

EPA/600/D-87/185
NTIS PB 87 199170

ASPECTS OF LIQUID AND VAPOR FLOW IN RETORTED OIL SHALE

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Presented at the 1986 Eastern Oil Shale Symposium,
Lexington, Kentucky
November 19-21, 1986

Notice

The development of the information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement CR812225 to Colorado State University. It has been subject to the Agency's peer and administrative review, and it has been approved for publication.

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Abstract

Reclamation and impact analysis of retorted oil shale piles will require prediction of water and solute transport rates over the entire water content range down to and including the relatively dry region. Experimental measurements of water transport coefficients in relatively dry oil shales have brought forward long-standing questions concerning the mechanics of combined liquid/vapor flow. In an attempt to ensure proper interpretation of experimental data, a new analytical solution has been obtained for combined liquid and vapor flow with solute transport. The solution shows that the relative magnitudes of the separate transport coefficients produce many of the flow features seen in experimental data, and significant liquid transport can occur in regions without apparent solute transport. This development is new and represents a significant addition to understanding solute transport. As such its methods and results can be applied to other problems in multiple phase transport and to materials such as high volume mining wastes and some hazardous waste disposal sites. The paper shows that an earlier conclusion reached by the authors, that a critical water content exists in retorted oil shale below which solute transport ceases, is unjustified.

Introduction

Research into the movement of water and dissolved constituents in retorted oil shale has been motivated by the adverse impacts that can be anticipated if leachate is generated and left uncontrolled in the large disposal piles planned. Accurate prediction of water and solute movement through disposal piles will require measurements of both water and solute transport over the entire range of solution contents, down to and including the relatively dry region. Dry region transport phenomena are of concern for two reasons. First, retorting produces a shale that is oven dried, and it is expected that only enough water to control dust and aid compaction will be added before placement, and much of that may rapidly be lost to evaporation. Thus, the pile initial condition before infiltration of precipitation will probably be relatively dry, and leaching may be strongly influenced by transport processes near the initial condition. Second, an earlier study by Golder Associates¹ has proposed that piles be designed to eliminate pile leachate by evaporating all excess infiltration. Such evaporation would of course require the portion of the pile near the evaporating interface to remain quite dry.

In a previous study by the authors^{2,3} the hydraulic and solute transport characteristics of Lurgi retorted oil shale were measured from saturation ($0.49 \text{ cm}^3/\text{cm}^3$) down to almost zero solution content. These measurements were carried out by use of a dual source gamma ray system^{4,5,6} which can simultaneously measure water content and solute concentrations during column sorption experiments. The experiments showed, as expected from earlier studies^{7,8,9,10,11}, that water vapor diffusion becomes the dominant water transport mechanism in the retorted material at low solution contents. Empirical examination of the data indicated that the liquid water and solute transport ceased at $0.066 \text{ cm}^3/\text{cm}^3$ volumetric solution content and that all water transport was by vapor diffusion.

As soon as these results were obtained, questions arose as to the accuracy of the data interpretation. More specifically, it was questioned if the solute transport observed was a function more of the test conditions, and if liquid transport actually ceased at a finite solution content. Examination of the literature showed that a considerable number of questions remained about the interactions of combined

liquid/vapor flow^{12,13,14} and unexplained solute transport phenomena which occur near low water contents¹⁴.

In an attempt to ensure proper interpretation of the experiment data a theoretical model of two-phase water and solute transport in a pore was developed. The model allows analytical numerical solutions to the unsteady sorption of solution. The model solutions are able to produce many of the flow features seen in the experimental data. From the results it can be concluded that the relative magnitude of the separate liquid and vapor transport coefficients produce the solute profiles seen, and that significant liquid transport can occur in a region without apparent solute transport.

Phenomena of Interest

In this paper two experimentally observed phenomena will be examined. These phenomena have been either unexplained or explained by thresholds of transport processes which have not been rigorously proven to exist.

Critical Water Content

Several experimenters have observed or speculated on the existence of a "critical" water content below which liquid conduction of solute ceases. From sorption or solute diffusion in dry media, Grismer et al.⁶, McWhorter and Brown^{2,3}, Rose¹⁰, and Porter et al.¹⁵ speculated that the liquid phase becomes discontinuous at low water contents. From sorption at high solution contents, Krupp et al.¹⁶, Laryea et al.¹⁷, and Robin et al.¹⁸ postulated the existence of an immobile layer of water near the solid surface, while Van Schaik and Kemper¹⁹, Smiles and Gardiner²⁰, and Bond et al.²¹ concluded that significant anion exclusion effects were occurring.

Most of the above conclusions were based on unsteady infiltration of solution. Typical results of such an experiment are taken from McWhorter and Brown² and are shown in Fig. 1. In this experiment NaI solution was injected into a completely dry column. Water and I⁻ were tracked by dual source gamma ray. After significant inflow the water was observed to develop a gradually varying profile, but the solute was restricted to water contents above 0.06 (cm³/cm³).

Solute Concentration Humps

Smiles et al.¹⁴ observed, as shown in Fig. 2, that, on infiltrating soil with a low initial solution content, there was not perfect piston-like displacement of the resident fluid, as would be expected. A small increase or hump in the resident solute concentration was formed ahead of the wetting front where the solute concentration was increased above the initial. This hump could not be explained, as no single convective or dispersive process can explain an increase in solute concentration in a region of increasing solution content. The same hump can be seen in the data but was not noted by Smiles and Phillip²².

Likewise McWhorter and Brown^{2,3} observed large increases in the invading solute

concentration behind the wetting front. They attributed the hump to evaporation.

The theoretical model, which is detailed in the Appendix, will be applied to determine if these two phenomena can be explained by the two-phase transport processes without the aid of transport thresholds such as a critical water content.

Method of Analysis

The phenomena of interest will be explained by appeal to a theoretical solution of liquid and vapor flow with solute transport in a porous media of known hydraulic properties. To obtain the theoretical solution new equations of water and solute transport have been developed. The derivation of these transport equations is secondary to the purpose of this paper. Therefore, only the assumptions and final results, will be presented here, while a brief derivation is presented in the Appendix.

