Direct estimation of transport coefficients during the dissolution of an hydrocarbon pollutant in water saturated porous media. Laboratory-scale experiments and interpretation

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Abstract

Experiments on the dissolution and transport of trapped residual NAPLs in water saturated homogeneous porous media were carried in a laboratory column. Saturation fields among the column (1D) were measured by the gamma ray attenuation technique and the effluent pollutant concentration was measured by gas chromatography. A numerical macroscopic model based on the averaged pore-scale mass balance equations was used to simulate experiments. The model takes into account convection, dispersion and interfacial mass transfer. The mass transfer coefficient was calculated in pore-scale periodic unit cells containing the solid phase, an immobile phase (pollutant), and a flowing phase (water) by the means of averaging theory results. Confrontation of experimental and numerical results allowed the direct estimation of the mass transfer coefficient, and the construction of a unit cell which is representative of the pore-scale geometry of trapped NAPL blobs.

1. Background

The occurrence of hydrocarbons in the subsurface is a serious environmental problem. Because of their very high toxicity and their low solubility in water, they represent a long-term contamination source. Most important sources of such aquifer contamination are (Abriola [1]) : leaking storage tanks and
pipelines, improper surface disposal and accidents during gasoline transport. Following its release in the subsurface, the pollutant migrates through the unsaturated zone and then reaches the aquifer (Figure 1). Lighter than water NAPLs tend to accumulate at the water table while more dense NAPL migrate through the saturated zone until they are trapped at residual saturation by the capillary forces (Hunt et al. [2]). The pollutant is then transported by active dispersion, i.e., dispersion in the presence of pollutant sources at the pore scale.

Figure 1: Migration of a NAPL in the subsurface

One fundamental problem in the study of hydrocarbon transport is the local equilibrium assumption which depends mainly on the pore-scale fluid distributions, the chemical and physical properties of the pollutant and the water flow velocity. As a consequence, two sorts of models have been developed to simulate the transport of NAPLs in the saturated zone: local equilibrium models and mass transfer models. However, mass transfer models can produce the same results as the equilibrium models provided that the mass transfer coefficient is high enough.

The transport in a binary system (in our case water-toluene) is often modelled using Eq. 1, where $C$ is the macroscopic average NAPL mass fraction in the water phase; $C_{eq}$ is the equilibrium mass fraction; $\rho$, $S$ and $V$ are respectively the aqueous phase density, saturation and filtration velocity; and $\varepsilon$ is the porosity.

$$\varepsilon \frac{\partial (\rho SC)}{\partial t} + \nabla \cdot (\rho VC) = \nabla \cdot (\rho D \cdot \nabla C) - \rho \alpha (C - C_{eq})$$ (1)

The mass transfer coefficient $\alpha$ and the dispersion tensor $D$ are both of crucial importance for the pollutant transport description. Many scientists tried to propose phenomenological correlations for those coefficients but their
results (specially in terms of the mass transfer coefficient) vary over several orders of magnitude (Miller et al. [3], Powers et al. [4,5], Imhoff et al. [6]).

The approach presented in this work, consists on the comparison between the experimental dissolution of pure NAPLs in water saturated porous media (section 2) and the predictions of a macroscopic model (section 3) based on the pore-scale averaged mass balance equations in which values of $\alpha$ and $D$ are computed theoretically as described in Quintard & Whitaker [7]. The comparison gives the foundation for a search of a geometrical configuration that is representative of the fluid distribution at the pore-scale in the experimental column. Preliminary results of this approach can be found in Radilla et al. [8].

2. Experimental set-up and procedure

The main piece of the set-up (Figure 2) is an aluminum column (4 cm diameter, 10 cm length) filled with a calibrated silica sand (mean grain size 70 $\mu$m, permeability $4 \cdot 10^{-12}$ m$^2$) by the means of a vibrating apparatus. The column is positioned vertically between a displacing device formed by a radioactive source ($^{241}$Am, 435 mCi) and a scintillator detector (NaI) coupled to a photomultiplier. This gamma-ray apparatus allows the measure of porosity and saturation fields along the column.

