The mechanism of NAPL layer formation in a microfluidic device with dual-permeability: experiments and numerical simulation

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Abstract. In-situ remediation is an important technique for non-aqueous phase liquid (NAPL) contamination remediation in soils. Understanding the formation and distribution of NAPL contaminated layers in heterogeneous soils is essential to propose cost-effective remediation methods. Therefore, a two-dimensional microfluidic device with dual permeability zones was designed to simulate the soil-groundwater system and experimentally investigated the formation process of the NAPL contamination layer. Numerical modeling of phase field coupled with laminar flow was used to simulate the distribution of NAPL in soil-groundwater system, and the formation of NAPL contamination layer under typical groundwater flow rate and wetting angle was evaluated. The NAPL in the low permeable zone formed a stable contamination layer, while the NAPL in the high permeable zone was washed out to varying degrees and mainly resided in the junction of high-low-permeability regions of the chip, with residues of 42.2% and 23.3% in the chip high permeable region at groundwater velocities of 6.17 m/d and 10.16 m/d, respectively, the numerical simulation results were consistent with the experimental observations. This retention was diminished in the high permeable zone as the NAPL-to-wall wetting angle increased. In addition, when the contact angle was increased from 33° (lipophilic) to 108° (hydrophilic), the residual NAPL content in the high permeable zone decreased from 48.86% to 28.22%. This paper provides a reliable visualizable experimental platform for the study of NAPL pollution formation at micro-scale in heterogeneous groundwater system, and lays a foundation for the subsequent optimization of the remediation strategy.

1. Introduction

In recent years, crude oil spills have occurred frequently and large amounts of toxic substances have entered the soil, making soil oil contamination a global problem [1-3]. Crude oil, as a typical non-aqueous phase liquids (NAPLs) pollutant, is extremely hazardous to human health. It has low solubility in water, weak chemical activity, and a high octanol/water partition coefficient (Kow). Strong binding capacity to soil organic matter and high resistance to desorption allow crude oil to persist in the soil for long periods of time [4-6]. Some in-situ remediation techniques for soil-groundwater NAPL contamination such as physical, chemical and biological techniques have been
proposed accordingly for NAPL contamination in soil-groundwater systems [7-9]. However, due to the heterogeneity of the soil-groundwater system, it is difficult for the restoration agent to make sufficient contact with the NAPL contaminants in the low permeable zone, resulting in poor remediation. For example, the 1989 Exxon Valdez oil spill contaminated a large beach area with gravels in Prince William Sound, Alaska. The U.S. government and Exxon spent three years cleaning up local crude oil pollution, but in 2003, investigators re-tested the beach crude oil content, revealing that approximately 55.6 tons of crude oil remained in the low permeable zone at the bottom of the beach[10]. The low seepage zone, in which crude oil persists as a source of pollution, continues to endanger local ecological safety [11, 12].

Therefore, understanding the formation mechanism of NAPL contamination layer in soil-groundwater is essential to propose cost-effective remediation solutions. Microfluidic models allow real-time observation of multiphase fluid flow and distribution in porous media [13], and thus are widely used to study correlations in inhomogeneous porous media [14-16]. In this work, a microfluidic chip with dual permeability was designed to simulate a heterogenous soil-groundwater system to study the formation and distribution of the NAPL contamination layer in soil through experimental and numerical models.

2. Experimental and numerical simulation

As shown in Figure 1, a two-dimensional microfluidic chip with dual permeable regions was designed. The chip has a high permeable region (indicated by the yellow circles) in the center and two identical low permeable regions on the two sides (indicated by the blue circles), which is designed to simulate a heterogeneous subsurface aquifer. The porosities ($\phi$) of the high and low permeable regions are 0.462 and 0.303. In this article we calculate the permeability $k$ using the Kozeny-Carman formula[17], The permeability of the high and low permeable regions are 0.462 and 0.303, respectively.