Model Assumptions

The developed model assumes one-dimensional horizontal adsorption of liquid solute into a nearly dry column of porous media as typical with most laboratory experiments of interest here. Solution is transported by gradients of hydraulic pressure, but it is assumed that the water characteristic can be used to transform Darcy's conductivity to a diffusivity where the liquid flow is driven by gradients of water content. The vapor transport is assumed to be driven by vapor diffusion but again it is assumed that the vapor adsorption isotherm can be used to transform the driving gradient to the liquid water content. These well established transformations are routinely used by investigators in this field. The liquid and vapor phases are assumed to be in instantaneous local equilibrium; i.e., where kinetic effects of evaporation and condensation are negligible.

Solutes are present in both the initial solution and the invading solution, but at different concentrations. Solute is transported only in the liquid phase. The solute is not adsorbed by the solid phase and moves with the mean velocity of the liquid phase. This last assumption implies miscible displacement; i.e., the initial and invading solutes are mixed by only small-scale dispersive processes.

The column has a uniform, low initial solution content. At the start and during the remainder of the adsorption the column inlet is maintained at a constant solution content. The invading solution enters the column with a constant concentration. This is a slightly different boundary condition than used in some experiments.^{2,3}

Diffusivities

Using the concept of liquid and vapor diffusivities it can be stated that the total water flux expressed as liquid volume is

$$q_c = - \left[\frac{D_v(\theta)}{C_w} \frac{d\rho_v}{d\theta} + D_l(\theta) \right] \frac{\partial \theta}{\partial x} \quad \text{or (1a)}$$

$$q_c = - D_c(\theta) \frac{\partial \theta}{\partial x} \quad \text{(1b)}$$

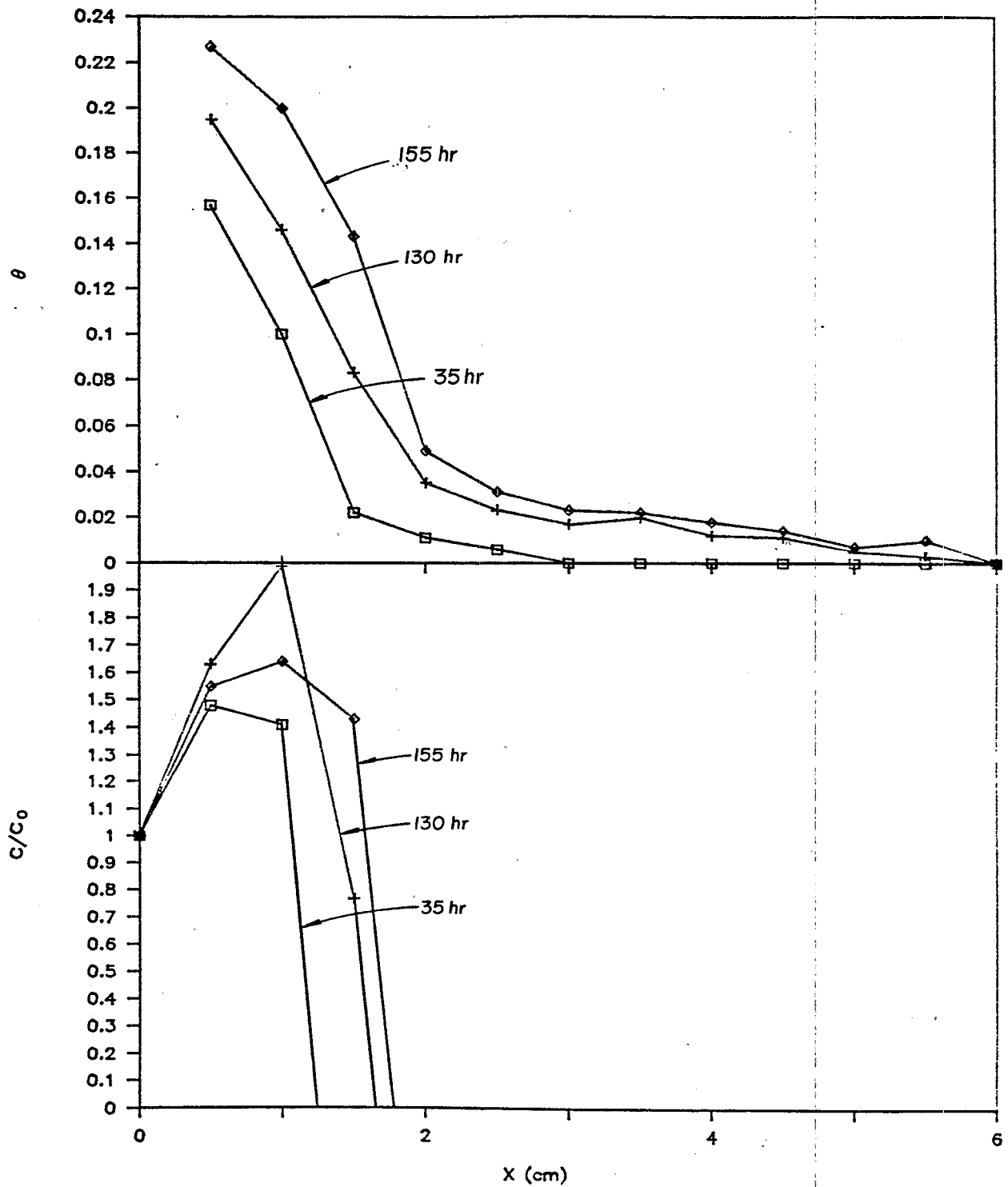


Figure 1. Solution Content (θ) and Relative Invading Solute Concentration (C/C_0) Versus Column Position (x), After Various Times. These Results Are from an Unsteady, Constant-Flux Experiment Performed by McWhorter and Brown²

