_g, is often referred to as the porous media factor and lumped into a single parameter which when multiplied by the free-space diffusion coefficient results in an effective diffusion coefficient. Since the tortuosity coefficient and the porosity are always less than 1, the gas saturation is a maximum of 1, and the porous media factor is always much less than 1, the rate of vapor diffusion in a porous media should be much less than the diffusion rate in free space.

For isothermal conditions and linear vapor pressure profiles, Equation (1) can be written (in an integrated form) in terms of relative humidity and saturated vapor pressure:

$$j = -D^c_{eff}\frac{P_{sat}}{RT}\frac{(RH_1 - RH_2)}{\Delta Z} \qquad (2)$$

where j is the mass flux of water vapor (kg/m^2-s), D^c_{eff} is the effective diffusion coefficient (m^2/s), P_{sat} is the saturated vapor pressure (Pa) at the system temperature, T(K), R is the gas constant for water vapor (462 J/kg-K), RH is the relative humidity, and ΔZ is the vertical length over which the diffusive process of interest occurs. The subscripts 1 and 2 refer to the boundaries of the domain. Equation (2) assumes a one-dimensional steady state process with constant effective diffusion coefficient. For a dry porous medium the effective diffusion coefficient, D^c_{eff}, is the product of the free space diffusion coefficient, gas phase saturation, porosity, and tortuosity as indicated above.

The effective diffusion coefficient is known to be a function of temperature. Vargaftik [12] presents the following relationship:

$$D^c_{eff} = \tau\phi S_g D^o_C \frac{P^o}{P}\left(\frac{T}{273}\right)^\theta \qquad (3)$$

where D^o_C is the binary diffusion coefficient (also referred to as the free space diffusion coefficient) for water vapor and air at standard conditions (P^o = 1 bar). Vargaftik gives D^o_C = 2.13×10^{-5} m^2/s at T=273 K, P=1 bar, and $\theta = 1.8$.

Under nonisothermal conditions the transport of water in a porous medium can be affected by temperature gradient through the Soret effect [13] as well as the gradient in partial pressure or concentration. In addition, as discussed earlier, diffusion may be enhanced as a result of the presence of the liquid phase through pore-scale evaporation/condensation mechanisms. For nonisothermal conditions Equation (1) can be rewritten as follows:

$$j = -\tau\phi S_g (D_C \rho_g \nabla\omega + D_T \nabla T) \qquad (4)$$

The approximate average non-isothermal vapor flux in a region bounded by fixed conditions at 1 and 2 can be written in a form analogous to Equation (2):

$$j = -\frac{\overline{D^c_{eff}}}{\Delta Z R}\left(\frac{RH_2 P_{sat(2)}}{T_2} - \frac{RH_1 P_{sat(1)}}{T_1}\right) - \overline{D^t_{eff}}\frac{(T_2 - T_1)}{\Delta Z} \qquad (5)$$

where the overbar implies an averaged or integrated result. For porous media the effective diffusion coefficients are related to the free space diffusion coefficients through the following relationships:

$$D^c_{eff} = \tau\phi S_g D_C \quad (6)$$

$$D^t_{eff} = \tau\phi S_g D_T \quad (7)$$

The average effective diffusion coefficient $\overline{D^c_{eff}}$ may be approximated by integrating the effective diffusion coefficients from temperature T_1 to T_2.

$$\overline{D^c_{eff}} = \frac{1}{T_2 - T_1}\int_{T_1}^{T_2} D^c_{eff}\,dT \quad (8)$$

