

Removal of a Single-Component NAPL under Nonequilibrium Condition: a Zero Mass Flux Moving Boundary

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ABSTRACT

A new zero flux moving boundary conditions to solve the non-equilibrium single-component dispersion-advection transport problem containing NAPL have been introduced. The resultant model can overcome many approximations in the model which is done by previous study and give more precise analytical solution to the aqueous (or gas) phase concentration profile, NAPL saturation and the moving front speed. From the results, it is clear that the number of pore volumes (P), which are required for removing all NAPL under equilibrium conditions, plays a role in the differences between the two models' predictions. The NAPL saturation profile predicted by the two models is the same. At very low P the predicted value of the front speed by the present model is half of the value predicted by Brouwers and Augustijn model and increases gradually with P. It reaches 0.99 when P is 100.

Keywords: analytical solution; NAPL; moving boundary

ازالة السائل ذو الطور اللامائي والمركب الواحد تحت ظروف عدم الأتزان:
ظروف حدودية متحركة ذات تدفق كتلي صفري

الخلاصة

تم اعتماد ظروف حدودية متحركة ذات تدفق كتلي صفري للحل الرياضي لمسألة الحمل-الانتشار ولمركب واحد وتحت ظروف عدم الأتزان. يتجاوز الموديل الرياضي الناتج عدة تقريبات للحل الذي تم في دراسة سابقة. ويعطي حل تحليلي ادق لتركيز الطور المائي (الغازي) وكذلك لتركيز الطور السائل اللامائي وسرعة تقدم الجبهه المتحركة. تشير النتائج الى ان P، عدد مرات حجم الفراغات في التربة من

المائع النظيف واللازمة لأزالة كل الطور السائل الامائي وتحت ظروف الأتزان، يلعب دورا في الأختلافات بين تنبؤات كل من الموديلين. يعطي كلا الموديلين حلا متشابهها لتركيز الطور السائل اللامائي. عند القيم الصغيرة جدا الى P فأن سرعة الجبهة التي يعطيها الحل في هذا البحث هي نصف القيمة التي يعطيها الحل السابق وتزداد هذه النسبة مع زيادة قيمة P. تصل قيمة هذه النسبة 0,99 عندما تكون قيمة P 100.

Nomenclature

C	concentration in the aqueous (gas phase) solution (Kg m^{-3})
C_s	equilibrium concentration in the aqueous (gas phase) solution (Kg m^{-3})
C^*	C/C_s
D	hydrodynamic dispersion coefficient ($\text{m}^2 \text{sec}^{-1}$)
k	modified first-order mass-transfer rate coefficient (sec^{-1})
K_1	conventional first order mass-transfer coefficient
L	characteristic length (m)
n	soil porosity
P	$C_s/(\rho_N S_{NO})$
P_e	vL/D
P_e'	$P_e \cdot (1 - u/v)$
S_N	NAPL saturation ($\text{m}^3 \text{m}^{-3}$)
S_{NO}	initial NAPL saturation ($\text{m}^3 \text{m}^{-3}$)
S^*	S_N/S_{NO}
t	time (sec)
u	speed of moving front (m sec^{-1})
v	interstitial ground water (gas phase) velocity (m sec^{-1})
ω	kL/v
ω'	$\omega/(1 - u/v)$
ω''	$\omega/(u/v)$
ρ_N	density of NAPL (Kg m^{-3})
x	distance in the main direction of flow (m)
x_m	location of moving boundary (m)
z	distance from moving front (m)
Z	z/L

INTRODUCTION

Subsurface contamination by non-aqueous phase liquids (NAPL's) is one of the important issues to environmental problems. NAPLs act as a source for groundwater pollution in saturated zone and a potential source for groundwater pollution when they are immobilized in unsaturated zone. The maximum contaminant levels of these fluids in drinking water often more than two orders of magnitude less than their solubility in water [1]. Remediation is often necessary.