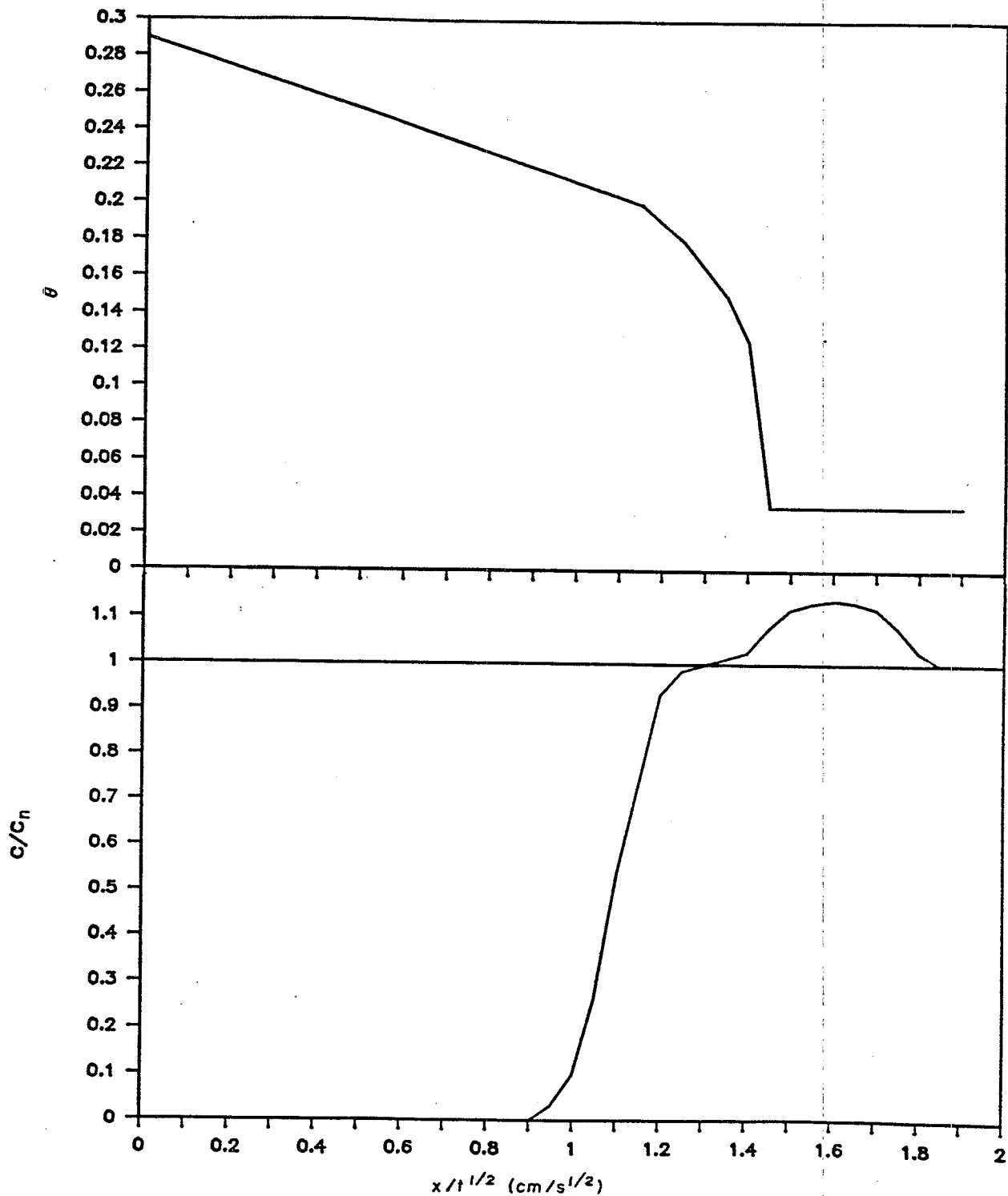


Figure 2. Solution Content (θ) and Relative Resident Solute Concentration (C/C_n) Versus Relative Column Position ($x/t^{1/2}$). These Results Are From an Unsteady Constant Concentration Experiment Performed by Smiles et al.¹⁴ (Curves Are Best Fit to Reported Data)

where q_t - total equivalent liquid volumetric flux,
 $D_v(\theta)$ - vapor diffusivity,
 C_w - concentration of water in solution,
 $d\rho_v/d\theta$ - slope of vapor adsorption isotherm,
 $D_l(\theta)$ - liquid diffusivity,
 θ - solution content,
 $D_t(\theta)$ - total water diffusivity, and
 x - horizontal position.

As noted both D_l and D_v are functions of θ . With Eq. (1a) it is clear that the total water flow is the sum of the two components, bulk liquid flow and vapor diffusion. The fraction of water transport in either phase at a particular position is simply the ratio of the phase diffusivity to the total.

Assumed Diffusivities

Values of the individual diffusivities must be assumed to achieve a flow solution. Figure 3 presents the assumed values. In the figure the horizontal axis is the solution volumetric content, θ , over the range of interest 0.02 to 0.10, while the vertical axis is the diffusivity.

