Controlling transport processes during NAPL removal by soil venting

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Soil venting is a widely used technique to remediate unsaturated soils contaminated with organic contaminants. A fundamental concern in the remedial design is to predict the performance of the venting system in terms of the contaminant vapor removal rates and the clean-up limits that can be achieved at a site. In this paper, a mass transport model to simulate the evaporation of non-aqueous phase contaminants from the unsaturated soil during venting is presented. In particular, the dependence of NAPL evaporation on the resistance due to diffusional transport within the liquid phase is discussed in detail. Various limiting mechanisms that control the contaminant removal from NAPL phase have been identified. Results from numerical simulations have indicated that interfacial concentration can be overpredicted by models employing complete mixing assumption when the mass transfer coefficients are high and the interface transfer rates are limited by the diffusional transport within the liquid layer. Venting scenarios were simulated using a multi-component numerical model in which diffusional resistance in the liquid layer was included. The predicted vapor concentrations in the outlet air have been found to be in good comparison with experimental data.

INTRODUCTION

Soil venting is recognized as an effective technology in the removal of hazardous organic contaminants from the subsurface soils. This technology has received wide attention over the past decade due to the need of an in-situ, cost-effective method to address the numerous contamination problems created by subsurface leakages. Although significant developments have been made in terms of installation, monitoring of venting systems at field sites based on the knowledge gained through several case studies on field venting operations, there is still a lack of complete understanding of the governing processes that take place in a realistic field situation.

Modeling efforts carried out in this direction focused mainly on simplified representations of venting systems that can be used as screening tools in the design and optimization at the field scale. Past modeling studies in this field have indicated that in order to predict the performance of soil venting in remediating various sites and to successfully design a remedial system that can achieve the ultimate goal of closure, one needs thorough understanding of fluid flow created in the subsurface as well as the transport processes occurring during soil venting.

Various gas flow models were developed to describe the fluid flow created in the vicinity of the vapor extraction wells. These include a single well radial model by Johnson et al. and a three-dimensional gas flow model by Sepehr & Samani. These models have either ignored the consideration mass transfer processes in the soil or implemented very simplified equilibrium based partitioning laws to describe the mass transfer. Many of the soil venting models assume that the local partitioning of the contaminant into various phases is governed by equilibrium constraints (Johnson et al.; Baehr et al.; Rathfelder et al.). Laboratory scale experimental work carried out to verify this assumption indicated that contaminant removal from NAPL as well as aqueous phases follow the equilibrium constraints due to the high interphase mass transfer coefficients. However, field data gathered from several sites show that the contaminant vapor concentrations differ significantly from the equilibrium based predictions. Also, contaminant removal rates were found to be close to the saturation values at the initial venting periods but to decrease significantly to lower values as the venting
progresses. This results in a longer remedial action to clean-up the site and sometimes may even need a redesign of the system to be able to reach the clean-up limits set by the regulatory criteria.

A number of mathematical models have been presented which incorporate rate-limited mass transfer to the vapor phase (Armstrong et al.\textsuperscript{1}, Rathfelder et al.\textsuperscript{14}, Sleep & Sykes,\textsuperscript{19} Brusseau et al.\textsuperscript{4}). These models have incorporated macropore and micropore transport and partitioning processes between the mobile gas phase and immobile aqueous and NAPL phases and used first-order interphase mass transfer descriptions to determine the mass transport. Gierke et al.\textsuperscript{7} conducted laboratory experiments to study the vapor transport in unsaturated soil columns and their results have indicated that vapor extraction performance in moist, aggregated soils will be affected by nonequilibrium transport. An experimental study performed by Wilkins et al.\textsuperscript{21} examined factors influencing rate-limited NAPL-vapor phase mass transfer in unsaturated porous media. They found that deviations of vapor phase concentrations from local equilibrium values can occur at gas-phase velocities typically encountered in soil vapor extraction systems and more significant mass transfer rate-limitations would be expected over extended periods of volatilization.

In this work, we have attempted to focus on the transport processes that occur at a microscopic level and govern the removal of contaminants from the soil by venting. These processes include resistance to species transport from the bulk liquid phase to the evaporating interface due to diffusional constraints.

**THEORETICAL ANALYSES**

One of the major processes that affects the performance of soil venting systems is the interphase mass transfer of contaminant fractions under advective flow conditions created by the subsurface pressure gradients. Determination of mass transport within the soil requires a clear understanding of partitioning of the contaminant fractions into various phases and the subsequent transport of these fractions in the gaseous phase. Various numerical models that have been developed to simulate the remedial performance of venting systems employ mass transfer modules that assume local equilibrium between various phases. The justification of such assumption stems from the fact that the transfer factors for the interphase mass transfer in porous media are usually very high. In the following analyses, we are taking a closer look at the diffusional resistance offered by the liquid phase during the species evaporation from non-aqueous phase contaminants. The objective of this work is to explain the deviations in the contaminant vapor concentrations measured during multi-component contaminant evaporation from the predictions of existing soil venting models. In this work, we will present a brief description of a mass transport model for soil venting systems. The details of a complete non-isothermal, multi-component model for soil venting systems is reported in previous work by Lingineni & Dhir\textsuperscript{10} and is provided as an appendix at the end of this paper.