One of in-situ remedial technologies may be applied to a saturated zone is pump and treat process. In this technology a clean ground water acts to dissolve the NAPL [2]. In the unsaturated zone a traditional in-situ remediation practice for contaminated soil is soil vapor extraction (SVE) in the case when the NAPL has a relatively high vapor pressure [3]. In SVE technology a clean air acts to enhance volatilization the NAPL. The pump and treat and SVE processes are characterized by a moving depletion front of NAPL moves in the direction of water (or gas) flow. The speed and location of the depletion front give clear evidence about the extent of the success of the remediation process Many non-equilibrium transport models have been presented to describe the rate-limited mass transfer between the NAPL and aqueous (or gas) phase [4, 5, 6, 7, 8, 9, 10]. These models often adopt first-order kinetics for the interphase mass transfer between NAPL and aqueous or gas phase. Numerical solution of NAPL dissolution and NAPL volatilization transport models are presented by [3, 11, 12, 13]. Most of the existing models for simulating the depletion of NAPL in soils employ specific boundary conditions at fixed boundaries in the problem domain. The objective of this paper is to develop a model to solve the non-equilibrium, single-component transport model containing NAPL by introduction of zero flux moving boundary conditions to overcomes many approximations done by Brouwers & Augustijn [14] and to predict the concentration distributions of aqueous or gas phase as well as the migration of the moving front of NAPL.

Methods

Problem description

The problem considered in this work was conceptualized as shown in Figure (1). A semi-infinite one-dimensional homogenous saturated soil system was contaminated with a single component soluble organic material. The organic material exhibits three different



Figure (1): Conceptual model used in this study.

phases (namely, aqueous (gas), sorbed and residual NAPL phases) in the saturated soil. The liquid phase is uniformly distributed in the soil with an initial NAPL saturation S_0 . The sorbed phase is negligible when compared to the mass of the NAPL. The NAPL saturation is assumed to be small, so that the volume of the transporting fluid in the contaminated region can be considered constant. The NAPL-containing soil is flushed with clean water (air). The NAPL volume declines and eventually disappears and edges where clean water (air) enters the contaminated zone. The edge (moving boundary), will move with a constant speed in the direction of flow. Ahead of the moving boundary it is assumed that the aqueous phase concentration profile remains the same (wave like), just shifts in the direction of flow beginning at the moving boundary. Dissolution (volatilization) of NAPL is described by a linear mass-transfer. The mass-transfer rate coefficient is assumed constant.

Model formulation

The one-dimensional mass transport equation of the aqueous (gas) phase in the NAPL-contaminated soil is [14]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - k(C - C_s) \quad \dots (1)$$

where C (Kg m^{-3}) is the concentration in the aqueous (gas phase) solution, t is time (sec), D is the hydrodynamic dispersion coefficient ($\text{m}^2 \text{sec}^{-1}$), x is the main direction of flow (m), v is the interstitial ground water (gas phase) velocity (m sec^{-1}), k is a modified first-order mass-transfer rate coefficient (sec^{-1}) ($k = K_l/n$, where K_l is the conventional first order mass-transfer coefficient that is a function of the specific interfacial area between NAPL and water (gas phase) in contact with a single-component NAPL).

The change of the NAPL mass is described by

$$\rho_N \frac{\partial S_N}{\partial t} = k(C - C_s) \quad \dots (2)$$

where ρ_N is the density of the NAPL (Kg m^{-3}), S_N is the NAPL saturation which is defined as the fraction of pores occupied by the NAPL ($\text{m}^3 \text{m}^{-3}$).