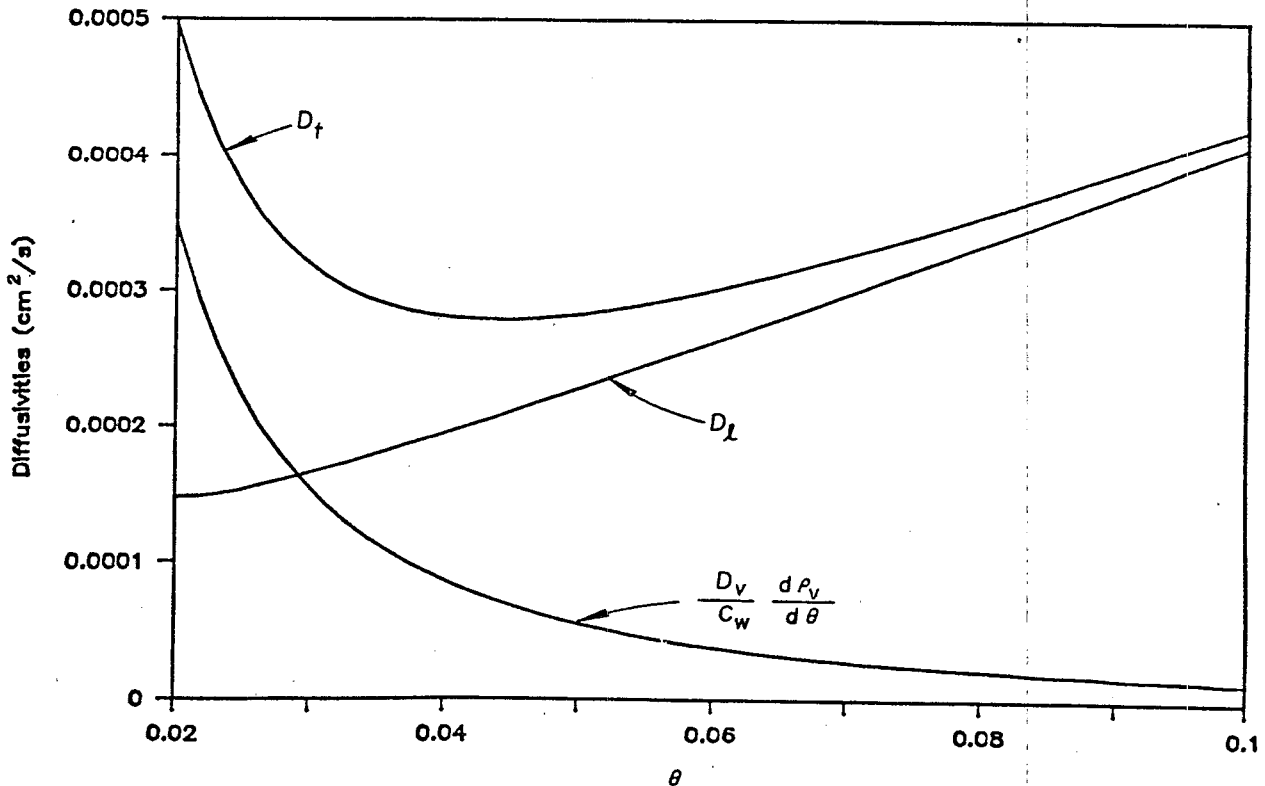


Figure 3. Assumed Values of Liquid (D_l), Vapor (D_v), and Total (D_t) Diffusivities. Note That Vapor Has a Maximum at Low Solution Contents; The Liquid, at High Solution Contents; and the Total, a Minimum at an Intermediate Content

Note that the vapor diffusivity is greatest at the lower solution contents, while the liquid diffusivity dominates as solution content increases. Nowhere in the range of interest is either transport coefficient zero. The total diffusivity has the characteristic double maximum of most porous media. These functions were obtained from a theoretical model for a set of plate capillaries, but for this analysis any set of values could be used as long as they had the same general shape. A different set of transport coefficients would only change the numerical results, not the general conclusions.

From the Appendix, the general equation for the water flow is

$$-\frac{\lambda}{2} \frac{d\theta}{d\lambda} - \frac{d}{d\lambda} \left(D_t \frac{d\theta}{d\lambda} \right) \quad (2)$$

where $\lambda = x/t^{1/2}$, and

t = time from start of sorption.

Equation (2) is subject to

$$\theta(\lambda=0) = \theta_0; \text{ a constant, and} \quad (3)$$

$$\theta(\lambda=\infty) = \theta_n; \text{ a constant.} \quad (4)$$

The use of the transformed Boltzman coordinate, $\lambda=x/t^{1/2}$ is possible due to the boundary conditions used, and "normalizes" the solution. That is, it allows the solution content profiles from different times to be collapsed onto one another. For ease of reference, λ can be

thought of as a horizontal scale which stretches uniformly (like a rubber band) with time.

The evaporation and condensation along the column can be determined by the relation:

$$e(\lambda) = \left[\frac{dA(\theta)}{d\theta} - \frac{\lambda}{2} \right] \frac{d\theta}{d\lambda}, \quad (5)$$

where e = the phase transfer, and

$A(\theta)$ = transport function.

The transport function is calculated during the solution procedure and is a function of the diffusivities and boundary conditions. The phase transfer variable e is positive for condensation and negative for evaporation.

The solute concentration along the column can be determined by solution of the following differential equation:

$$C(\lambda)e + \left[A(\theta) - \frac{\lambda\theta}{2} \right] \frac{dC(\lambda)}{d\lambda} = \frac{d}{d\lambda} \left[\theta D_s(\theta) \frac{dC(\lambda)}{d\lambda} \right], \quad (6)$$

subject to:

$$C(\lambda=0) = C_o, \text{ and} \quad (7)$$

$$C(\lambda \rightarrow \infty) = C_n, \quad (8)$$

where $C(\lambda)$ = solute concentration,

$D_s(\theta)$ = coefficient of solute dispersion,

C_o = inlet concentration of invading solute, and

C_n = initial concentration of resident solute.

The left-hand side of Eq. (6) represents phase transfer and convective effects, while the right-hand side represents dispersion.

Results and Discussion

Flow Solution

Figure 4 presents the solution of Eq. (2) for solution content profiles for the initial and boundary conditions given by Eqs. (7) and (8). In Fig. 4 the vertical axis is solution content and the horizontal axis the normalized distance, $x/t^{1/2}$. As could be expected the solution content falls from the boundary condition at the inlet ($x/t^{1/2} = 0$), to the initial solution content at about $x/t^{1/2} = 0.07$. As in all sorption experiments where vapor transport plays a role, a "vapor nose" elongates the profile. This nose is due to the secondary diffusivity maximum at the low solution contents as shown in Fig. 3. This theoretical profile is similar and consistent with experimentally observed profiles.