**MACROSCOPIC MASS TRANSPORT MODEL FOR SOIL VENTING**

In the following section, we will present governing equations to describe transport of contaminant species from the gas-liquid interface into the gas flow created during soil venting. The macroscopic transport of the contaminant fractions in the gaseous phase is described by the following species conservation equation:

\[
\frac{\partial C_{k,g}}{\partial t} + v_g \cdot \nabla C_{k,g} - \frac{D_{k,g}}{\sigma_{g}} \nabla^2 C_{k,g} = R_{k, n \rightarrow g}
\]

where \(C_{k,g}\) is the concentration of the \(k\)th species in the gaseous phase, \(v_g\) is the local velocity of the air and \(D_{k,g}\) is the diffusion coefficient of \(k\)th species in the gaseous phase. The terms on the right-hand-side of eqn (1) represent interphase mass transfer fluxes into the gaseous phase from solid, aqueous and non-aqueous phases, respectively. In order to describe the evaporation of a multicomponent NAPL mixture, the interphase mass transfer rate, \(R_{k, n \rightarrow g}\), can be represented as

\[
R_{k, n \rightarrow g} = h_m A_l (C_{k, sat} - C_{k,g})
\]

where \(C_{k, sat}\) is the gas phase concentration of the \(k\)th species at the NAPL-gas interface, \(C_{k,g}\) is the \(k\)th species concentration in the bulk gas phase, \(h_m\) is the mass transfer coefficient and \(A_l\) is the interfacial surface area of the evaporating liquid.

The interphase mass transfer rate of contaminant fraction from the liquid phase to gaseous phase as described by eqn (2) strongly depends upon the concentration of that fraction at the gas-liquid interface. The saturation vapor concentrations of each individual species at the NAPL-gas interface, according to Raoult's law, can be expressed as

\[
C_{k, sat} = x_k C_k^* = \frac{w_k T}{\sigma T} p_k^* = \frac{w_k T}{\sigma T} p_k^* = \frac{w_k T}{\sigma T} p_k^*
\]

where \(x_k\) is the mole fraction of \(k\)th species in the bulk liquid and \(C_k^*\) is the saturation vapor concentration of pure \(k\)th species at mixture temperature.

By assuming that the gas phase behaves as an ideal gas (a good approximation at environmental temperatures and pressures), a relationship between pressure and concentration can be written as

\[
\frac{w_k}{\sigma T} p_k^* = \frac{w_k}{\sigma T} p_k^* = \frac{w_k}{\sigma T} p_k^* = \frac{w_k}{\sigma T} p_k^*
\]

where \(w_k\) is the molecular weight of the \(k\)th species, \(\sigma\) is the universal gas constant, \(T\) is temperature and \(p_k^*\) is...
the saturation vapor pressure over pure liquid. The saturation vapor pressure \( p_k^* \) as a function of temperature is calculated using Antoine vapor pressure correlation

\[
\ln p_k^* = \alpha - \frac{\beta}{T + \gamma}
\]  

(5)

where the constraints \( \alpha, \beta, \gamma \) depend upon the \( k \)th species and \( T \) is the absolute temperature of the interface. The above equation predicts the vapor pressure over a flat surface.

### DETERMINATION OF MASS TRANSFER COEFFICIENT AND INTERFACIAL SURFACE AREAS

When the saturation values of the liquid contaminant are equal to or less than the residual saturation, pendular configuration of liquid is believed to exist in the soil. Rose\(^6\) presented a method to determine the volumes and surface areas of pendular rings that exist in the soil interstices. Assuming that the interfacial surfaces of pendular rings can be regarded as arcs of circles, the volume of the pendular rings that rest at zero contact angle can be determined according to the equation

\[
V_{\text{ring}} = 2\pi r_p^3 \left\{ 2 - 2 \cos \theta - \tan \theta \times \left[ 2 \sin \theta - \tan \theta \left( \frac{\cos \theta}{\cos \theta} \right)^2 \right] \right\}
\]  

(6)

where \( \theta \) is the defining angle shown in Fig. (1).