In this study, the NAPL was mineral oil (No. 100, Moringa) and its viscosity is 83.3 $mPa\cdot s$. The mineral oil was stained using Oil Red O (Sigma-Aldrich) for easier visualization of the contaminated layers formation. It has been shown that the addition of Oil Red O does not affect the viscosity and contact angle of the mineral oil [18]. A diagram of the experimental setup is shown in Figure 2. Debubbled mineral oil was injected into the chip manually using a 5 mL medical syringe to saturate the chip with mineral oil. Next, deionized water was injected into the chip at typical groundwater flow rates of 10.16 m/d and 6.17 m/d, respectively, through a micro-syringe pump (LSP-01-1A Boaz) and a 100 $\mu$L micro-syringe (Shanghai Pigeon). During the experiment, CCD was used to take pictures of the chip every 30 second which connected to the computer, and the imaging results were recorded by AJ-VERT software.
ImageJ software was used for image processing. Taking the high permeable zone as an example: the center of the high seepage region was selected using the rectangular selection tool in the software, and the grayscale values of $L_n$ (n is the image sequence number, and n = 0 stands for time 0 when the chip was filled with oil) were measured. Subsequently, a blank area on the chip was selected and its grayscale value $B_{n,0}$ was measured as the blank background. Same method was used to obtain the grayscale values of the corresponding regions of the control experimental pictures (chip was filled with water), $L_w$, $B_{w,0}$, respectively, so the residual oil saturation normalization process could be calculated using eq 1:

$$\lambda = \frac{(L_n - B_{n,0}) - (B_z - B_{z,0})}{(L_0 - B_{1,0}) - (B_z - B_{2,0})}$$

(1)

where $L_n-B_{1,0}$ and $B_z-B_{2,0}$ are intended to eliminate the background light intensity.

The Cahn-Hilliard and Navier-Stokes equations provide an accurate description of the process of driving two-phase fluids in heterogeneous porous media. We used COMSOL Multiphysics 5.3a to solve the phase field equation and Navier-Stokes equation, and the two 2D modules in this simulation was incompressible laminar flow module used to solve the velocity profile, and the phase field module used to solve the tracked water-NAPL phase interface.

3. Results

3.1. Effect of heterogeneity on NAPL contamination layer formation at different flow rates

The effect of heterogeneity on the formation of NAPL contamination layer was observed at both experimental flow rates and the NAPL residual amount ($S_{or}$) in the chip was analyzed at two flow rates. Four images taken different time for the two flow rates were selected and shown in Figure 3A, 3B, respectively. It was found that the NAPL in the low permeable regions of the chip was not washed out under both flow rates, as shown by the “flat” trend of gray and green data points in Figure 4. In addition, the results from the two experimental flow rates had no significant difference in NAPL residuals in the low permeable zones, which was confirmed by two-way ANOVA with $p = 0.517 > 0.05$. This can be attributed to the small pore size and low permeability, resulting the high critical inlet pressure in the low permeable region of the chip. Water flow under the experimental conditions could not overcome the critical capillary pressure into the low permeable zones, which is the main reason of NAPL contamination layer formation in the hypotonic zone in soil.

![Figure 3](image_url)

**Figure 3.** (A) Experimental images at 6.17 m/d from 0 min to 9.6 min, (B) experimental images at 10.16 m/d from 0 min to 4.3 min, where the flow is from left to right.

![Figure 4](image_url)

**Figure 4.** Experimental processing data for A, B “▲” = breakthrough time at 10.16 m/d”, “■ = breakthrough time at 6.17 m/d”, The long black bars indicate the standard variance.

It can be seen from Figure 4 that the residual NAPL in the central high permeable region of the chip tends to stabilize at 4.3 min (at the red triangle in the figure), and then slowly declines until it reaches pseudo-stability after 8 min, and the final NAPL residual amount is about 23.3% at flow...
velocity of 10.16 m/d. When the water flow rate is 6.17 m/d (shallow blue square in Figure 4), the water flow took longer to break through the chip compared to 10.16 m/d (complete at 9.6 min, red square in the diagram), and the final NAPL residual amount is about 43.2% at flow velocity of 6.17 m/d. When the flow broke through the high permeable zone, a dominant flow channel was formed, and the pressure drop in the whole model became smaller. At the same time, the contact area between water and NAPL was reduced by the dominant channel, resulting in no further obvious decrease of the residual NAPL. We will explain this phenomenon in details in the following context.