Next, solving Eq. (5) for the evaporation and condensation of water vapor along the column provides the data plotted in Fig. 5. In Fig. 5 the vertical axis is the normalized phase

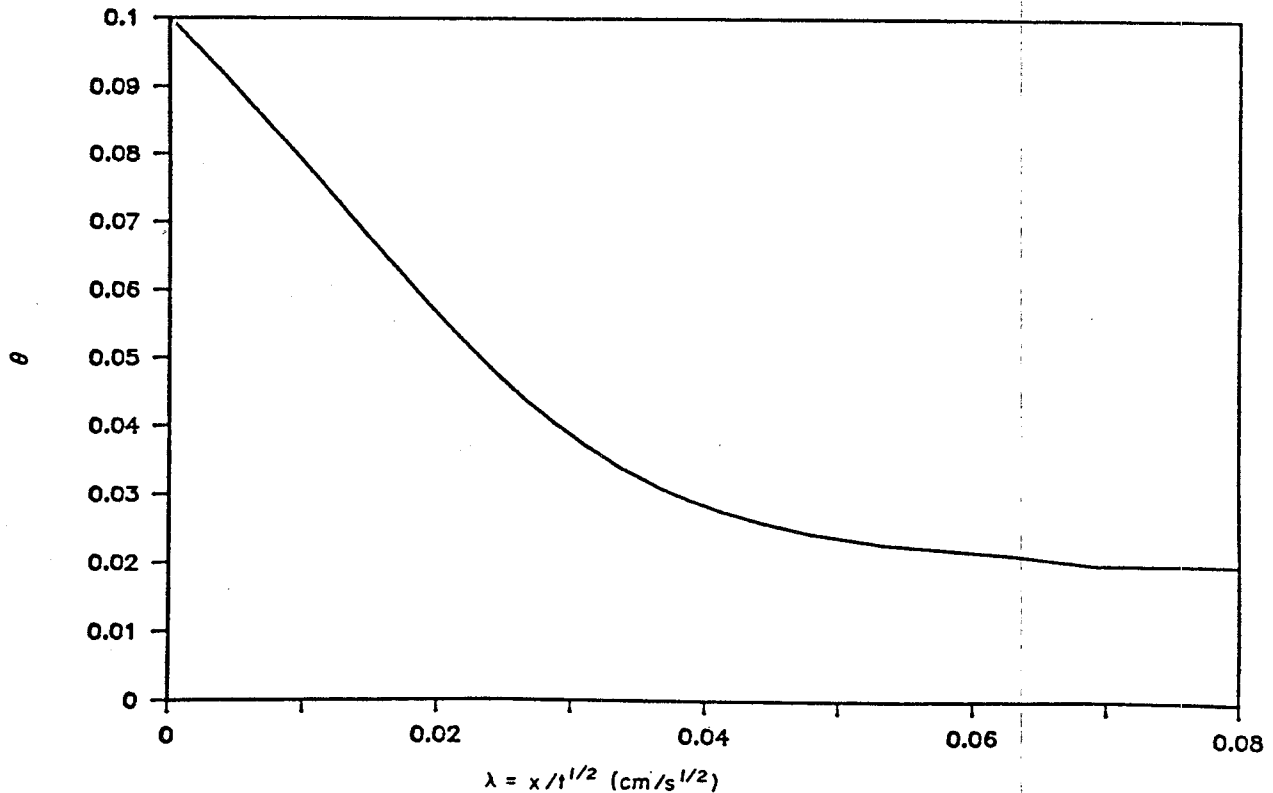


Figure 4. Calculated Solution Content (θ) Versus Relative Position ($x/t^{1/2}$)