The radius of curvature of the liquid contaminant can be related to the particle size and the defining angle \( \theta \) through geometric relations, such as

\[
r_1 = r_p \left( \frac{1 - \cos \theta}{\cos \theta} \right).
\]  

(7)

Thus, at a given liquid saturation level, the volume of a single pendular ring can be calculated by assuming a regular packing for the soil. For example, consider a soil matrix with uniform size particles of radius \( r_p \) and assume that the soil particles are arranged in a cubic packing. Figure (1) shows a unit cell of such packing, which is a cube of dimension \( 2r_p \). Each unit cell consists of twelve contact locations where liquid can exist in the form of pendular rings and the total volume of the liquid within the cell amounts to three complete rings. Thus, the volume of each pendular ring can be written as

\[
V_{\text{ring}} = \frac{2}{3} r_p^3 \varepsilon S_i
\]  

(8)

where \( \varepsilon \) is the porosity of the soil and \( S_i \) is the liquid saturation. The defining angle \( \theta \) can be determined from the volume of the pendular ring, using the relationship given by eqn (6), which can then be used to calculate the radius of curvature of the gas–liquid interface. Using the above relations for the uniform sized particles, the specific surface areas of the pendular rings are calculated by numerical integration.

The overall mass transfer coefficient \( h_m \) can be estimated from the relations for mass transfer in packed beds of cylindrical pellets. One such relation proposed based on experimental data on mass transfer in packed beds of spheres and cylindrical pellets with single-phase fluid flow [Sherwood et al.\(^{18}\)] is used to determine the mass transfer coefficient at the gas–liquid interface and can be expressed as

\[
h_m = \frac{1}{v_p S_c^{-2/3}} \cdot 1.17 Re^{-0.415}
\]  

(9)

where \( S_c \) is the Schmidt number and \( v_p \) is the superficial velocity of the fluid in porous medium.

The vapor concentrations at the interface as described by Raoult’s law or Henry’s law etc. are dependent upon the mole fractions of the individual contaminant species at the interface. The existing models of venting systems determine the mole fractions at the evaporating interface by assuming that the contaminant species in the liquid phase are completely mixed at all times. However, if a particular species is being depleted from the liquid phase by evaporation, its concentration at the interface will
decrease in comparison to its concentration in the interior of the liquid film (or bulk liquid phase). The concentration gradient thus created across the liquid film will initiate diffusional transport of that species from the bulk liquid to the interface and the rate at which such transport can occur will determine the concentration levels at the interface. In the following section, the assumption of complete species mixing in the liquid phase as compared to the diffusion governed transport in the liquid phase is examined for a simple geometry of a one-dimensional thin liquid layer comprised of a two-species miscible contaminant mixture.

DIFFUSIONAL TRANSPORT IN THE LIQUID PHASE

Consider the evaporation of a thin layer of liquid consisting of two miscible species of different volatilities as shown in Fig. (1). The initial concentrations of the species within the layer are assumed to be uniform and specified as $C_{A,0}$ and $C_{B,0}$. The following governing equations can be written to describe the diffusional transport of each species from the bulk liquid phase to the interface:

Component A

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial z^2}. \quad \text{(10)}$$

Initial and boundary conditions:

$$C_A(z, 0) = C_{A,0}, \quad 0 \leq z \leq \delta$$

$$\left( \frac{\partial C_A}{\partial z} \right)_{0,t} = 0, \quad t > 0$$

$$-D_A \left( \frac{\partial C_A}{\partial z} \right)_{\delta,t} = h_m (C_{A,\delta} - C_{A,\infty}), \quad t > 0.$$

Component B

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial z^2}. \quad \text{(11)}$$

Initial and boundary conditions:

$$C_B(z, 0) = C_{B,0}, \quad 0 \leq z \leq \delta$$

$$\left( \frac{\partial C_B}{\partial z} \right)_{0,t} = 0, \quad t > 0$$

$$-D_B \left( \frac{\partial C_B}{\partial z} \right)_{\delta,t} = h_m (C_{B,\delta} - C_{B,\infty}), \quad t > 0.$$

In writing the above boundary conditions, it is assumed that the lower boundary of the liquid layer is impermeable for species transport and the evaporation rate from the upper surface is described by the product of mass transfer coefficient $h_m$ and the concentration difference between the interface and the bulk gas phase $C_{\infty}$.

