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## Effects of thermal and chemical enhancements on the recovery of heavy chlorinated compounds in saturated porous media: Treatability tests and modeling

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**Key-words:** treatability tests, free product recovery, heavy chlorinated solvents, drainage-imbibition experiments, radius of influence (ROI), two-phase flow numerical models, Time Domain Reflectometry (TDR) probes, geophysical probes (induced polarization), imaging technique (Light Reflected Method-LRM)

### Objectives

Recovery of chlorinated solvents (CSs) as a free product generally relies on pumping and pumping/skimming (Perez *et al.*, 2014). However, this technique is time consuming and does not allow major recovery of CSs as free product and associated dissolved emissions (McGuire *et al.*, 2006). Our study focuses on the beneficial effects of thermal and chemical enhancements for recovering free product composed of heavy chlorinated compounds (mixture composed mainly of Hexachlorobutadiene, Hexachloroethane, Perchloroethylene, Pentachlorobenzene, Trichloroethylene...).

This study is part of the SILPHES project, financially supported by ADEME (French Agency for Environment and Energymanagement) in the framework of the program “Investing for the Future” (“Investissements d’Avenir”).

### Innovative nature of the proposed topic

In this study, the rheological parameters of the Dense Non-Aqueous Phase Liquid (DNAPL) were characterized: i.e., density, dynamic viscosity, interfacial tension (water/DNAPL) and contact angles (water/DNAPL). First, the imbibition-drainage tests were conducted in a small cell to determine the capillary pressure-saturation functions. Then, tests were performed in a column (1D tests) in order to validate the numerical model. Finally, pumping tests at different flow rates were carried out in a tank (2D tests), in order to optimize the processes. These tests were carried out using glass beads of different diameters (0.1 to 1 mm) to fulfil homogeneously the three type of setups (cell, column and tank) with glass beads of only one diameter per experiment, under two temperature conditions (10 and 45 °C) and with the application of four different surfactants (SDBS, Triton X-100, Aerosol MA-80, and Tween 80). DNAPL flow was monitored using Time Domain Reflectometry (TDR) probes, geophysical probes (induced polarization) as well as an imaging technique (Light Reflected Method-LRM).

Numerical models were developed using COMSOL Multiphysics® for 1D and 2D cases and the experimental data were compared with simulation results.

The results show that increasing the temperature from 10 to 45°C decreases the dynamic viscosity of DNAPLs (respectively, from  $5.50\pm 0.20$  to  $2.80\pm 0.08$  mPa.s) and has a limited influence on the interfacial tension (12 mN/m) and the contact angles ( $70^\circ$ ). The surfactants were found to reduce the interfacial tensions from 12 mN/m to 1 mN/m, depending on surfactant nature and concentration.

Retention curves of the two-phase system (capillary pressure as a function of water saturation) obtained using small cells were compared to various analytical models (Chen *et al.*, 2006). The best correlations were obtained with the van Genuchten - Mualem model and the Brutsaert - Burdine model.

These retention curves show that: (i) residual DNAPL saturation decreases by 30% when temperature increases from 10 to 45°C; (ii) surfactant addition globally decreases the irreducible saturation of water by 25% (i.e., the surfactants can, at constant pressure, increase the mobility of DNAPLs) and; (iii) some surfactant decrease the residual saturation by 24%.

The pumping experiments in the 2D tank allows (using geophysical and image interpretation) estimating the radius of influence (ROI) as well as the optimal pumping flow rate (PFR). The ROI of pumping increases significantly with the thermal and chemical enhancements (e.g., twice larger using surfactants). On the other hand, at higher PFRs, the beneficial effect of enhancement is less significant.

Figure 1 presents the results of pumping tests with and without surfactant.

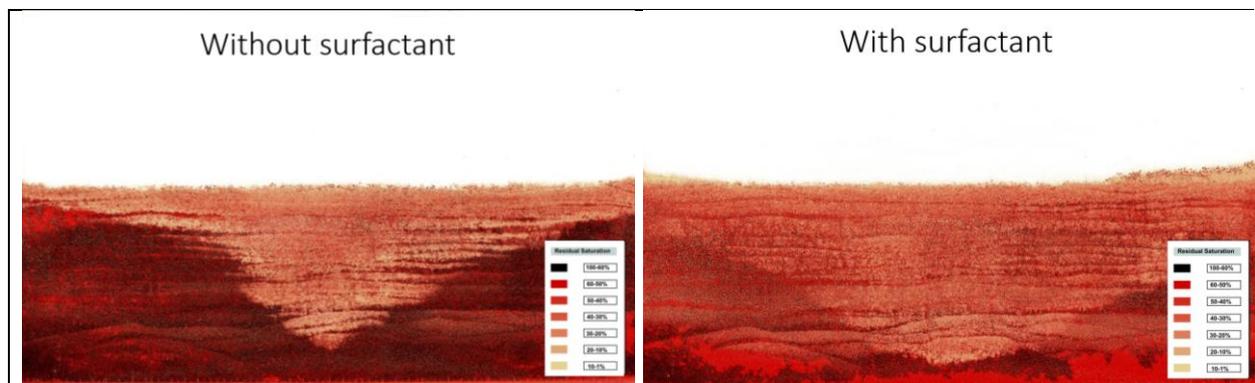


Figure 1: pumping tests with and without surfactant

Finally, the developed numerical models of two-phase flow in porous media accurately reproduce the experiments data. In particular, the model can predict the displacement of the water-DNAPL interface.

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