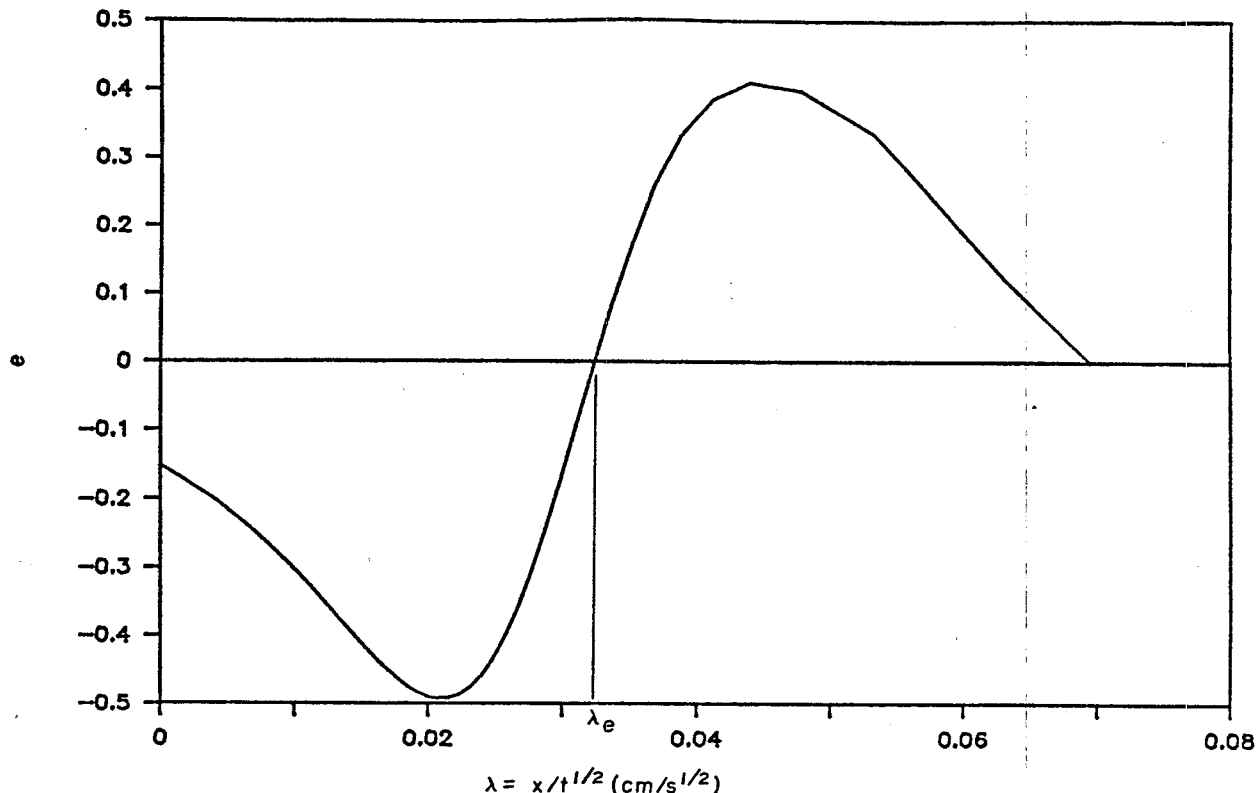


Figure 5. Calculated Evaporation and Condensation (e) Versus Relative Position ($x/t^{1/2}$)

transfer, e , with condensation positive and evaporation negative. Again the horizontal axis is the normalized distance $x/t^{1/2}$. The point labeled λ_e , where e is zero at about $0.03 \text{ cm/s}^{1/2}$, separates the regions of evaporation and condensation. In consideration of solute transport it can be stated that the evaporation behind λ_e will tend to increase the solute concentration, while the condensation ahead of the point will tend to reduce solute concentrations. The maximum evaporation rate occurs at about $0.021 \text{ cm/s}^{1/2}$, while the maximum condensation occurs at about $0.044 \text{ cm/s}^{1/2}$.

Finally, Eq. (6) must be solved to obtain the solute concentration along the column. For illustrative reasons Eq. (6) is solved assuming that the dispersive term on the right-hand side is zero. This allows the clear presentation of the convective and evaporation effects without the blurring caused by dispersion. Figure 6 presents these results. In Fig. 6 the vertical axis is the normalized solute contents C/C_o and C/C_n . The invading solution has only advanced to a position, labeled λ_s , of about $0.018 \text{ cm/s}^{1/2}$. From the inlet the invading solution concentration, C/C , rises from its injection value, 1, to a maximum of about 1.5 at λ_s . This increase in concentration is due to both evaporation and convective effects.

Possibly of greater interest is the concentration of the resident fluid, C/C_n . While condensation at the far end ahead of λ_n dilutes the resident solution, as could be expected, convective and evaporative effects between λ_s

and λ_e have the net effect of first increasing the concentration above 1 and then reducing it to about 0.8. If dispersion were added, these concentration profiles would be blurred by the smoothing effect of the dispersion, but the trend would still be present.

Explanation of Phenomena of Interest

We can now explain the two phenomena of interest. First re-examine Fig. 6. Looking only at the invading solute concentration profile (McWhorter and Brown^{2,3}) it could be argued that a "critical" water content occurred at position λ_s , which (from the solution content profile, Fig. 5) would be estimated to have a value of about 0.06. Thus it would be concluded that liquid diffusivity dropped to zero at that point. But this, of course, would be wrong. From Fig. 3 it can be seen that the liquid diffusivity is about four times the vapor value at that solution content. The solute is limited to the region behind λ_s simply because that position is as far as convection will transport it during a given infiltration time. Also note that λ_s is not an explicit function of the evaporation. The evaporation front, λ_e , is well ahead of λ_s , and λ_s is also slightly behind the position of maximum evaporation.

Now examine the resident solution content profile. The increase in solute concentration ahead of λ_s is similar to the unexplained observation of Smiles et al.¹⁴. Thus their data can be explained as the effects of combined liquid and vapor flow which they did not consider.

