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Thermal and chemical enhanced recovery of heavy chlorinated organic
compounds in saturated porous media: 1D cell drainage-imbibition experiments

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Abstract

Chemical and thermal enhanced recovery of pure heavy chlorinated organic compounds (DNAPL; dense non-aqueous phase liquids) were investigated by using lab-scale 1D cells. Temperature was increased to reduce DNAPL viscosity (and hence increase its mobility), while surfactant was added to decrease capillary forces involved in the entrapment of DNAPL in porous media. Laboratory scale experiments, based on mass balance and indirect monitoring methods (*i.e.*, permittivity, electrical resistivity and optical density), were conducted to quantify the effects of these enhancements. Heating the DNAPL up to 50 °C decreased its viscosity by a factor of two. The addition of a surfactant; *i.e.*, Sodium Dodecyl Benzene Sulfonate (SDBS), at its Critical Micelle Concentration (to prevent DNAPL solubilization), decreased interfacial tensions by a factor of 12. Drainage-imbibition experiments performed in 1D cells provided retention curves (capillary pressure as a function of water saturation) of a two-phase (DNAPL-water) system in experimental glass bead porous media. The observed reduction of residual saturation (S_{rn}) obtained with SDBS was 28% for 0.5 mm-diameter glass beads (GB) and 46% for 0.1 mm GB. No significant decrease in S_{rn} was observed with thermal enhancement. The van Genuchten – Mualem model was found to satisfactorily reproduce the measured retention curves. Indirect measurements of water saturations (S_w) showed that: i. measured permittivities were very close to values modeled with the Complex Refractive Index Model (CRIM); ii. Archie's Law was less successful in reproducing measured electrical resistivities; iii. optical densities provide accurate estimations of S_w . At field scale, the combined monitoring of electrical resistivity (which provides a global picture) and permittivity (which yields locally precise but spatially limited information) is expected to significantly improve the collection of information on residual saturations S_{rn} .

27

28 **Keywords**

29

30 Dense Non-Aqueous Phase Liquids, chemical enhancement, thermal enhancement,
31 permittivity, electrical resistivity, optical density

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33

34 **1. Introduction**

35 Chlorinated Organic Compounds (COCs) have been produced in large quantities since the middle
36 of the 20th century, mostly for chemical, pharmaceutical and agricultural applications [Cohen and
37 Mercer (1993); Kueper et al. (2003)]. Due to their high hydrophobicity and their density higher than
38 that of water, COCs may infiltrate aquifers vertically and form DNAPL (Dense Non-Aqueous Phase
39 Liquid) pools [Schwille (1988); Cohen and Mercer (1993)]. Their dispersion (by solubilization and
40 volatilization) from the pollution source zone may generate large contaminant plumes leading to
41 severe groundwater contamination [Stupp and Paus (1999)]. These particularly toxic pollutants, may
42 permanently affect soil, indoor air and groundwater quality [ADEME and Ernst & Young (2014);
43 NIEHS (2015); IARC (2018)].

44 Treating such contaminant sources is therefore a priority in order to avoid the migration of DNAPL
45 to groundwater over very long periods of time, leading to a buildup of contaminant plume
46 concentrations and plume spreading [Sale (2001); Stroo et al. (2003); Falta et al. (2005a); Falta et al.
47 (2005b); McDade et al. (2005); Newell and Adamson (2005); McGuire et al. (2006); Huang et al.
48 (2015)].

49 The recovery of COC free-phase (mobile) product is typically performed using pump and treat
50 methods. Due to COC high density, low solubility and strong interfacial tension with water, pump and
51 treat operations are time-consuming (*e.g.*, commonly in excess of 30 years). They are also not very
52 effective in the long term due to the slow release from the residual saturation and the low remediation
53 yield [Mackay and Cherry (1989); Travis and Doty (1990); Berglund and Cvetkovic (1995); Pankow
54 and Cherry (1996); Falta et al. (2005b); McDade et al. (2005); McGuire et al. (2006); Harkness and
55 Konzuk (2014)]. Typical recovery yields following pumping do not exceed 60% [ITRC (2002); Stroo
56 et al. (2012)]. DNAPL mobilization only starts when the sum of viscous and buoyancy forces exceed
57 capillary forces within the contaminated medium [Pennell et al. (1996); Duffield and Ramamurthy
58 (2003)].

