A non-isothermal three-phase pollutant transport model, theoretical formulation and numerical applications.

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Abstract

The purpose of this paper is the simulation of the non-isothermal flow and transport of contaminants in ground water systems. A system of six fully coupled non-linear partial differential equations were developed, in which the coupled flow of water, water vapour and heat is assumed to be governed by Philip and de Vries theory. The space discretisation is carried out using a modified Galerkin weighted residual finite element method with asymmetric shape functions. The resulting transient equations are then solved temporally by the generalised mid-point method, resulting in a system of six non-linear equations, in which the unknowns are the three fluid pressures, the temperature and the solute and gas NAPL concentrations. The accuracy and correctness of the model has been verified on a variety of isothermal and non-isothermal conditions. The results of subsets of problems analysed are shown to be in good agreement with analytical and other model simulators.

1 Introduction

It is generally recognised that waste disposal and spill sites, in addition to leaking underground storage tanks, can constitute a serious environmental health hazard (Yong et al. [1]). It is, therefore, of great importance to both understand the processes of groundwater contamination and to check the effectiveness of the remediation method. To this end, numerical modelling can complement the laboratory, centrifuge, and field experiments. Several numerical formulations, mainly two-phase systems, have been devised for predicting the transport and fate of contaminants, especially NAPL. The majority of the numerical codes
developed to date consider passive air phase approximation and isothermal conditions (e.g. Abriola and Pinder [2]). Non-isothermal conditions can, however, be due to several causes, such as seasonal temperature variations, technique of remediation and emplaced radioactive wastes. The effect of the temperature on the contaminant transport in three-phase unsaturated porous media has been investigated by only a few authors, e.g. Falta et al. [3]. Almost all the investigators established a formulation without including the water vapour. It is, however, well established that under temperature gradients, gas movement should take into account water vapour diffusion (Philip and De Vries [4], Ewen and Thomas [5]). Therefore the objective of this paper is the development of a general three-phase non-isothermal formulation for simulating contaminant transport, along with Philip and De Vries theory. The formulation incorporates biodegradation, volatilisation and dissolution of NAPL.

2 Governing equations

The mathematical model is composed of six conservation equations, i.e. three equations for the three phases, one of energy and two transport equations of the solute and NAPL vapour. We should note here that a rigid porous matrix is assumed for simplicity. Moreover, the system variables are the three fluid pressures, the temperature and the two NAPL concentrations in water and gas.

2.1 Mass conservation of the liquid water and water vapour

The conservation of mass for both the liquid water and water vapour is given by:

\[
\frac{\partial}{\partial t} \left( \rho_w \phi S_w \right) + \frac{\partial}{\partial t} \left( \rho_n \theta_n \right) = -\nabla \left( \rho_w V_w \right) - \nabla \left( \rho_n V_n \right) - \nabla \left( \rho_v V_g \right) + \phi S_w \lambda_w \left( \overline{C_{wi}} - C_{wi} \right) - \phi S_g \lambda_{wg} \left( H \ C_{gi} - C_{gi} \right) - Q_w
\]

Where \( V_w, V_g, V_n \) and \( V_a \) are the velocities of water, gas, vapour and NAPL respectively. \( V_w, V_g \) and \( V_n \) are defined as:

\[
V_a = -K_a \left( \nabla P_a + \rho_a g \nabla z \right)
\]

With

\[
K_a = \frac{k_{ra} k_{ra,0}}{\mu_a}
\]

\( \mu_a \) is temperature dependent. The following vapour flux is defined according to Ewen and Thomas [5] and Thomas and King [6]:
Expanding the RHS of eqn (1), incorporating the velocity expressions and rearranging gives:

\[
V_v = -\frac{D_{av} \nu_a}{\rho_w} \left\{ \rho_0 \frac{\partial h}{\partial P_w} \nabla P_w + \rho_0 \frac{\partial h}{\partial P_g} \nabla P_g + \frac{(\nabla T)_a}{\nabla T} \left( \rho_0 \frac{\partial h}{\partial T} + h_\beta \right) \nabla T \right\}
\]  

(5)