![Figure 2: Experimental set-up](image)

Fluids are injected in the column by a precision pump. A differential pressure transducer measures the pressure drop in the column during the experiments. Samples of 2 cm$^3$ (1 pore volume = 50 cm$^3$) are collected in the
column effluents and concentration measurements are carried with a gas chromatograph.

First, the column is saturated with deionized deaired water and then NAPL is injected until the irreducible water saturation is obtained. Afterwards, water is injected to displace NAPL until its residual saturation is reached. At this point, water injection continues and NAPL is transported only as a dissolved species (active dispersion). The dissolution requires hundreds of pore volumes of clean water to be injected.

NAPL saturation $S_n$, is calculated using Eq. 2, where $a_w$ and $a_n$ are the attenuation coefficients of water and NAPL, and $I^d$, $I^w$ and $I$ are respectively the dry, water saturated, and water-NAPL saturated column count rates.

$$ S_n = \frac{a_w}{a_n - a_w} \cdot \frac{\ln(I^w / I)}{\ln(I^d / I^w)} $$ (2)

Figures 3a and 3b present respectively saturation fields versus vertical position in the column and effluent normalized concentration versus pore volumes of clean water injected in the column.

These results where obtained for the dissolution of toluene and correspond to a flow Peclet number of 0.77. Peclet number is defined by equation (3) in which $D_m$ is NAPL molecular diffusivity in water and $d_p$ is the mean grain size.

$$ Pe = \left( \frac{||V||d_p}{D_m} \right) $$ (3)

3. Numerical model

The complete transport model involves four averaged mass balance equations associated with the two phase binary system (one equation for each species in each phase). Thus, we have:
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in the aqueous phase

\[
\varepsilon \frac{\partial \rho C}{\partial t} + \nabla \cdot (\rho \mathbf{V} C) = \nabla \cdot (\rho \mathbf{D} \cdot \nabla C) - \rho \alpha (C - C_{eq})
\]  

(4)

\[
\varepsilon \frac{\partial \rho S(1-C)}{\partial t} + \nabla \cdot (\rho \mathbf{V}(1-C)) = \nabla \cdot (\rho \mathbf{D} \cdot \nabla (1-C)) - K_w^w
\]  

(5)

in the non aqueous phase

\[
\rho_o \varepsilon \frac{\partial (1-S)C_o}{\partial t} = \rho \alpha (C - C_{eq})
\]  

(6)

\[
\rho_o \varepsilon \frac{\partial (1-S)(1-C_o)}{\partial t} = K_w^w
\]  

(7)

where \( K_w^w \) is the water exchange between the aqueous and the non aqueous phase; \( \rho_o \) and \( C_o \) represents the density and the NAPL mass fraction in the non aqueous phase. These equations are completed by Darcy's law applied to the flowing aqueous phase.

\[
\mathbf{V} = -\frac{\mathbf{K}(S)}{\mu} \cdot (\nabla P - \rho \mathbf{g})
\]  

(8)

Here, \( \mathbf{K}(S) \) is the permeability tensor, \( \mu \) is the aqueous phase dynamic viscosity, \( P \) is the mean pressure in the aqueous phase and \( \mathbf{g} \) is the gravity vector. The water exchange term \( K_w^w \) will be eliminated from these equations by assuming that the NAPL phase is completely saturated by water, which completely determines \( C_o \).

Permeability as a function of aqueous phase saturation is computed by using Wyllie's correlation (Wyllie [9], Morrow et al. [10]) :

\[
K(S) = K_w k_r(S) = K_w \left( \frac{S - S_i}{1 - S_i} \right)^n
\]  

(9)

in which \( K_w \) is the sand permeability to water, \( k_r \) is the relative permeability, \( S_i \) is the aqueous phase irreducible saturation and \( n \) is a real number. Both \( n \) and \( S_i \) are determined experimentally. The former with the drop pressure measures and the latter by the gamma attenuation device.