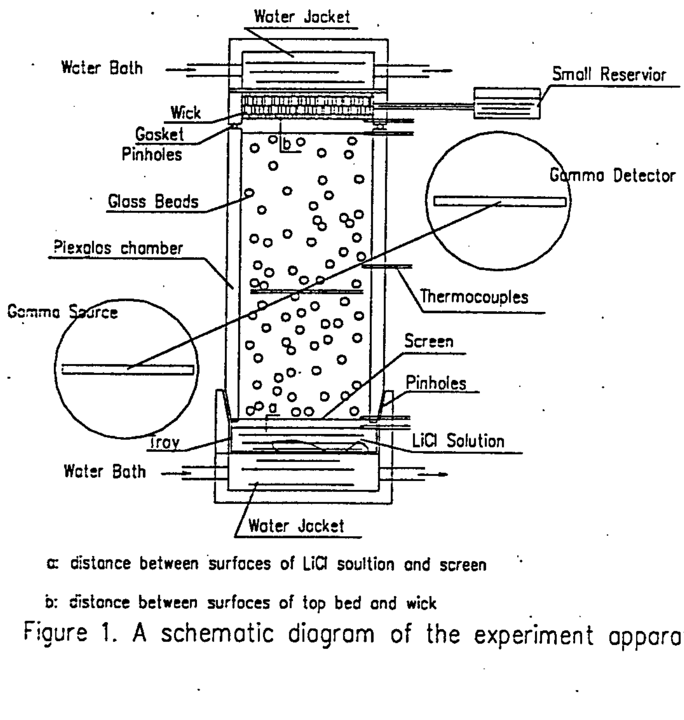
Equations (2) through (8) provide the theoretical background that will be utilized in presenting and interpreting the experimental results.

DESCRIPTION OF EXPERIMENT

The experimental apparatus is illustrated in Figure 1. The apparatus consists of a 51 mm wide × 51 mm deep × 95 mm high chamber constructed from acrylic. A bed of glass beads within the chamber serves as the porous medium. The chamber is capped with a jacket through which water can be circulated at a fixed temperature. Immediately below the water jacket is a fibrous wick which is connected to an external reservoir. The wick provides a supply of saturated water at a fixed temperature. An electronic balance is utilized to monitor the water loss from the reservoir. The top is clamped to the chamber for easy disassembly.

The bottom of the chamber consists of a desiccant tray and a water jacket. The tray can be removed for weighing. The central section of the chamber which contains the bed is slip fit into the lower desiccant chamber. A wire screen at the bottom of the chamber supports the glass beads. Five thermocouples measure the temperature at the wick, the top of the bed, the middle of the bed, the bottom of the bed, and the top of the desiccant. The entire apparatus is insulated with 2.54 cm of foam insulation. The water jackets at the top and bottom of the apparatus are supplied with water from constant temperature baths. A gamma attenuation system is available to measure the saturation profile in the packed bed during the experiment.

For isothermal experiments the entire apparatus was placed in an environmental chamber maintained at the desired temperature. Dry glass beads (450 μm beads were utilized except where indicated) were carefully packed in the acrylic container a small amount at a time while shaking the container. A very consistent average porosity of from 0.37 to 0.374 was achieved using this technique. The porosity for each experiment was determined using measurements of bed volume and weight. At the bottom, a saturated LiCl solution was utilized as the desiccant to provide a constant relative humidity of 0.13, while at the top the saturated wick maintains a relative humidity of unity. Because of the small amount of mass required the wick does not need a continuous supply of water from the attached reservoir for the isothermal experiments. The vapor diffusion rate can be determined by weighing the wick to determine the mass loss and by weighing the desiccant to determine the mass gain. In addition the bed can be weighed to detect any liquid build up in the bed and check the overall mass balance.



a: distance between surfaces of LiCl soultion and screen

b: distance between surfaces of top bed and wick

Figure 1. A schematic diagram of the experiment apparatus

The electronic balance used for these measurements has an accuracy of ±0.01 grams. Weights were recorded every 12 or 24 hours depending on the mass transfer rates. The atmospheric pressure was also recorded twice daily.

For nonisothermal experiments the water circulated through the upper water jacket was maintained at a fixed temperature greater than that circulated through the lower water jacket. Hence, the temperature gradient resulted in a stable density distribution to eliminate natural convection. Two constant temperature baths were used to supply the water to the jackets. Since the nonisothermal experiments were run for several days, the upper reservoir was utilized to maintain a water supply to the wick. A gamma attenuation system [14] was used to measure the liquid saturation profile in the bed. During nonisothermal experiments water vapor diffusing from the top boundary continuously condenses in the cooler regions of the bed. The mass flux of vapor into and out of the packed bed can be determined by weighing the desiccant and the bed.

RESULTS AND DISSCUSSION

Several isothermal experiments were conducted in free space in order to test the experimental apparatus and technique. By setting τ, the tortuosity coefficient, ϕ, the porosity and, S_g, the gas phase saturation to unity, Equation (2) yields the isothermal mass diffusion coefficient if the mass flux is measured.