Expanding the RHS of eqn (1), incorporating the velocity expressions and rearranging gives:

\[
C_{11} \frac{\partial P_w}{\partial t} + C_{12} \frac{\partial P_g}{\partial t} + C_{13} \frac{\partial P_n}{\partial t} + C_{14} \frac{\partial T}{\partial t} + C_{15} \frac{\partial C_{gi}}{\partial t} + C_{16} \frac{\partial C_{wi}}{\partial t} = \nabla \left( k_{11} \nabla (P_w) \right) + \nabla \left( k_{12} \nabla (P_g) \right) + \nabla \left( k_{13} \nabla (P_n) \right) + \nabla \left( k_{14} \nabla (T) \right) + \nabla \left( k_{15} \nabla (C_{gi}) \right) + \nabla \left( k_{16} \nabla (C_{wi}) \right)
\]  

(6)

In which \( C_{ij} \) and \( k_{ij} \) are the capacities and transmissibilities coefficients.

2.2 Mass conservation of dry air

Applying the principle of mass conservation to the dry air yields:

\[
\frac{\partial}{\partial t} \left( \phi C_{ga} \{ S_g + H_a S_w \} \right) = \nabla \left( D_{ga} + H_a D_{wa} \nabla C_{ga} \right) - \nabla \left( C_{ga} \left( V_g + H_a V_w \right) \right) - Q_a
\]  

(7)

Expanding the RHS of eqn (7), incorporating the velocity expressions and rearranging gives:

\[
C_{21} \frac{\partial P_w}{\partial t} + C_{22} \frac{\partial P_g}{\partial t} + C_{23} \frac{\partial P_n}{\partial t} + C_{24} \frac{\partial T}{\partial t} + C_{25} \frac{\partial C_{gi}}{\partial t} + C_{26} \frac{\partial C_{wi}}{\partial t} = \nabla \left( k_{21} \nabla (P_w) \right) + \nabla \left( k_{22} \nabla (P_g) \right) + \nabla \left( k_{23} \nabla (P_n) \right) + \nabla \left( k_{24} \nabla (T) \right) + \nabla \left( k_{25} \nabla (C_{gi}) \right) + \nabla \left( k_{26} \nabla (C_{wi}) \right)
\]  

(8)

2.3 Mass conservation of NAPL

The conservation of mass for the NAPL in the case of a single component contaminant is given by

\[
\frac{\partial}{\partial t} \left( \phi \rho_n S_n \right) = -\nabla ( \rho_n V_n ) - \phi S_w \lambda_w \left( C_{wi} - C_{wi} \right) - \phi S_{gi} \lambda_{gi} \left( C_{gi} - C_{gi} \right) - Q_n
\]  

(9)

The second and third terms on the RHS characterise the dissolution and volatilisation processes respectively (Sleep and Sykes, [7]). The last equation can be written as follows after substitution and transformation:

\[
C_{31} \frac{\partial P_w}{\partial t} + C_{32} \frac{\partial P_g}{\partial t} + C_{33} \frac{\partial P_n}{\partial t} + C_{34} \frac{\partial T}{\partial t} + C_{35} \frac{\partial C_{gi}}{\partial t} + C_{36} \frac{\partial C_{wi}}{\partial t} = \nabla \left( k_{31} \nabla (P_w) \right) + \nabla \left( k_{32} \nabla (P_g) \right) + \nabla \left( k_{33} \nabla (P_n) \right) + \nabla \left( k_{34} \nabla (T) \right) + \nabla \left( k_{35} \nabla (C_{gi}) \right) + \nabla \left( k_{36} \nabla (C_{wi}) \right)
\]  

(10)
2.4 Heat transfer

The conservation of energy for the soil is given by:

\[ \frac{\partial \dot{H}}{\partial t} + \nabla Q = -Q_n \]  

(11)

Where \( \dot{H} \) is the heat content expressed as follows:

\[ \dot{H} = H(T - T_s) + \phi S_g \theta L \]  

(12)