In their analytical solution [14], it is assumed that "at $t = 0$ a clean solution ($C = 0$) enters the contaminated zone. While the water passes through the contaminated zone, the NAPL dissolves into the water phase. After the flushing of a few pore volumes, a constant concentration profile is developed such that the steady state ($\partial C / \partial t = 0$) can be assumed". When the moving boundary develops "the concentration profile remains the same, only shifted in the direction of flow beginning at the moving boundary". Brouwers and Augustijn [14] did not prove the correctness of this assumption. Moreover, in their derivation of the moving boundary speed Brouwers and Augustijn depends on the overall mass balance a confined contaminated region (x ranges from moving boundary to L (m), length of contaminated zone) [14]. In this derivation, the right hand side of Eq. (37) is divide by x_m (m) (location of moving boundary) [14], but x_m may equal zero. To get a straight forward steady state solution to the problem, zero aqueous phase

contaminant mass flux and zero NAPL saturation is assumed to be at the moving front. So, the following boundary conditions can be applied:

$$vC - D \frac{\partial C}{\partial x} = 0 \quad , \quad \text{at } x(t) = \text{moving front} = u \cdot t \quad \dots(3)$$

$$S_N = 0 \quad , \quad \text{at } x(t) = \text{moving front} = u \cdot t \quad \dots(4)$$

u is the speed of the moving front (m sec⁻¹).

and

$$\frac{\partial C}{\partial x} = 0 \quad , \quad x \rightarrow \infty \quad \dots (5)$$

$$S_N = S_{N0} \quad , \quad x \rightarrow \infty \quad \dots (6)$$

Due to the assumption that C has a wavelike profile which moves with a constant speed and the moving boundary has zero flux, it is reasonable to use the following transformation:

$$\text{Let } z = x - u \cdot t \quad \dots(7)$$

Combining Eq's. (1) and (7) yields:

$$D \frac{\partial^2 C}{\partial z^2} - (v - u) \frac{\partial C}{\partial z} - k(C - C_s) = 0 \quad \dots (8)$$

Rewriting Eq. (8) in dimensionless form yields:

$$-\frac{1}{P_e} \frac{\partial^2 C^*}{\partial Z^2} + \frac{\partial C^*}{\partial Z} + \omega' C^* = \omega' \quad \dots (9)$$

and for Eq. (2)

$$\frac{\partial S^*}{\partial Z} = -\frac{\omega''}{P} (C^* - 1) \quad \dots (10)$$

$$C^* - \frac{1}{P_e} \frac{\partial C^*}{\partial Z} = 0 \quad \text{at } Z = 0 \quad \dots (11)$$

$$S^* = 0 \quad \text{at } Z = 0 \quad \dots(12)$$

and

$$\frac{\partial C}{\partial Z} = 0 \quad \text{when } Z \rightarrow \infty \quad \dots(13)$$

and

$$S^* = 1 \quad \text{when } Z \rightarrow \infty \quad \dots(14)$$

where

$$C^* = \frac{c}{c_s} \quad \dots(15)$$

$$P_e' = P_e \cdot \left(1 - \frac{u}{v}\right) \quad \dots(16)$$

$$P_e = \frac{vL}{D} \quad \dots(17)$$

$$Z = \frac{z}{L} \quad \dots(18)$$

$$\omega' = \omega \cdot \frac{1}{\left(1 - \frac{u}{v}\right)} \quad \dots(19)$$

$$\omega = \frac{kL}{v} \quad \dots(20)$$

$$S^* = \frac{S_N}{S_{NO}} \quad \dots(21)$$

$$P = \frac{c_s}{\rho_N S_{NO}} \quad \dots(22)$$

$$\omega'' = \omega \cdot \frac{1}{\left(\frac{u}{v}\right)} \quad \dots(23)$$

L is the characteristic length

The solution of Eq. (9) will be:

$$C^* = a \cdot e^{\lambda_1 Z} + b \cdot e^{\lambda_2 Z} + 1 \quad \dots(24)$$

$$\lambda_{1,2} = \frac{1}{2} \left(P_e' \pm \sqrt{P_e'^2 + 4\omega' P_e'} \right) \quad \dots(25)$$

Applying boundary conditions Eq. (11) and Eq. (13) in Eq. (24) yields:

$$C^* = 1 + \frac{\lambda_2 \cdot e^{\lambda_2 Z}}{\omega'} \quad \dots(26)$$

Substitute Eq. (26) into Eq. (10) yields:

$$\frac{\partial S^*}{\partial Z} = -\frac{\omega''}{P} \left(\frac{\lambda_2 \cdot e^{\lambda_2 \cdot Z}}{\omega'} \right) \quad \dots (27)$$