Simulations are carried in a one-dimensional vertical domain and the boundary and initial conditions associated with equations 4 to 8 are :

top \((z=0)\)

\[
\mathbf{V}(z,t) = U
\]  

(10)

\[
C(z,t) = 0
\]  

(11)

bottom \((z=L)\)

\[
P(z,t) = P_0
\]  

(12)

\[
\frac{\partial C(z,t)}{\partial z} = 0
\]  

(13)

initial time \((t=0)\)

\[
C(z,t) = C_{eq}
\]  

(14)
The mass transfer coefficient $\alpha$ and the dispersion tensor $D$ are computed over periodic unit cells by using the averaging theory applied to a classical pore-scale dispersion equation and by solving appropriated local problems (Quintard & Whitaker [7]). Some of the unit cells are presented in figure 4.

All the cells in figure 4 have the same porosity (0.4) and the same NAPL saturation (0.2). It is important to note that NAPL is supposed to be immobile and that the water flow takes place from the left to the right. Four identical cells are represented in each case to better illustrate the corresponding periodic media. Calculations are done for values of NAPL saturation in the range of 0 to 0.2 and for Peclet numbers in the range of 0.01 to 1000. Results for the mass transfer coefficient are presented in Figure 5 for a Peclet number of 0.77.

Although cells may look simplistic if one compares them to a real porous medium, they are rich in information on the pore-scale fluid distribution as our
results show for example that cell d provides more realistic (lower) values of the mass transfer coefficient than the other cells. This is due to the presence in cell d of preferential pathways and to the consequent by-passing of the pollutant sources. Several pore-scale studies (Ng et al. [11], Conrad et al. [12], Mayer & Miller [13]) on fluid distribution for residual NAPLs have shown that most of trapped hydrocarbons are contained in blobs spanning five or more pore bodies, resulting in a limited mass transfer (Conrad et al. [12]). Our results confirm that such variations in the geometry can explain such limitations.

4. Comparison between experiments and simulations

Saturation fields obtained experimentally (section 2) give very poor information in terms of pore-scale fluid distribution which has been shown to be a determining factor for the mass transfer coefficient. The best fit between experimental results and model predictions for different unit cells can be used to estimate a pore-scale representative fluid distribution configuration.

Figures 6a and 6b present the comparison between experimental results and numerical simulations with the best estimated α. Observed variations are in the range of 0.001 to 0.01 s⁻¹, which is ten times lower than results for cell d. This suggests that blobs should be interconnected and that the area of the interface water-NAPL which is in contact with the flowing water should be smaller.

Given these results, our approach seems to be correct and the comparison is encouraging. In particular, the average time necessary for the complete pollutant dissolution observed experimentally is well predicted by the model as well as the shape of the dissolution front.

However, differences are observed at the end of the dissolution (figure 6b). Such discrepancies may be attributed to several mechanisms including sorption/desorption, dissolution fingering (Imhoff et al. [14]), and of course to
inaccurate description of the representative unit cell because of computer memory and speed limitations. In the absence of more precise data, our predictions are satisfactory.

5. Conclusion

A new approach is proposed to determine the mass transfer coefficient involved in the transport of residual one component NAPLs in water saturated porous media. This approach combines experimental results with predictions of a macroscopic transport model. The mass transfer coefficient is calculated theoretically in various periodic unit cells which represent different pore-scale fluid distributions. The best fit between experimental data and model predictions is used to estimate a pore-scale representative fluid distribution configuration. Model predictions fit well the experimental data and our results are in good agreement with previous studies on the pore-scale fluid distribution of residual NAPLs in water saturated porous media.

Acknowledgement: Financial support from PRH-INSU and Institut Français du Pétrole is gratefully acknowledged.

References