In which \( L \) is the latent heat and \( H \) is the heat capacity of the soil given by:

\[ H = (1 - \phi) \rho_s C_{ps} + \phi \rho_w C_{pw} + \phi \rho_v C_{pv} + \phi S_g C_{ga} C_{pa} + \phi S_g C_{gi} C_{pgi} \]

\[ + \phi S_n \rho_n C_{pn} + \phi S_w C_{wi} C_{pw} \]  

(13)

The heat flux per area \( Q \) is given by:

\[ Q = -\lambda \nabla T + \left( \rho_w \lambda' + \rho_v \lambda'' \right) L + \left( T - T_s \right) \]

\[ C_{pw} \rho_w V_w + C_{pv} \rho_v V_v + C_{pgi} \rho_g V_g \]  

(14)

Here an instantaneous thermal equilibrium is assumed among the phases. Eqn. (14) can also be rewritten as follows:

\[ C_{41} \frac{\partial P_w}{\partial t} + C_{42} \frac{\partial P_g}{\partial t} + C_{43} \frac{\partial P_{wi}}{\partial t} + C_{44} \frac{\partial T}{\partial t} + C_{45} \frac{\partial C_{gi}}{\partial t} + C_{46} \frac{\partial C_{wi}}{\partial t} = \nabla (k_{41} \nabla (P_w)) \]

\[ + \nabla (k_{42} \nabla (P_g)) + \nabla (k_{43} \nabla (P_{wi})) + \nabla (k_{44} \nabla (T)) + \nabla (k_{45} \nabla (C_{gi})) + \nabla (k_{46} \nabla (C_{wi})) \]  

(15)

2.5 NAPL vapour transfer

The mass conservation equation for the NAPL vapour yields:

\[ \frac{\partial}{\partial t} \left( \rho C_{gi} \left( S_g + H_i S_w \right) \right) = \nabla \left( D_{gi} \nabla C_{gi} \right) - \nabla \left( F_{gi} \phi_{gi} + H_i V_w \right) \]  

(16)

Where \( D_{gi} \) is the hydrodynamic dispersion coefficient in gas. Eqn (16) can also be written as follows after substitution and some manipulations:
\[ C_{S1} \frac{\partial P_w}{\partial t} + C_{S2} \frac{\partial P_g}{\partial t} + C_{S3} \frac{\partial P_n}{\partial t} + C_{S4} \frac{\partial T}{\partial t} + C_{S5} \frac{\partial C_{gi}}{\partial t} + C_{S6} \frac{\partial C_{wi}}{\partial t} = \nabla (k_{S1} \nabla (P_w)) + \nabla (k_{S3} \nabla (P_n)) + \nabla (k_{S4} \nabla (T)) + \nabla (k_{S5} \nabla (C_{gi})) + \nabla (k_{S6} \nabla (C_{wi})) \] 

(17)

\[ + \nabla (k_{S7} \nabla (z)) + k_{S3} C_{gi} + k_{S9} C_{wi} + k_{S10} \] 

(17)

2.6 Solute mass transfer

The mass conservation equation for the solute can be written as:

\[ \frac{\partial}{\partial t} (\phi C_{wi} S_w) = \nabla (D_{wi} \nabla C_{wi}) - \nabla C_{wi} V_w + \phi S_w \lambda_d \left( C_{wi} - C_{wi0} \right) - \phi S_w \lambda_{nw} (HC_{wi} - C_{gi}) - \lambda_{bw} \phi S_w C_{wi} - Q_{wi} \] 

(18)

Where \( D_{wi} \) is hydrodynamic dispersion-diffusion coefficient in water. As for the NAPL vapour transport equation, eqn. 18) can be written as follows:

\[ C_{S1} \frac{\partial P_w}{\partial t} + C_{S2} \frac{\partial P_g}{\partial t} + C_{S3} \frac{\partial P_n}{\partial t} + C_{S4} \frac{\partial T}{\partial t} + C_{S5} \frac{\partial C_{gi}}{\partial t} + C_{S6} \frac{\partial C_{wi}}{\partial t} = \nabla (k_{S1} \nabla (P_w)) + \nabla (k_{S3} \nabla (P_n)) + \nabla (k_{S4} \nabla (T)) + \nabla (k_{S5} \nabla (C_{gi})) + \nabla (k_{S6} \nabla (C_{wi})) \] 