Integrating Eq. (27) and applying boundary condition in Eq. (14) yields:

$$S^* = -\frac{\omega''}{P} \left(\frac{e^{\lambda_2 \cdot Z}}{\omega'} \right) + 1 \quad \dots(28)$$

An expression for the speed of the front u can be obtained by substituting boundary condition in Eq. (12) into Eq. (28):

$$\frac{u}{v} = \frac{1}{P+1} \quad \dots (29)$$

The location of the evaporation front at any time = $u \cdot t$

Substituting for u into Eq.'s (16), (19) and (23) and combining these equations with Eq. (26) and Eq. (28) to get an expression for C^* and S^* respectively.

$$C^* = 1 + \left(\frac{P}{P+1} \right) \cdot \frac{\lambda_2 \cdot e^{\lambda_2 \cdot Z}}{\omega} \quad \dots (30)$$

$$S^* = 1 - e^{\lambda_2 \cdot Z} \quad \dots (31)$$

Where

$$\lambda_2 = \frac{1}{2} \left(P_e \cdot \left(\frac{P}{P+1} \right) - \sqrt{P_e^2 \cdot \left(\frac{P}{P+1} \right)^2 + 4\omega P_e} \right) \quad \dots (32)$$

For practical applications, if the aqueous phase

(gas phase) concentration profile C^* can be measured, Eq. 30 can be rewritten as:

$$\ln(1 - C^*) = \ln \left(-\frac{P}{P+1} \cdot \frac{\lambda_2}{\omega} \right) + \lambda_2 \cdot Z \quad \dots(33)$$

If we plot $\ln(1 - C^*)$ versus Z , λ_2 can be obtained from the slop of the straight line. The profile of the residual NAPL saturation can be obtained by substituting the value of λ_2 into Eq. 31.

A summary of comparison between the present model solution with that presented in ref [14] is given in Table 1. It is clear that the parameter P plays a role in the difference between the two models predictions. The NAPL saturation S^* profile which is predicted

by the two models is the same.

Table (1): Present and Brouwers & Augustijn, 2001 Model expressions.

Present Model	Brouwers & Augustijn
$C^* = 1 + \left(\frac{P}{P+1}\right) \cdot \frac{\lambda_2 \cdot e^{\lambda_2 \cdot Z}}{\omega}$	$C^* = 1 + \frac{\lambda_2 \cdot e^{\lambda_2 \cdot Z}}{\omega}$
$S^* = 1 - e^{\lambda_2 \cdot Z}$	$S^* = 1 - e^{\lambda_2 \cdot Z}$
$\frac{u}{v} = \frac{1}{P+1}$	$\frac{u}{v} = \frac{1}{P}$
$\lambda_2 = \frac{1}{2} \left(P_e \cdot \left(\frac{P}{P+1}\right) - \sqrt{P_e^2 \cdot \left(\frac{P}{P+1}\right)^2 + 4\omega P_e} \right)$	$\lambda_2 = \frac{1}{2} \left(P_e - \sqrt{P_e^2 + 4\omega P_e} \right)$

Results and discussions

Figure 2 shows the way in which the moving front speed changes with the number of pore volumes (P), which are required for removing all NAPL under equilibrium conditions. At very low P the predicted value of the front speed by the present model is half of the value predicted by Brouwers and Augustijn model and increases gradually with P. It reaches 0.99 when P is 100. Practically, The migration speed of the front gives clear evidence about the success of the remediation process.