In order to see the conditions under which the diffusional resistance in the liquid phase is negligible such that the complete mixing assumption is valid, a numerical simulation was performed to determine the evaporation rates of contaminant liquid consisting of a lighter component A (ethanol) and a heavier component B (propylene glycol), whose properties are given in Table 1. The initial liquid composition is assumed as 20% ethanol and 80% propylene glycol. The initial thickness of the liquid layer was taken to be 100 $\mu$m. The concentration of these species in the bulk gas phase are assumed to be zero. The concentration profiles of the lighter fraction A in the liquid layer are plotted in Fig. (2) at different time levels for a mass transfer coefficient of 0.001 m s$^{-1}$. The profiles shown in Fig. (2) indicate a decrease in the mass fraction of component A with time as the evaporation progresses and a concentration gradient being set up within the liquid layer. The concentration of component A at the interface is set at a value where the diffusional transport from the bulk liquid to the interface is sufficient to maintain the evaporation rates at the interface. In this case, due to the low mass transfer coefficient, the concentration profiles in the liquid layer are relatively flat. The removal rates of the lighter component are limited by the convective mass transfer from the interface to the bulk gas phase. In Fig. (3), the actual concentrations at the interface as predicted by the diffusional transport model are compared with those calculated by assuming that the components are completely mixed in the liquid layer. The interface concentrations obtained through the mixing assumption are higher than the actual concentrations.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular weight (kg kmole$^{-1}$)</th>
<th>Boiling Point at 1 atm (C)</th>
<th>Latent heat of vaporization (cal mole$^{-1}$)</th>
<th>Liquid density kg m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>46.07</td>
<td>78</td>
<td>201</td>
<td>789</td>
</tr>
<tr>
<td>Propanol</td>
<td>60.1</td>
<td>97.4</td>
<td>166</td>
<td>804</td>
</tr>
<tr>
<td>Butanol</td>
<td>74.19</td>
<td>117.9</td>
<td>139</td>
<td>810</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>76.10</td>
<td>215.6</td>
<td>170</td>
<td>1053</td>
</tr>
</tbody>
</table>
Next, consider another case with similar geometry and composition of liquid layer as above, but with a higher mass transfer coefficient of 0.01 m s$^{-1}$. In this case, the evaporation rate at the interface is much higher than the rate at which the lighter component A is transported from the bulk liquid by diffusion. This results in a rapid reduction in the concentrations of component A at the interface, as shown in Fig. (4). Although, at initial stages, the evaporation rates of component A are higher due to the high mass transfer coefficient, the removal rates reduce significantly at a later time due to the diffusional resistance offered by the liquid phase and are limited by the concentration gradients set within the liquid phase. The predictions of the mixing model in such a case will provide a much higher interfacial concentration and a correspondingly high evaporation rate by neglecting the diffusional resistance, although the actual evaporation rate predicted by the diffusion limited model is much smaller as shown in Fig. (5).

In both of the cases described above, the heavier component is assumed to have negligible evaporation rates. Now, we will consider the effect of increasing volatility of component B. When the removal rates of lighter components are limited by the diffusional transport, the evaporation rates diminish with time quite
(1) One of the limiting rates for the contaminant removal is by virtue of the air passing through the contamination zone being saturated with the contaminant vapor. This limit is set by the air flow rates created in the contamination zone and the saturation vapor concentrations of the contaminant fractions which in turn depend upon the local soil temperatures.

(2) The second limiting process governing the contaminant removal rate is the convective transport of contaminant fractions from the interface to the bulk gaseous phase. The convective rates of transport depend upon the air velocities and the interfacial geometry which in turn set the value of the mass transfer coefficient, the interfacial surface area of the contaminant and the interfacial concentrations.

(3) The third limiting rate for the contaminant transport is the rate at which contaminant fractions can be transported in the liquid phase to provide the required concentrations to the interface to sustain evaporation. This limit is set by the diffusion coefficients of the contaminant fractions in the liquid phase and the effective thickness of the liquid layer.

In predicting the effectiveness of a soil venting system design, it is very important to identify the rate determining process from one of three limiting rates described above so that the most optimum operation parameters can be chosen. For example, if the diffusional transport in the liquid phase is the rate determining step, it will be a futile attempt to improve the remediation by increasing the air flow rates through the soil. Under such circumstances, techniques such as pulsed venting may be more effective. Similarly, if the required clean up levels are not achievable for certain lighter fractions due to the slow rates of removal of heavier fractions, it may be required to use some type of in-situ heating method to improve the evaporation rates of the heavier fractions.

### MULTI-COMPONENT SOIL VENTING EXPERIMENTS

Let us now consider the effect of including diffusional resistance within the liquid phase on the remedial predictions made by the soil venting system models. Consider the remediation of a one-dimensional cylindrical soil column that consists of a miscible NAPL contaminant at residual saturations. The contaminant mixture was prepared by mixing equal volumes of three species namely, ethanol, propanol and butanol. The properties of these contaminant species are listed in Table (1). The residual saturation of the contaminant mixture was measured to be about 16%.