(19)

3 Numerical solution procedures

The set of six PDE established in the previous sections are first discretised in space using a modified Galerkin weighted residual finite element Method with asymmetric functions (Huyakorn and Nilkuha, [8]) applied to the spatial terms. The set of ordinary differential equations obtained after use of Green’s theorem is then discretised in time using the generalised mid-point \( \theta \) method. These procedures applied for instance to the first PDE eqn. (6) yields after some manipulations:

\[ \begin{align*}
& A_{11} P_w + A_{12} P_g + A_{13} P_n + A_{14} T + A_{15} C_{gi} + A_{16} C_{wi} = \\
& B_{11} P_w + B_{12} P_g + B_{13} P_n + B_{14} T + B_{15} C_{gi} + B_{16} C_{wi} + B_{17} \\
& \text{for } t=\Delta t, t=2\Delta t, \ldots, t=10\Delta t 
\end{align*} \]

(20)

In eqn. (20), the left upper index indicates the time step and \( A_{ij} \) and \( B_{ij} \) are coefficients. The same procedures are applied to the five other PDE, however the results are not displayed for the sake of clarity as similar equations are obtained. Finally, the governing non-linear equations are solved simultaneously using the conjugate gradient solver, with the non-linearities handled using the iterative
Picard Method. An under-relaxation technique is used between two successive iterations in order to increase the convergence rate.

4 Numerical results

A variety of problems constituting a subset of the general formulation have been simulated. Good agreements were obtained between this model and the analytical solutions of Carslaw and Jaeger [9] for the case of both one-dimensional and two-dimensional transient heat transfer. In order to not lengthen the presentation, the results are not displayed. The correctness of the general model will be illustrated by presenting the results of two analyses constituting a subset of the general problem.

4.1 Two-dimensional three-phase oil spill problem

This problem concerns the spill of a light hydrocarbon into a two-dimensional partially saturated medium with an inclined water table. The geometry and the mesh of the problem are displayed in Figure 1. The initial water table is at four meter depth on the left boundary and four meter and half depth on the right boundary. The material properties can be found in Katyal et al. [10]. The initial conditions are chosen to ensure that the NAPL saturations are initially zero. Boundary conditions for oil are a constant head of \(-0.1\) m until the accumulated oil reaches 1.0 m\(^3\) and no flow is allowed elsewhere. For the water phase, boundary conditions are no flow on the on the top and bottom boundaries and the lateral boundaries are under prescribed heads. In addition, the constitutive model used is the extended Van Genuchten three-phase model (Parker et al. [11]). Figure 1 shows a comparison of the results obtained without upwinding by the present model and the model MOFAT of Katyal et al. [10]. We can notice good agreement between the two codes.
For the case of this two-dimensional problem, it was found that the front advance is mainly conditioned by the approximation of the permeabilities and capacities during the weighting process in the finite element discretisation. Indeed the permeabilities and the capacities have to be written in terms of the basis functions and the nodal values as follows:

\[
K(x, y) = \sum_{i=1}^{n} K_{ii} N_{ii}^{i} \quad (21)
\]

\[
C(x, y) = \sum_{i=1}^{n} C_{ii} N_{ii}^{i} \quad (22)
\]

Where, \( n \) is the node number per element

\( C_{ii} = C(P_{\alpha\beta,ii}) \) and \( K_{ii} = K(P_{\alpha\beta,ii}) \), \( P_{\alpha\beta} \) being the capillary pressure between the \( \alpha \) and \( \beta \) phases. \( ii \) is the element node number.