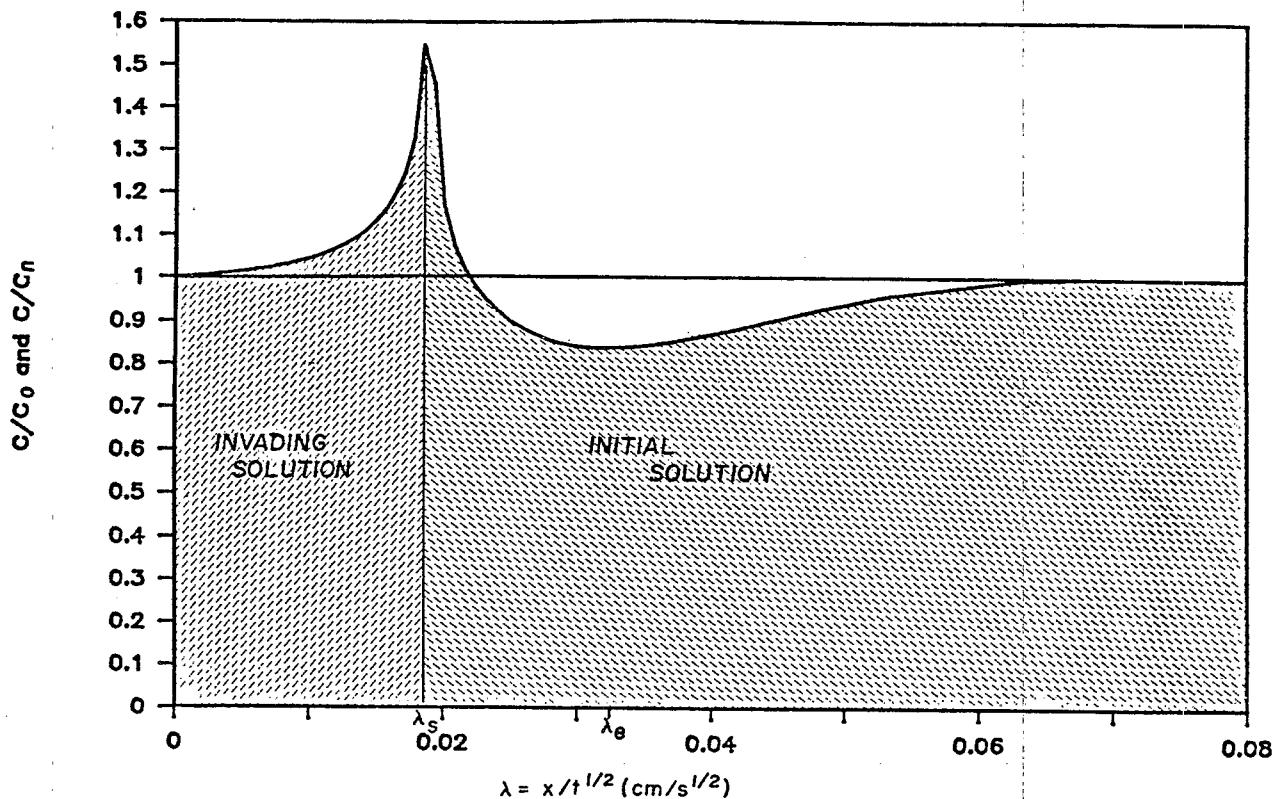


Figure 6. Calculated Solute Concentration (C/C_0 and C/C_n) Versus Relative Position ($x/t^{1/2}$)

Finally note that in this case the minimum resident solution content occurs not where condensation is a maximum but instead where the phase transfer is zero. This point demonstrates clearly that the solute concentration is a function of both convection and phase transfer, and that at some positions convection alone can produce concentration changes.

Conclusions

This analysis has shown that, in relatively dry retorted oil shale, proper interpretation of experimental solute transport data requires careful theoretical considerations. The vapor transport of water, while small when compared to liquid flow, nevertheless induces convective transport processes in the liquid phase which can increase or dilute the concentration of solutes. Without a clear understanding of the effects of evaporation and condensation on solute convection it is easy to misinterpret experimental data.

Additional analyses of liquid and vapor flow with solute transport have been performed. These included the constant concentration with dispersion, the constant flux boundary with and without dispersion, and a case with actual measured oil shale liquid and vapor diffusivities. Results of these analyses will be published at a later date.

Notice

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Appendix

Theoretical Development

This appendix presents a development of the equations of water, vapor, and solute transport in porous media. This development has been kept as brief as possible and is limited to the case of constant concentration adsorption of solution. Solutions for desorption and constant flux sorption have been obtained by similar methods, but are beyond the scope of this paper. A complete development of this theory will be published at a later date.

This development is new and represents a significant addition to understanding solute transport. As such its methods and results can be applied to other problems in multiple phase transport.

For one-dimensional sorption of water vapor the mass flux of vapor, F_v , is given by:

$$F_v = -D_v \frac{d\rho_v}{d\theta} \frac{\partial \theta}{\partial x} \quad (A-1)$$

where

D_v = vapor diffusivity,

ρ_v = vapor density,

θ = volumetric water content, and

x = horizontal distance.

The vapor diffusivity is a function of the free space molecular diffusion coefficient, the tortuosity, the porosity, and the solution content. The ratio $d\rho_v/d\theta$ is used to transform the driving gradient for diffusion from vapor concentration to water content. Its use assumes that a unique isothermal equilibrium exists between the vapor and liquid phases. Continuity of vapor phase on a control volume of porous media yields:

$$\frac{\partial}{\partial t} (\phi - \theta) \rho_v - \frac{\partial}{\partial x} D_v \frac{d\rho_v}{d\theta} \frac{\partial \theta}{\partial x} - E \quad (A-2)$$

where

ϕ = porosity,

E = mass transfer to the liquid phase, and

t = time.

The source term, E , in general is assumed to be a function of x and t .

For one-dimensional horizontal sorption of liquid solution, the mass flux of water, F_l is given by the relation:

$$F_l = q_l C_\omega - C_\omega D_l \frac{\partial \theta}{\partial x} \quad (A-3)$$

where

q_l = liquid volumetric flux,

C_ω = water concentration in solution, and

D_l = liquid diffusivity.

The liquid diffusivity is related to the hydraulic conductivity and is a strong function of solution content. Continuity of liquid phase on a control volume of porous media yields:

$$\frac{\partial}{\partial t} (C_\omega \theta) - \frac{\partial}{\partial x} C_\omega D_l \frac{\partial \theta}{\partial x} + E \quad (A-4)$$

Adding Eqs. (A-2) and (A-4) yields the total water continuity:

$$\frac{\partial}{\partial t} (\phi - \theta) \rho_v + \frac{\partial}{\partial t} (C_\omega \theta) - \frac{\partial}{\partial x} \left(D_v \frac{d\rho_v}{d\theta} + C_\omega D_l \right) \frac{\partial \theta}{\partial x} \quad (A-5)$$

Note in Eq. (A-5) the source terms have cancelled. Using typical vapor adsorption isotherms, it is simple to show that $\partial/\partial t (\phi - \theta) \rho_v \ll \partial/\partial t (C_\omega \theta)$, and thus, the first term can be dropped. Likewise for dilute solutions, it can be shown that $C_\omega \approx \text{constant} = 1$. With these assumptions Eq. (A-5) becomes:

$$\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} \left(\frac{D_v}{C_\omega} \frac{d\rho_v}{d\theta} + D_l \right) \frac{\partial \theta}{\partial x} \quad (A-6)$$

Now a combined diffusivity, D_t , is defined as:

$$D_t = \frac{D_v}{C_\omega} \frac{d\rho_v}{d\theta} + D_l \quad (A-7)$$

Equations (A-6) and (A-7) yield a simple equation of water flow:

$$\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} (D_t \frac{\partial \theta}{\partial x}) \quad (A-8a)$$

$$\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} q_t \quad (A-8b)$$

where q_t is the total water volumetric flux expressed as solution. For constant concentration sorption, the initial and boundary conditions are:

$$\theta(x, 0) = \theta_n \quad (A-9)$$

$$\theta(\infty, t) = \theta_n \quad \text{and} \quad (A-10)$$

$$\theta(0, t) = \theta_o \quad (A-11)$$

Flow Solution Method

McWhorter²³ and Phillip²⁴ showed that Eq. (A-8b) could be solved by a method of fractional flow where the flux at any $\theta(x, t)$ is defined as a fraction, $F(\theta, t)$, of the influx at $x=0$, or:

$$q_t(x, t) = F(\theta, t) q_o(t) \quad (A-12)$$

where $q_o(t)$ is the inlet volumetric flux.