The images right at the water breakthrough and at the end of the experiment at two flow rates in the high permeable zone were chosen, as shown in Figure 5, in order to illustrate the effect of flow rate on the residual NAPL and its distribution in the model, with the water current flowing from left to right. When the water flow rate was 10.16 m/d, the distribution of NAPL in the high permeable zone basically reached a pseudo-steady state after the water flow breakthrough, and after that, the decrease of NAPL droplets was observed only in the lower right corner of the picture (shown in the dashed red circle in Figure 5A). When the water flow rate was 6.17 m/d, the NAPL residual amount stabilized at 43.2% when the water flow broke through, and no change in NAPL droplets was observed at the end of the experiment at t=17 min.

Four residual forms of NAPL in the high permeable zone were found, including NAPL membranes, NAPL clusters, NAPL bridging clusters, and NAPL cones. (1) NAPL clumps are the main reason for the formation of NAPL contamination layer, as shown in the red circle in Figure 5, NAPL clumps are concentrated at the junction of high and low permeable zone and decrease with the increase of water flow velocity. (2) The NAPL bridging clusters are present in the pore throats (green area in Figure 5). This pattern of NAPL droplets is induced by the bypass channels on both sides of the substrate formed by the water flow, which is the predominant form of NAPL contamination in the high permeable zone, and the NAPL bridging clusters decrease as the water flow rate increase. (3) The NAPL membrane is wrapped around the circular substrate (yellow area in Figure 5), which is widely present in the high permeable region. (4) In the experiment, the NAPL cone was present only at 10.16 m/d, as shown in the purple region in Figure 5B, which is due to the destruction of the NAPL membrane and NAPL bridging clusters after the increase of flow rate and thus NAPL cones forming behind the substrate.

![Figure 5. Experimental images in the high permeable zone at two flow rates. The black areas represent NAPL. Flow direction is from left to right, and the red scale bar is 1 mm.](image)

3.2. Numerical analysis of the parametric effects on NAPL residuals

A full chip model with all the pore details was created and applied for the simulation at the early stage, and the results revealed that the NAPL in the low permeable zone was not washed out at all (Figure 6), which is consistent with the experimental phenomenon. However, the fine mesh of the low permeable zone led to tremendous amount of unnecessary calculations, so in the subsequent work, we only kept a small portion of the low permeable zone, and mainly used the central high permeable zone for the numerical simulation.
Figure 6. Simulation of oil (red)-water (blue) interface distribution in the complete chip. Blue indicates water and red indicates NAPL.

The simulation of the high permeable zone in Figure 7 better explained the experimental phenomena in Figure 3 and 5. During the simulation, the water flow broke through the central high permeable zone at about 4 min at flow rate of 10.16 m/d and the final NAPL residual amount was 20.1% (as shown by the orange dashed line in Figure 4). The results were in good agreement with the experimental results. While at the lower flow rate of 6.17 m/d, the simulation results (shallow blue dashed line in Figure 4) showed that the water flow breakthrough time was about 10 min and the final residual oil amount was 39.8%, which was also in good agreement with the experimental results. The residual NAPL volume fraction and pressure diagram (Figure 7) show that the maximum pressure drop occurred at the front edge of the oil-water interface before the water flow broke through, and the pressure difference at phase interface was the greatest driving force to push the oil phase liquid to overcome the capillary resistance and viscous forces. In the pressure diagram of Figure 7A, we could easily find that the pressure at the drive-out front edge was 37.41 Pa when t=2.0 min, while this value was only 4.19 Pa when t = 3.6 min. This is a good explanation why most of the NAPL in Figure 5 remained downstream of the chip, and the pressure drop at the front edge was no longer sufficient to push more NAPL from the pore when it reaches downstream.

Figure 7. Volume fraction graph and pressure distribution in the model at the two flow rates. A represents the simulation results at the water flow rate of 10.16 m/d and B represents 6.17 m/d.
When the flow broke through, the pressure in the model decreased dramatically, with the maximum pressure drop occurring at the inlet (the inlet pressure equals to 0.478 Pa at a flow rate of 10.16 m/d and 0.053 Pa at 6.17 m/d) and the pressure decreased along the whole flow pathway. Therefore, the remaining pressure drop in the model did not reach the pressure required to drive the NAPL residuals. This is why the NAPL residuals in the chip did not change much after the water flow broke through the channel.