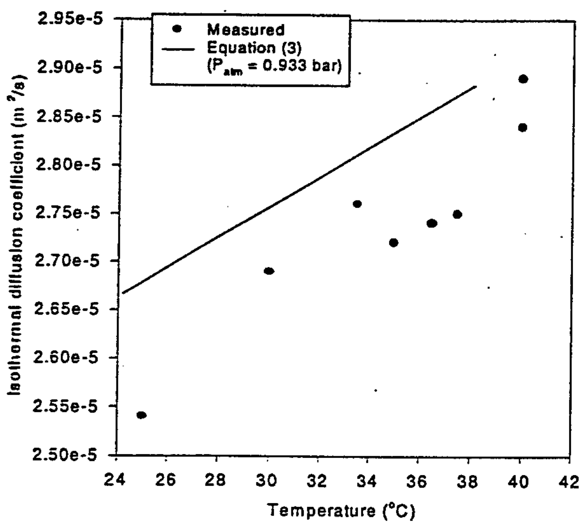


Figure 2. Isothermal mass diffusion coefficient in free space

Figure 2 shows the measured values of D_C compared with those reported by Vargaftik [12] (Equation (3)). The results, which span the temperature range from 25 °C to 40 °C, are within 3.6% of Equation (3) and confirm the 1.8 power law dependence on temperature. The uncertainty in these results is estimated to be 3.2% with the primary contribution coming from the measurement of mass flux (through weight).

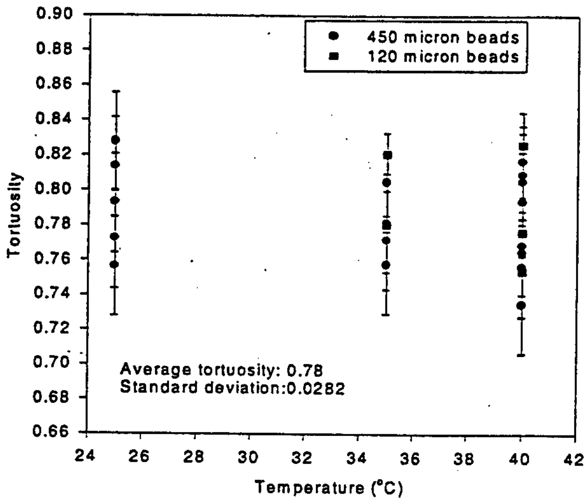


Figure 3. Measured tortuosity at different temperatures

With the free space diffusion coefficient measured, the next step was to measure the tortuosity coefficient for an isothermal packed bed. There are two small free-spaces (see Figure 1) above and below the packed bed. As the relative humidity is known to be unity at the wick and 0.13 at the desiccant, Equations (2) and (3) for free space conditions can be utilized to back calculate the relative humidity at the top and bottom of the packed bed. Equations (2) and (3) can then be utilized to determine the tortuosity for the bed given the measurement of mass flux. Figure 3 shows experimental results for the tortuosity measured over the temperature range from 25 °C to 40 °C and for two different sizes of glass beads (120 and 450 microns). The data indicate that particle size does not have a strong effect on the tortuosity coefficient. The measured tortuosity has an average value of 0.78 with a standard deviation of 0.0282. This value is in reasonable agreement with those in use by soil scientists [15], 0.66, and in drying predictions [16], 0.70. The experimental uncertainty for these results is estimated to be 0.046 which is consistent with the standard deviation reported above. The largest contributor to the estimated uncertainty is the measured mass flux. However, the effect of liquid or adsorbed water in the bed was not considered in the estimation of the uncertainty. The question of how much water must be in the bed before it might enhance the diffusion will be addressed later in the paper. The water loss from the upper reservoir and wick assembly, the water gain in the bed, and water gain in the desiccant tray indicate that mass is conserved. Figure 4 shows the ratio of water accumulation rate in the bed and in the desiccant tray at different temperatures. These ratios are, with two exceptions, below 0.1.