The contaminant evaporation rates are determined by carrying out simulations using a non-isothermal, multi-component model (Lingineni & Dhir\textsuperscript{10}). The numerical implementation of the diffusional transport is done as a two-step process. The conceptual model given for liquid diffusional transport in a planar geometry is explicitly coupled with the flow and transport model for soil venting. Each discretized cell in the main soil venting model is associated with an imaginary bin containing the species concentrations and masses existing in that cell. For each time step, the macroscopic equations for species transport are solved to determine the species fluxes from the liquid phase into gaseous phase as driven by the mass transfer coefficient and interface concentration. The interface mass concentration for this step is taken from the boundary value concentrations at the previous time step of the imaginary bin. Each bin itself is...
discretized into a number of one-dimensional divisions, for which the simple diffusional transport equations given by (10) and (11) are applied and solved for time dependent concentrations. At the end of each time step, the species concentration in the one-dimensional bin are updated using the fluxes given by the transport simulator and new values for the interfacial conditions are determined for the next time step of the transport simulator.

For an air flow rate of 7 SCFH, the resulting mass fractions of the three contaminant fractions in the outlet air are shown in Fig. (7). This first set of simulations were carried out with no diffusional resistance in the liquid phase. The corresponding mass fractions in the outlet indicate the following trends: The initial concentrations of all three fractions are equal to the saturation concentrations set by the contaminant characteristics and the initial composition of the contaminant mixture. The concentrations of the lightest fraction i.e. ethanol remains at this initial value as the venting progresses and gradually falls to zero at the final stages. As the concentrations of ethanol reduce, the concentrations of propanol and butanol increase due to the increased mole fractions of these components at the evaporating interfaces. Similar increases in the butanol concentrations are observed when the propanol concentrations starts reducing at later stages of venting.

To see the effect of diffusional transport on the vapor concentrations in the outlet air, a second numerical simulation was carried out. The resulting outlet vapor concentrations of all three fractions are also shown in Fig. (7). Comparing these vapor concentrations with the concentrations predicted by complete mixing model, it can be noticed that due to the diffusion resistance offered by the liquid phase, the vapor concentrations of ethanol at later stages of venting are less than the predictions made by a completely mixing assumption. Also, the deviations from the saturation concentrations are observed at earlier time levels when diffusional resistance is included in the model. The corresponding effect of lower ethanol concentrations at the liquid–gas interface, is to increase the mole fractions of propanol at the interface. Thus, propanol vapor concentrations at the outlet air are found to increase to a higher value compared to simulation 1, for a time period between about 10,000 and 17,500 s. After this time level, the diffusional resistance to the propanol transport within the local liquid layer becomes the limiting process and the vapor concentrations of propanol start to tail off. No significant effects of diffusional resistance are noticed in the case of butanol due to its very low evaporation rates and the contaminant mixture being predominantly single component after a time level of 25,000 s. The results also indicate that the effect of diffusional resistance in the liquid phase is to increase the remediation times of the lighter fractions in the contaminant.

A second set of numerical simulations were performed to study the importance of diffusional resistance in the liquid phase at different air flow rates. Two simulations were carried out with venting flow rates of 1 SCFH and 15 SCFH. The resulting vapor concentrations in the outlet air in each of these cases are shown in Figs 8 and 9. It can be seen from these results that at a lower flow rate of 1 SCFH, the vapor concentrations predicted by the mixing models produce essentially identical results to those predicted by including the diffusional transport. This is due to the fact that at low air flow rates, the mass transfer coefficients are lower and the resulting evaporation rates at the NAPL–gas interface are slow. Under such circumstances, the contaminant species within the liquid layer have sufficient residence times to create a flat concentration gradient and thus be very close to the completely mixed limit. However, at higher air flow rates (Q = 15 SCFH) rapid evaporation occurs at the NAPL–gas interface and steep concentration gradients are set within the liquid layers. Thus the remediation times of lighter fractions of the contaminants as predicted by the complete mixing models will be very much underpredicted as compared to the realistic situation where significant tailing in the vapor concentrations is observed.

**COMPARISON WITH GASOLINE EXPERIMENTS**

Following the previous discussion on the importance of diffusional resistance in the liquid phase and the simple
numeral simulations, we will use the non-isothermal, multicomponent model to predict the removal rates of selected fractions in gasoline. These simulations are performed using both of the approaches discussed earlier i.e. complete mixing assumption and the diffusion limited transport in the liquid phase. The results from these simulations will be compared with one-dimensional column experiments conducted in the laboratory.

A brief description of the experimental apparatus and the procedure used in carrying out the gasoline experiments (Katsumata and Dhir\textsuperscript{9}) is described below. The one-dimensional column experiments were conducted in a cylindrical test section filled with 360 μm glass beads. The experimental column was made of transparent acrylic and was 30 cm long with a 11.4 cm inside diameter. The glass beads filled 20 cm of the column's height leaving 10 cm open at the top. The porosity of the glass beads was measured using a gamma densitometer and found to be 38%. The experiments were conducted using gasoline as the contaminant and initial conditions in the test section were set such that uniform residual saturations exist within the test section. The residual saturations of the contaminant in the test section, as measured by the gamma densitometer were found to be approximately 16%. This value was also compared with the total volume of gasoline trapped in the test section as determined through a volume balance of liquid gasoline.