The following formulation was found to give rise to unrealistic results and almost no front advancing in highly non-linear problems:

\[
K(x, y) = K\left(P_{\alpha\beta,ii} N_{ii}^{i}\right) \quad (23)
\]

\[
C(x, y) = C\left(C_{\alpha\beta,ii} N_{ii}^{i}\right) \quad (24)
\]
4.2 A high-level radioactive waste disposal problem

This hypothetical non-isothermal problem has been studied by Pollock [12] and is used to analyse the effect of a high-level radioactive waste deposited in a two-phase unsaturated medium. A four metre thick repository, consisting of 10 year old canisters is located 100m underneath the ground surface. The heat and flow problem was simulated by a 475m column subdivided by eight node quadrilateral elements. A Passive air pressure of $10^5 \text{Nm}^{-1}$ is assumed for this problem The material properties are presented in Table 2 and the constitutive relationships are as follows (Permeabilities and retention relationships):

$$k_{rw} = \frac{(S_w - 0.1)^7}{0.9^7} \quad \text{for } 0.1 < S_w < 1.0 \quad (25)$$

$$k_{rw} = 0.0 \quad \text{for } 0.0 < S_w < 0.1 \quad (26)$$

$$\psi = P_w - P_g = -1.0 \times 10^5 \exp(-15.27S_w + 6.062) \quad \text{for } 0.1 \leq S_w \leq 1.0 \quad (27)$$

$$\psi = -1.0 \times 10^5 \exp \left(314.84 S_w^2 - 72.84 S_w + 9.21 \right) \quad \text{for } 0.0 \leq S_w < 0. \quad (28)$$

The initial conditions for the temperature consists of a linearly increasing temperature with depth at a rate of 0.03 $^\circ\text{C m}^{-1}$. The temperature at the surface is 20 $^\circ\text{C}$. The initial water saturation is assumed to follow a hydrostatic condition above the water table, which is 500 meter below the ground surface. The boundary conditions are as follows:

For $z=0m$ T=20 $^\circ\text{C}$ and no water flux.

For $z=-475m$ $T=34.25 \, ^\circ\text{C}$ and $\psi=-2.4525 \times 10^5 \, \text{N m}^{-2}$

The profiles of the liquid saturation and the temperature for both the present model and Pollock’s simulation are shown in Figures 2 to 5. It can be seen that good agreement is obtained for the temperatures at 10, 50, 500 and 1000 years. Although some differences in the water saturation results arise at the surface and near the depository, globally the results are quite good mainly with increasing depth. In addition, the effect of the latent heat transfer by water vapour is reproduced in both simulations causing the temperatures to be limited at 100 $^\circ\text{C}$ in the wet zones and 120-125 $^\circ\text{C}$ in the dry zones in which evaporation is insignificant.
Table 1: Material parameters. Radioactive waste problem.

<table>
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<th>Material Parameter</th>
<th>Value</th>
<th>Material Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
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<td>Cₐ</td>
<td>1000.0 J kg⁻¹°C⁻¹</td>
</tr>
<tr>
<td>Φ</td>
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<td>Cₗ</td>
<td>1900.0 J kg⁻¹°C⁻¹</td>
</tr>
<tr>
<td>(0)</td>
<td>0.35</td>
<td>Cₒ</td>
<td>4184.0 J kg⁻¹°C⁻¹</td>
</tr>
<tr>
<td>(1)</td>
<td>0.5 W m⁻¹°C⁻¹</td>
<td>Tₘ</td>
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</tr>
<tr>
<td></td>
<td>2.0 W m⁻¹°C⁻¹</td>
<td>w</td>
<td>1000.0 kg/m³</td>
</tr>
<tr>
<td>Cₜ</td>
<td>837.0 J kg⁻¹°C⁻¹</td>
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</table>

5 Conclusion

A theoretical framework describing three-phase flow and transport of NAPL in non-isothermal porous media has been presented. Verification of the model using a variety of examples in isothermal and non-isothermal conditions shows that the mathematical model and procedures are applicable. The results of subsets of problem analysed are shown to be in good agreement with analytical and other model simulators. It has been shown that for highly non-linear spill problem in two-dimensional problems, it is mainly the method of approximation of the permeabilities and capacities that governs the front advance. The upwinding scheme is found to only speed up the oil infiltration. The coupled heat and mass transfer problem analysed, corresponding to a radioactive waste simulation, has shown the importance of the latent heat transfer by water vapour. The simulation showed that latent heat is causing the temperatures to be limited at 100 °C in the wet zones and 120-125 °C in the dry zones around the repository in which evaporation is insignificant. However, the validation of the model against field data is still required. This issue is being currently addressed.
6 References