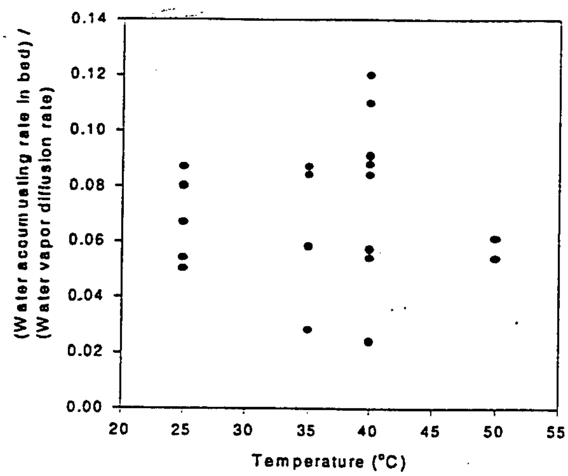


Figure 4. Ratio of water accumulation rates in bed and in the desiccant

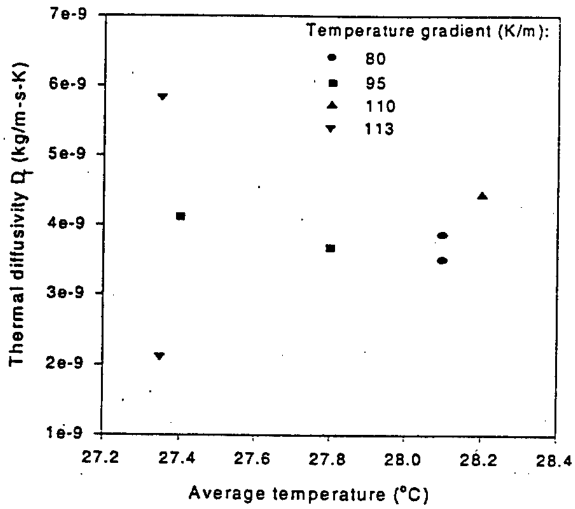


Figure 5. Thermal diffusivity D_T at free space

Before doing nonisothermal experiments involving a packed bed, the equivalent experiments were performed without the glass beads in order to determine the Soret coefficient, D_T, in Equation (7). With D^c_{eff} in Equation (5) measured, D_T can be determined by again measuring the mass flux for free space subjected to a prescribed temperature gradient. These results are shown in Figure 5. Compared to the isothermal measurements (Figure 2) there is considerable scatter in the data with no strong correlation to either the average temperature or the temperature gradient. The average measured value for D_T is 3.9 x 10^{-9} kg/m-K-s. For our experimental conditions approximately 5~8% of the total flux is contributed by the thermal (second) term in Equation (5). This coefficient appears to be high when compared to the Soret coefficient for other gaseous mixtures [13] . It is speculated that small amounts of condensation on the walls of the test chamber may be affecting these results. The uncertainty is estimated to be 5.8% which is somewhat less that the scatter indicated by the data. The primary contributor to the calculated uncertainty is the uncertainty in the isothermal mass diffusion coefficient and the measurement of the mass flux.

Before presenting results for experiments involving enhanced vapor diffusion an enhancement factor must be defined. Previous investigators have used two different definitions for the enhancement parameter, one normalized using the effective diffusion coefficient for a dry porous medium which will be termed η and one normalized using the free space diffusion coefficient termed β. Mathematically the effective diffusion coefficients can be expressed as:

$$D^c_{eff} = \eta S_g \phi \tau D_C \quad \text{and} \quad D^t_{eff} = \eta S_g \phi \tau D_T \qquad (9)$$

$$D^c_{eff} = \beta D_C \quad \text{and} \quad D^t_{eff} = \beta D_T \qquad (10)$$

Utilizing Equations (9) - (10) in conjunction with the measured mass flux, the isothermal effective diffusion coefficient, D^c_{eff}, and effective thermal diffusion coefficient, D^t_{eff}, the enhancement factors η and β can be determined.

Because of the continuous condensation of vapor in the bed, the measurements of the enhancement factor were made under transient conditions. It was possible to establish quasi steady conditions (for periods of 6 - 10 hours) by adjusting the boundary conditions (temperature) during the course of the experiment. For transient experiments it is noted that the enhancement factor could be based on three different mass fluxes - all of which were measured - the flux entering the bed, the flux exiting the bed, and the average flux. For the quasi-steady experiments the entering and exiting mass fluxes were equal and hence this problem did not exist.