Phillip and Knight²⁵ proved that, for constant concentration boundary condition (Eq. A-11), F was not a function of time. Thus, an exact solution for the flow can be found through a semi-analytical calculation of $F(\theta)$. For this boundary condition the inlet flux is given by:

$$q_o(t) = S/t^{1/2} \quad (A-13)$$

where S is the soil sorptivity constant calculated from the fractional analysis.

With use of Eqs. (A-12) and (A-13), Eq. (A-8b) is simplified further to:

$$\frac{\partial \theta}{\partial t} = - \frac{S}{t^{1/2}} \frac{\partial}{\partial x} F(\theta) \quad (A-14)$$

For the boundary conditions of Eqs. (A-9), (A-10), and (A-11) the Boltzman transformation will ease the solution of Eq. (A-14). A transform coordinate is defined as:

$$\lambda = x/t^{1/2} \quad (A-15)$$

Making this substitution into Eqs. (A-9), (A-10), (A-11), and (A-14) yields a differential equation of flow:

$$- \frac{\lambda}{2} \frac{d\theta}{d\lambda} - S \frac{d}{d\lambda} F(\theta) \quad (A-16a)$$

which is equivalent to:

$$- \frac{\lambda}{2} \frac{d\theta}{d\lambda} = \frac{d}{d\lambda} D_t \frac{d\theta}{d\lambda} \quad (A-16b)$$

Eq. (A-16) is subject to:

$$\theta(\infty) = \theta_n \quad \text{and} \quad (A-17)$$

$$\theta(0) = \theta_o \quad (A-18)$$

With Eq. (A-16) and the fractional flow analysis of $F(\theta)$, the flow profile at any time and position can be determined for given diffusivity functions D_v and D_l or D_t .

Of importance to this appendix is the determination of the seepage velocity, $v(\theta_i)$, of a particular solution content, θ_i . Using Eq. (A-14) and the definition of substantial derivatives, it can be shown that:

$$v(\theta_i) = q_o(t) \frac{dF}{d\theta} \Big|_{\theta_i} \quad (A-19)$$

Liquid Phase Analysis

With the total flow analysis, the water transport in either phase, the evaporation and the condensation can be determined. First, since all fluxes (liquid, vapor, and total) are driven by $\partial\theta/\partial x$, they can be related by the ratio of diffusivities:

$$q_l = \frac{D_l}{D_t} q_t \quad (A-20)$$

With Eqs. (A-12) and (A-13):

$$q_l = \frac{D_l}{D_t} FS t^{-1/2}, \text{ or} \quad (A-21a)$$

$$q_l = A(\theta) t^{-1/2}, \quad (A-21b)$$

where $A(\theta)$ is a transport function equal to $D_l FS/D_t$. Returning to the liquid continuity, Eq. (A-4):

$$\frac{\partial}{\partial t} (C_\omega \theta) = \frac{\partial}{\partial x} C_\omega q_l + E. \quad (A-4)$$

Again, assuming $C_\omega = 1$, making the Boltzman transform, and substituting Eq. (A-21b) yields:

$$-\frac{\lambda}{2} \frac{d\theta}{d\lambda} + \frac{dA}{d\lambda} = E'(x, t) t \quad (A-22)$$

Here E' is E/C_ω . Now note that the left-hand side is only a function of λ . It can be stated from inspection that:

$$E'(x, t) = e(\theta)/t. \quad (A-23)$$

Substituting Eq. (A-23) into (A-22) yields a relationship for the evaporation/condensation:

$$e(\theta) = -\frac{\lambda}{2} \frac{d\theta}{d\lambda} + \frac{dA}{d\lambda} \quad (A-24)$$

Solute Transport

With the known flow conditions it is now possible to predict the solute transport. Assuming solute is transported by convection and Fickian dispersion in the liquid phase a control volume analysis yields the equation of solute motion:

$$\frac{\partial \theta C}{\partial t} = -\frac{\partial}{\partial x} (C q_l) + \frac{\partial}{\partial x} (\theta D_s \frac{\partial C}{\partial x}), \quad (A-25)$$

subject to:

$$C(x, 0) = C_n, \quad (A-26)$$

$$C(0, t) = C_o, \quad (A-27)$$

$$C(\infty, t) = C_n, \quad (A-28)$$

where C is the solute concentration, and D_s is the coefficient of solute dispersion. Again, the Boltzman transform is applied and q_l is replaced by Eq. (A-21b) to yield:

$$-\frac{\lambda}{2} \frac{d\theta C}{d\lambda} + \frac{d}{d\lambda} (\theta C A) = \frac{d}{d\lambda} (\theta D_s \frac{dC}{d\lambda}), \quad (A-29)$$

subject to:

$$C(0) = C_o, \text{ and} \quad (A-30)$$

$$C(\infty) = C_n. \quad (A-31)$$

Applying the chain rule to Eq. (A-29) and regrouping produce:

$$\left(\frac{dA}{d\lambda} - \frac{\lambda}{2} \frac{d\theta}{d\lambda}\right) C + \left(A - \frac{\lambda\theta}{2}\right) \frac{dC}{d\lambda} = \frac{d}{d\lambda} (\theta D_s \frac{dC}{d\lambda}). \quad (A-32)$$

Now it can be noted that the first term can be replaced with phase transfer term $e(\theta)$ as given by Eq. (A-24):

$$eC + \left(A - \frac{\lambda\theta}{2}\right) \frac{dC}{d\lambda} = \frac{d}{d\lambda} (\theta D_s \frac{dC}{d\lambda}). \quad (A-33)$$

This is the basic equation of solute transport when water is transported in vapor and liquid phases, subject to the boundary conditions of Eqs. (A-30) and (A-31).