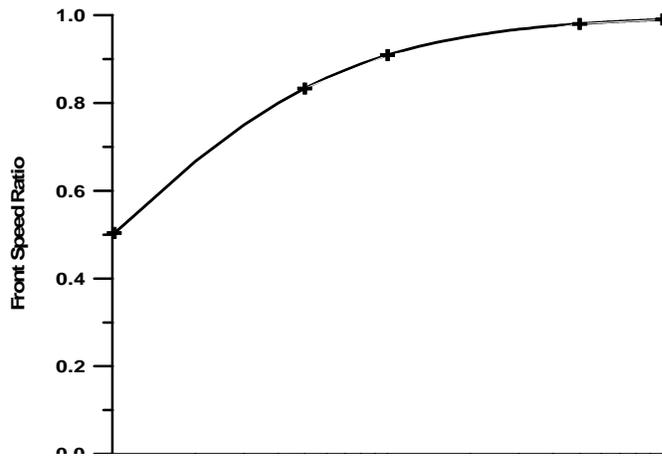


Figure (2): Ratio of front speed predicted by the present model to that predicted by the old model verses the dimensionless parameter P.

Figure (3) shows a comparison between the predicted NAPL aqueous phase

concentration profile at different distances from the moving front by the present and the old models. In this figure, P and w are chosen to be equal 10 and 1 respectively; and the dispersion coefficient is very small (the advection is dominant). It is clear that The predicted front speed by the present model is lower than one by the old model. From Figure 3, it can be seen that there is a slight difference in the concentration profile between the two models, since λ_2 in the case of the present model is a bit larger than that of old model when P is much larger than 1. At any distance from the moving front, the concentration that predicted by the present model is higher than that predicted by the old model.

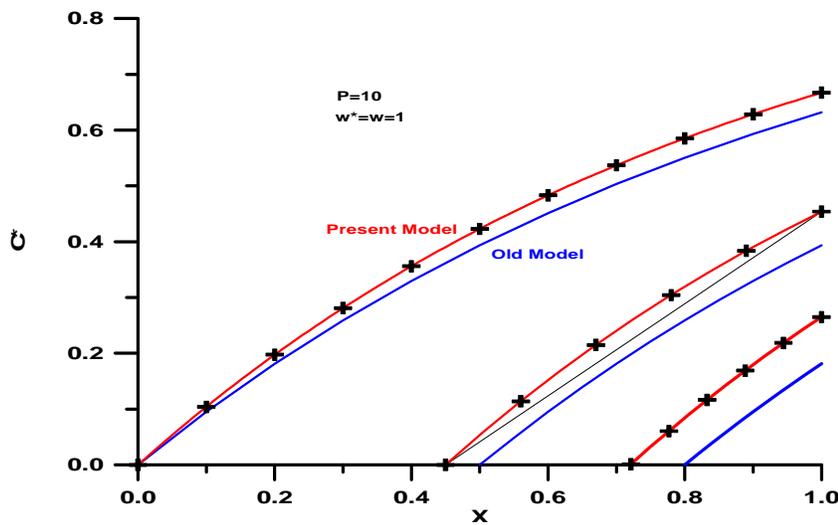


Figure (3): Aqueous phase concentration vs distance for different front propagation time

The importance of the dispersion on the aqueous concentration profile can be deduce from the effect of Pe on this profile. By Examining Eq. 32, it can be revealed that the value of λ_2 ranges from zero to $w \cdot \{(p+1)/P\}$ for a range of Peclet number (Pe) from zero to a very large value, respectively. This means that the value C^* (defined by Eq. 30) at the front varies from 1 (equilibrium conditions) to zero for a range of Pe from zero to a very high value, respectively. The aqueous concentration C^* shows steeper profile for high Pe than the case of low Pe .

CONCLUSIONS

A new zero flux moving boundary conditions to solve the non-equilibrium single-component dispersion-advection transport problem containing NAPL have been introduced. The resultant model gives more precise analytical solution to the aqueous phase concentration profile, NAPL saturation and moving front speed. Also, it gives better understanding to NAPL depletion. The analytical solution reveals significant

differences with that presented by Brouwers & Augustijn [14], especially when value of the initial NAPL saturation is relatively low (P less than 10). This may be met in practice when remediating soil with such low concentration of NAPL initial saturation value using pump and treat or soil vapor extraction process. However, this model can be considered a useful tool in many cases to assess the progress of remediation action, especially with soil and treat and soil vapor extraction process.

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