Five specific components of the gasoline were selected in this study and their vapor concentrations in the outlet air were measured at regular intervals. The selected fractions along with the relevant properties are listed in Table 2.

After residual saturation levels of liquid gasoline were established in the test section, a constant air flow of 25 SCFH was created in the test section using a compressed air source and a flow reservoir to stabilize any flow fluctuations. The vapor samples of the five

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Table 2. Properties of gasoline fractions chosen for laboratory 1-D experiments

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular weight (kg kmole(^{-1}))</th>
<th>Boiling point at 1 atm (°C)</th>
<th>Initial mass fraction in liquid</th>
<th>Liquid density kg m(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>72.15</td>
<td>36.2</td>
<td>0.413</td>
<td>626</td>
</tr>
<tr>
<td>Benzene</td>
<td>78.17</td>
<td>80</td>
<td>0.00585</td>
<td>874</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.1</td>
<td>111</td>
<td>0.02878</td>
<td>867</td>
</tr>
<tr>
<td>n-Octane</td>
<td>114.2</td>
<td>126</td>
<td>0.03665</td>
<td>703</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>106.2</td>
<td>138</td>
<td>0.00869</td>
<td>866</td>
</tr>
<tr>
<td>n-Propyl benzene</td>
<td>120.2</td>
<td>159</td>
<td>0.00514</td>
<td>862</td>
</tr>
<tr>
<td>Decane</td>
<td>142.3</td>
<td>174.3</td>
<td>0.50289</td>
<td>730</td>
</tr>
</tbody>
</table>
selected fractions were collected from the outlet air at regular intervals and analyzed using a HP 5890 gas chromatograph.

In order to perform the numerical simulations corresponding to these experiments, the multicomponent composition of the gasoline needs to be specified. The composition of the five species were taken directly from the measurements made in terms of mass fractions of each species in the liquid phase. However, these fractions only comprise of a small portion of the complete gasoline spectrum, with several additional components that are either lighter or heavier. Using a typical gasoline composition (Johnson et al.\(^8\)) as a basis, all of the lighter components are lumped into a single fraction whose properties are taken to be those of pentane. Similarly, the fractions in the heavier range are lumped into another single fraction whose properties are taken to be those of decane/pentane. Thus, the multi component nature of the gasoline is approximated by a total of seven fractions.

The diffusion coefficients for each of these fractions in gasoline are estimated using Wilke–Chang technique (Reid et al.\(^15\)) for estimating diffusion of a single species through a homogeneous solution of mixed solvents. The effective diffusion coefficient for the \(k\)th species in liquid phase is thus calculated using

\[
D_{k,1} = \frac{(\phi M)^{0.5} F}{\eta_m V_k^{0.5}}
\]

\[
\phi M = \sum_{j=1}^{n} x_j \phi_j M_j
\]

where \(x_j\) is the mole fraction, \(M_j\) is the molecular weight, \(\phi_j\) is the association factor of the \(j\)th species, \(V_k\) is the molal volume of solute fraction at its normal boiling temperature, and \(\eta_m\) is the mixture viscosity. An average association factor of 1.5 is assumed for all of the gasoline fractions.

Figures 10–14 show comparisons of vapor concentrations of selected fractions obtained from experiments with those obtained through numerical simulations. The following general trends can be noticed from these figures. The initial vapor concentrations of each species as measured in the experiments and as observed in simulations are very close to the values dictated by Raoult’s law as combined with the saturation vapor concentrations and initial composition of the liquid contaminant. Experimental data show a gradual increase in the vapor concentrations at the initial venting periods and tailing off in the concentrations after attaining the peak value. Within the group of contaminant fractions monitored, the lighter fractions attained the peak value followed by the heavier fractions. This can be attributed to the continuous changes in the liquid composition towards heavier fractions, thus increasing the mole fractions of the heavier fractions remaining in the liquid phase.

The results obtained from the first set of simulations carried out with the non-isothermal, multicomponent model where the assumption of complete mixing of all of the species in the liquid layer is invoked, show significant differences from the experimental data. Although the match-up is quite satisfactory at initial periods of evaporation, at later stages of venting, the trends, as well as magnitudes observed in the vapor concentrations as a function time were considerably different. The experimental data shows a very gradual decrease in vapor concentrations for very long periods of the order of \(10^3\) minutes or greater. The numerical simulations
show rapid reductions in the vapor concentrations and as a result much smaller remediation times.

The second set of simulations were carried out with the same input parameters and model but using a diffusional transport model to predict the interface concentrations. The inclusion of diffusional transport was found to be an additional resistance mechanism in the removal of selected fractions from the bulk phase, thus reducing the vapor concentrations and in turn increasing the tailing off period of the vapor removal. The results obtained with the diffusional transport model are in much closer agreement with the data from experiments.