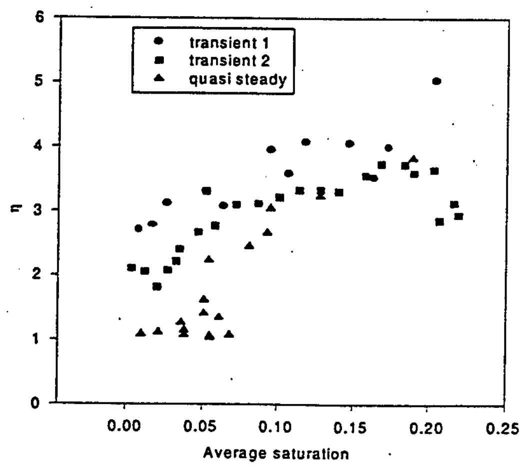


Figure 6. The enhancement factor η as a function of average saturation for different boundary conditions

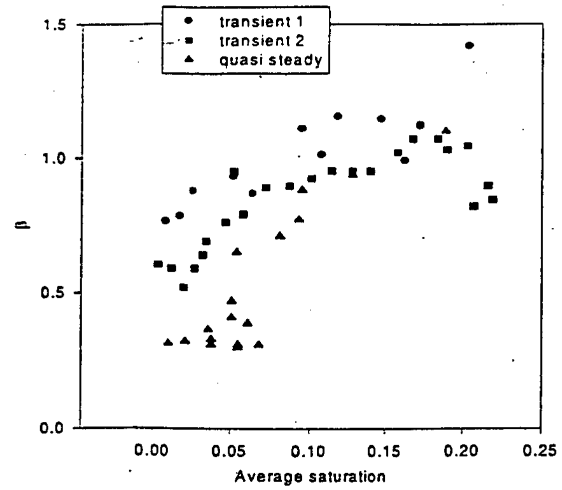


Figure 7. The enhancement factor β as a function of average saturation for different boundary conditions

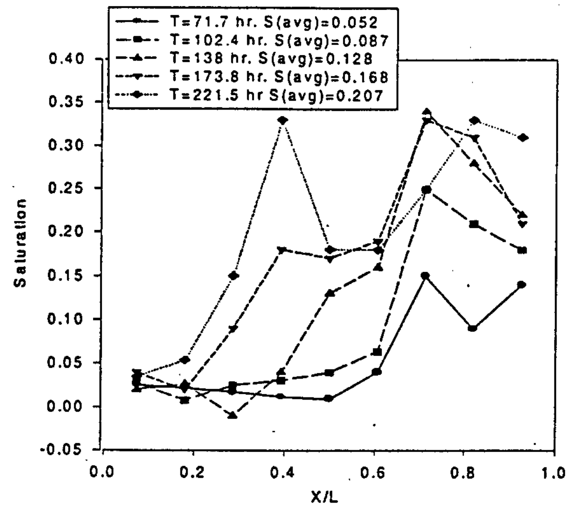


Figure 9. Saturation profiles at different times for transient 2 experiment

Figures 6 and 7 show experimental results for the two enhancement factors (based on the average of inlet and outlet mass fluxes) defined in Equations (9) and (10) as a function of average saturation for a number of quasi-steady cases and two transient experiments. The transient experiments were conducted using two different temperature differences. For the results identified as transient 1 the upper and lower bed temperatures were maintained at 39.5 and 27.1 °C, respectively, while for transient 2 they were maintained at 35.3 and 32.5 °C, respectively. Transient 1 spanned a period of 120 hours beginning with an initially dry bed and ending with an average saturation of 0.19. Transient 2 ran for 243 hours and ended with a saturation of 0.22. For the transient experiments enhancement factors are presented based on the average mass flux. The uncertainty in the enhancement factors presented is estimated to be 8.5%.