The contact angle of NAPL in the formation varies with different types of NAPL and the physical properties of specific formation [19]. To figure out the effect of stratigraphic wettability on the formation of NAPL-contaminated layers, we simulated the change of NAPL residual amount at different contact angles at a water flow rate of 8 m/d (Figure 8). Because the fluid is incompressible, the NAPL content decreased linearly with increasing injection time regardless of the contact angle prior to breakthrough [20]. When the model was hydrophilic, the front edge was more stable, more NAPL was driven, and NAPL residuals were consequently reduced. Nevertheless, as the model became lipophilic, NAPL was more likely to adhere to the surface of the model, and the front edge became unstable, in which case the water flow would form a bypass channel in the model, resulting in more NAPL remaining in the model. Moreover, the simultaneous adsorption of NAPL on the surface reduced the effective cross-sectional area of the water flow, and the water velocity would be faster at constant flow rates, so that the water flow breakthrough time was accelerated as the NAPL contact angle was reduced [14, 21].

The experimental data of wetting angle and NAPL residuals were extracted from Jung’s work using GetDate Graph Digitizer 2.22 (shown by green triangles and orange circles in the upper right-hand corner of the small graph in Figure 8) for further comparison, and the red squares in the figure indicate the results of this simulation. The three sets of data in the figure show that the NAPL residuals exhibited an exponential decreasing pattern with increasing NAPL contact angle, and that the NAPL residuals increased with increasing porosity. Then, each set of data was divided by the corresponding porosity to uniformly compare the changes of NAPL residuals with wettability. We find that the NAPL removal efficiency changed greatly when the wettability changed from strong oil wetting to weak oil wetting (left side of the light gray dashed line in Figure 9). According to the orange trend line in Figure 9 (fitted from our simulated data and Jung φ=0.3), the simulated data on the left side of the light gray dashed line fitted the Jung φ=0.3 data well, but the Jung φ=0.15 data deviated from the trend line significantly. When the model changed from weak oil wetting to strong water wetting (to the right of the light gray dashed line in Figure 9), the NAPL removal efficiency decreased, and the three sets of data on the right side of the dashed line agreed well with the trend line, indicating that there is a critical θ above which the porosity has less influence on the NAPL residual change.
4. Conclusions
In this study, a two-dimensional dual-permeability microfluidic chip was designed to study the formation mechanism of NAPL contamination layer in heterogeneous aquifer. The effects of various flow rates on the formation of NAPL-contaminated layers in heterogeneous strata were analyzed, and the influence mechanism of the NAPL wetting angle on NAPL contamination layer formation was quantitatively analyzed by numerical simulation. Two-way ANOVA revealed no significant change in NAPL residues in the low permeable zone under different experimental conditions, which indicates that the NAPL in the low permeable zone was basically not washed out at all. The NAPL residual amount decreased with increasing flow velocity in the high permeable zone of the micro-model, while the water flow breakthrough time was shortened. Four main NAPL residual morphologies were found in the experimental images and a large amount of NAPL remained in the downstream region of the chip. The simulation results were in good agreement with the experimental results for the relationship between NAPL residual amount and flow rate. The simulated pressure diagram shows that the maximum pressure drop was at the front edge of the substitution, and the phase interface pressure difference was the main reason for driving the NAPL to flow. At the same time, the pressure drop at the front edge decreased with time, resulting more NAPL remaining at downstream of the chip. The simulation also agreed well with the experimental results about the effect of flow rate on the formation of the NAPL contamination layer, and the simulated pressure graph provided a better explanation of the experimental phenomena. In subsequent simulations of the relationship between NAPL contact angle and contamination layer formation, the results were consistent with previously reported experimental trend [20].

Acknowledgements
This work was supported by the National Natural Science Foundation of China [Grant No. 51974341 and 51874330], the Opening Fund of Shandong Key Laboratory of Oilfield Chemistry and the Fundamental Research Funds for the Central Universities [Grant No. 19CX05006A].

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