SUMMARY

A non-isothermal, multi-component model with diffusion limited liquid phase transport has been used to describe soil venting systems. The model is used to quantify the possible overpredictions that an assumption of complete mixing of contaminant fractions can introduce in the determination of vapor recovery rates. The model results are compared with one-dimensional column experiments conducted with gasoline, in which vapor concentrations and the corresponding removal rates of five selected fractions were monitored. The results from experiments as well as numerical simulations show the deviations in vapor concentrations from the Raoult's law predictions, for extended periods of time.

REFERENCES

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**APPENDIX A: DETAILS OF NON-ISOTHERMAL, MULTICOMPONENT MODEL**

**Gaseous flow in subsurface environments**

Efficient design and operation of soil venting systems requires realistic predictive capability of gaseous flow created in the soil for the imposed subsurface conditions. Gas flow through soil is dependent on soil characteristics including porosity and permeability; gas properties such as viscosity and density; pressures and temperatures in the subsurface. The flow of gases due to pressure gradients consists of two parts, viscous flow and slip flow. Non-zero velocities at the pore walls result in slip flow. The importance of slip flow increases as the average pore radius decreases and as the pressure decreases. The effects of slip flow are found to be negligible for gas transport in most soil types including silts, sands and gravel under the conditions of typical soil venting systems (Massmann12). Hence, in the following analysis, the flow of gases through the soil medium is assumed to be dominated by viscous forces and thus described by Darcy's law. It should be noted that at high fluid velocities, inertial forces can no longer be neglected and the deviations occur from Darcy's law. Darcy's law is found to be in good agreement with the experimental data collected by various researchers for $Re = ud_p/\nu < 10$.

The mass continuity equation for the gas flow through porous media is given by

$$ \frac{\partial (\varepsilon_S \rho_g)}{\partial t} + \nabla \cdot (\varepsilon_S \rho_g \mathbf{v}_g) = Q $$

where $\mathbf{v}_g$ is the gas velocity, $\rho_g$ is the gas density, $\varepsilon$ is the porosity of the medium and $S_g$ is the local gas saturation. $Q$ denotes the mass per unit volume per unit time exchanged through a source or sink. In the above formulation, it is assumed that $Q$ is positive for a source and negative for a sink. $Q$ is defined to have a value only at locations corresponding to either vapor extraction wells or air injection wells. Also, in this type of formulation, the model expects input in the form of air flow rates through each of the wells. There is another equivalent formulation in which pressures imposed at wells can be provided as input. For the particular case of soil matrix being nondeformable and homogeneous, the above mass continuity equation can be written as

$$ \frac{\partial}{\partial t} (S_g \rho_g) + \nabla \cdot (\rho_g \mathbf{v}_g) = Q $$

The equation of motion for gas flow in soil as described by Darcy's law can be written as

$$ \mathbf{v}_g = -k \frac{k_{rg}}{\mu_g} (\rho_g \nabla S + \nabla P_g) $$

where $k$ is the intrinsic permeability of the medium which depends on the geometry of the medium solely. $k_{rg}$ is the gas phase relative permeability that represents the fraction of permeability available for gas flow in a multiphase system. The relative permeability, $k_{rg}$ is a function of gas phase saturation which in turn is dependent upon the liquid contaminant (NAPL) and soil water saturation. The dependence of relative permeabilities on
the fluid saturations is described by various formulations (Brooks & Corey; Parker et al; Farrell & Larson). One of the simplest ways of representing the increase in gas permeability with reduction in liquid saturation is by using a modified Brooks & Corey relationship shown by Falta et al. as

$$k_g = S_g^3$$  \hspace{1cm} (A4)

Darcy’s law may be substituted into the mass continuity equation to obtain a governing equation for gas pressures:

$$\frac{\partial S_g \rho_g}{\partial t} = \nabla \cdot \left( k_{rg} \frac{\rho_g \nabla z}{\mu_g} \nabla P_g \right) - Q_e.  \hspace{1cm} (A5)$$

The gas density, $\rho_g$, is a function of gas pressure and temperature and can be obtained by using the ideal gas law

$$\rho_g = \frac{P_g}{RT}$$  \hspace{1cm} (A6)

where $T$ is the absolute temperature and $R$ is the ideal gas constant.

The pressure distribution within the subsurface environment can be obtained by solving the nonlinear coupled eqns (A5) and (A6) along with the appropriate boundary conditions and source/sink conditions to represent the vapor extraction as well as air injection wells. The gas velocities at various locations in the soil can then be calculated by using eqn (A3). The governing equations posed in this section represent a rigorous way of determining pressure and velocity profiles in the contaminated soil for a given venting design.