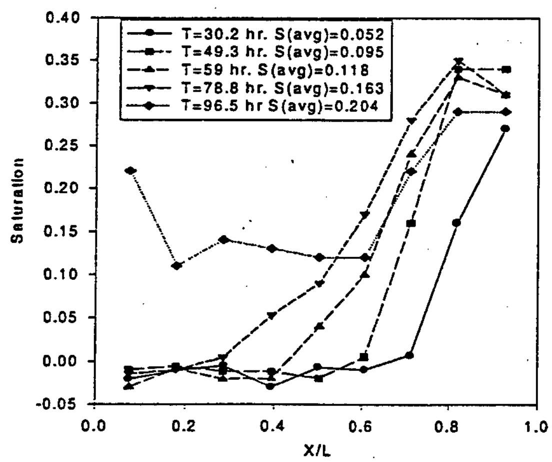


Figure 8. Saturation profiles at different times for transient 1 experiment

As can be seen in the figures the results for the quasi-steady measurements fall slightly below those for the transient experiments based on the average of inlet and outlet mass fluxes. The results are qualitatively similar to those of previous investigators [6] in that for very low liquid content (saturation less than 0.05) there is very little enhancement. As the saturation is increased to 0.20, where transport in the liquid phase should be expected to begin to contribute, the enhancement factor increases to approximately 1 when compared to free space (β) and approximately 4 when normalized to the diffusion coefficient for a dry porous medium (η). The temperature difference, or temperature gradient, does not appear to have a strong effect on the results. For the enhancement factors calculated using the average of the inlet and outlet mass fluxes for the two transient cases which have different imposed temperature gradients (Figure 10) the results are comparable. In this case transient 2 which has the smaller temperature difference results in higher enhancement factors.

Because of the nature of these experiments the saturation distribution in the bed is both nonuniform and time dependent. The saturation distributions as a function of time and space for the two transient experiments are shown in Figures 8 and 9. In these figures x/L = 0.0 is at the bottom of the bed. The uncertainty in the measurement of saturation is estimated to be 7.5% when saturation is 0.1, and 4.3% when saturation is 0.2. The primary contributor to this uncertainty is the variation in measured gamma counts. In both cases the saturation is high near the top of the bed due to condensation. This region of high saturation increases in thickness as the experiment progresses in time. The wet region is separated from the rest of the bed by a drying front which moves toward the bottom of the bed as time progresses. It appears that liquid phase transport begins to play a dominant role as the saturation approaches 0.3 since the saturation does not increase beyond this point. In both experiments the condensation rate exceeds the drying rate and hence the drying front eventually moves to the lower surface along with higher saturations.

The temperature distributions in the bed are shown in Figure 10 for the two transient experiments. As can be seen in the figure, the temperature distributions are not linear and change very little with time in contrast to the saturation distributions. Latent heat exchange and variations in thermal conductivity due to saturation variations both contribute to the non-linear temperature distribution. In the case of a small temperature difference the temperature in the middle of the bed (x/L = 0.5) is actually lower than the temperature at the bottom of the bed (x/L = 0.0) due to the dominance of the latent heat associated with evaporation.

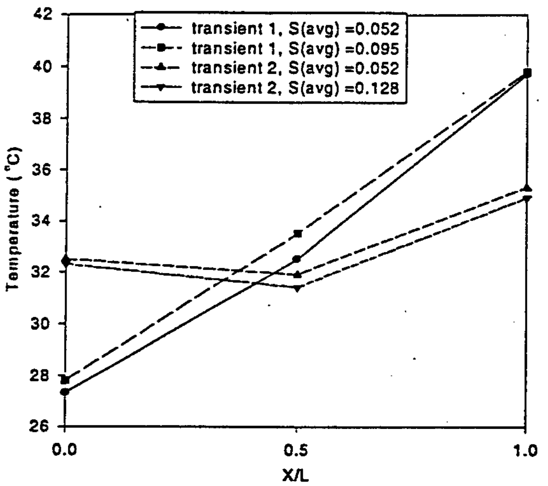


Figure 10. Temperature profiles of the packed bed

CONCLUSIONS

The dry tortuosity coefficient was measured under isothermal conditions in packed beds of glass beads having average diameters of 120 and 450 microns. For temperatures ranging from 25 °C to 40 °C the measured tortuosity coefficient was 0.78 ± 0.028. No correlation between bead size or temperature and the tortuosity coefficient is evident in the data.

Although measurements of the free space mass diffusion coefficient are in good agreement with those in the literature, measured values of the thermal (Soret) diffusion coefficient appear to be high, at least when compared to those for other gaseous mixtures. The thermal diffusion coefficient measured in this case was 3.9×10^{-9} kg/m-s-K.

Nonisothermal experiments in packed beds of glass beads confirmed the existence of enhanced vapor diffusion resulting from pore-scale condensation and evaporation. The data from these experiments have been utilized to extract enhancement factors which depend on the average saturation in the bed. Although the experimental data is complicated by the transient nature of the experiment and nonuniform saturation distribution, the results are qualitatively similar to those reported previously [6]. The measured enhancement factor defined as the effective diffusion coefficient normalized for a dry porous medium diffusion coefficient increases from 1.0 to approximately 4.0 as the average saturation increases from 0.0 to 0.2.

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