**Thermal regime in the subsurface environment**

Soil temperature is one of the most critical factors that influence various physical and chemical processes occurring within the soil during venting. In this section, the major processes influencing soil temperature are discussed and the corresponding energy transport equations are developed to predict soil thermal profiles as a function of time. Soil temperatures can vary during soil venting due to a variety of natural processes such as diurnal variations in soil temperature, latent heat absorption during contaminant evaporation, heat transport due to differences between ambient air temperatures and soil temperature. Soil temperatures can also be increased by employing in-situ heating techniques such as injection of preheated air into the soil, installation of buried heat sources in the soil, radio frequency soil heating and steam injection in order to enhance remediation.

To account for variations in the fluid phase properties and the interphase mass transfer rates with local soil temperatures, the propagation of thermal perturbations within the subsurface need to be modeled. Once the heat is deposited into the soil by a specific in-situ heating method, heat flow within the soil can occur mainly due to conduction, convection of heat by fluid flow and latent heat transfer.

The temporal and spatial variations of temperatures in the subsurface environment can be obtained by performing an energy balance on the soil phase and the gas phase of a differential soil volume element.

**Solid phase:**

$$\frac{\partial T_s}{\partial t} = \lambda_s \nabla^2 T_s - h A_s (T_s - T_g) - \sum_{k=1}^{N} m_{s,k} h_{s,k} f_1 + m_{w} h_{s,w} f_2. \hspace{1cm} (A7)$$

**Gas phase:**

$$\frac{\partial T_g}{\partial t} + \frac{\rho c_p}{\rho g} \frac{\nabla v_e}{\nabla T_s} = \lambda_g \nabla^2 T_g + h A_s (T_s - T_g) - \sum_{k=1}^{N} m_{s,k} h_{s,k} (1 - f_1) + m_{w} h_{s,w} (1 - f_2). \hspace{1cm} (A8)$$

Due to the fact that the liquid saturations are very low in vadose zone soils, the effect of liquid phase on the overall energy balance is very minimal. Heat flow to the solid phase can occur by conduction, interphase heat transfer from gaseous phase and latent heat transfer from phase changes occurring within the control volume. In the case of gas phase, the main heat transfer mechanisms are convection, interphase heat transfer from solid phase, and latent heat transfer. However, for the sake of completeness, conduction term is also included in the gas phase energy conservation equation. The amount of latent heat absorbed during the contaminant evaporation and the amount of latent heat released due to condensation of water vapor have to be partitioned between the solid and gas phases. This partitioning is represented by the fractions $f_1$ and $f_2$ in eqns (A7) and (A8). The interphase heat transfer rates from the gas phase to the solid phase is described by using an appropriate convective heat transfer coefficient for flow of gases in porous media. One such heat transfer correlation based on experimental data for spheres and short cylinders (Whitaker), is given by

$$Nu = \frac{h d_p}{\lambda_g} = (0.5 Re^{1/2} + 0.2 Re^{2/3}) Pr^{1/3} \hspace{1cm} (A9)$$

where $Nu$ is the Nusselt number, $d_p$ is the particle diameter and $Re$ is the Reynold number based on superficial gas velocity within the porous medium. For typical conditions in the soil, the transfer area available for heat transfer between the solid and gaseous phases is quite large. This would result in small temperature differences between solid and gas phases within a local soil element. Thus, it is reasonable to simplify the
thermal analysis by assuming that the temperatures of all phases in a differential soil element are equal. Then, an overall energy balance can be performed on all of the phases to obtain the following energy conservation equation:

\[
\left( \rho c_p \right)_m \frac{\partial T}{\partial t} = \lambda_m \nabla^2 T - \left( \rho c_p \right)_g y_g \cdot \nabla T - \sum_{k=1}^{N} m'_h h_{f,k} + m'_w h_{f,w}. \tag{A10}
\]

In performing the above overall energy balance, energy storage and conduction heat transfer rates are described by defining an effective thermal conductivity and heat capacity as

\[
\lambda_m = \lambda_v \varepsilon_v + \lambda_w \varepsilon_w + \lambda_n \varepsilon_n + \lambda_g \varepsilon_g
\]

and

\[
\left( \rho c_p \right)_m = \rho_g c_{pg} \varepsilon_g + \rho_v c_{pv} \varepsilon_v + \rho_w c_{pw} \varepsilon_w + \rho_n c_{pn} \varepsilon_n.
\]

The above expression for effective thermal conductivity of the soil is obtained by assuming that individual thermal resistances of each phase act in parallel. Similarly, an effective heat capacity for the soil matrix is defined as the sum of the heat capacities of various phases weighted by their volume fractions. The second term on the right-hand-side of the energy equation describes the heat transfer by gaseous advection. Third and fourth terms represent the latent heat absorbed during contaminant evaporation and the latent heat released by water vapor condensing from the incoming air.