59 The DNAPL studied herein was sampled from the subsurface of the Tavaux site; a large chloralkali
60 chemical plant located in the center-east of France. It is a mixture composed mainly of heavy

chlorinated organic compounds (weight percent; wt%): hexachlorobutadiene-HCBD (58%), hexachloroethane-HCA (14%), perchloroethylene-PCE (8%), and pentachlorobenzene (3.5%), carbon tetrachloride (4%), trichloroethylene-TCE (2%), hexachlorobenzene (1%) [Cazaux et al. (2014)]. Due to the accidental release of DNAPL, the subsurface of the Tavaux site is contaminated, with locally pure DNAPL present below the water table. Investigations aim therefore at optimizing the recovery of this free phase, either through thermal (heating) or chemical (surfactants) enhancements.

Surfactants addition aims to: a) decrease the interfacial tension (IFT) between the organic phase and water and b) increase NAPL solubility in water through micelle generation. Dissolution of contaminants into micelles arises when surfactant concentrations exceed the Critical Micelle Concentration (CMC) value in the pores [Rosen (1989)]. While the chlorinated compounds that are the most documented in the literature are PCE and TCE, the DNAPL investigated in the present study does not contain more than 15% (wt%) of these compounds. Also, there is a paucity of literature regarding the main compounds encountered on the Tavaux DNAPL (*i.e.*, HCB and HCA). Nonionic surfactants are effective for remediating chlorinated solvents such as PCE and TCE because of their ability to reduce the IFT and increase pollutant solubility [Taylor et al. (2001); Zhong et al. (2003); Zhao et al. (2006); Suchomel et al. (2007); Harendra and Vipulanandan (2011); Atteia et al. (2013); Pennell et al. (2014)]. Several surfactants (*i.e.*, Triton X-100, Tween 80, Aerosol MA-80 and SDBS) are able to solubilize and reduce the IFT for the TCE-water and PCE-water systems. For TCE, IFT has been reduced from 35.2 to 0.2 mN.m⁻¹ with Aerosol-MA-80 [Dwarakanath et al. (1999)] and from 35.2 to 10.4 mN.m⁻¹ with Tween 80 [Suchomel et al. (2007)]. For PCE, the system's IFT can be reduced by the Aerosol family of surfactants: from 47.8 to less than 0.01 mN.m⁻¹ [Dwarakanath et al. (1999); Sabatini et al. (2000); Childs et al. (2004)], or by Triton X-100 and Tween 80 [Taylor et al. (2001); Harendra and Vipulanandan (2011)]. In this work, the surfactants were introduced at concentrations well below their respective CMC concentrations, in order to avoid DNAPL dissolution and hence the need for costly water treatment technologies [Sabatini et al. (1998); Ahn et al. (2008); Atteia et al. (2013); Maire et al. (2018)].

Regarding temperature enhancement, it has been shown that the viscosity of a chlorinated solvent is generally reduced by 1% per degree Celsius incremental increase [Davis (1997)]. [Sleep and Ma

(1997)] observed a significant viscosity reduction with increasing temperature in the case of PCE. Such viscosity reduction increases DNAPL mobility and therefore decreases residual saturations. She and Sleep (1998) reported that increasing the temperature decreased residual PCE [She and Sleep (1998)]. Kong (2004) also demonstrated during imbibition-drainage experiments that residual coal tar saturations reduced when temperatures were increased from 22 to 50 °C (respectively $S_m = 31.4\%$ to 27.6% in F-70 sand and $S_m = 32.8\%$ to 21.8% in 20-30 mesh Ottawa sand) [Kong (2004)]. Indirect monitoring of these residual saturations can be performed using several methods.

Permittivity measurements using Time-Domain Reflectometry (TDR) probes have served as indicators of Dense Non-Aqueous Phase Liquid (NAPL) saturation (S_n) [Redman et al. (1991); Redman and DeRyck (1994); Kueper et al. (1993); Brewster et al. (1995)]. PCE samples spiked at controlled values of saturation were monitored by TDR, with results showing a good correlation between PCE saturation and permittivity interpreted using a mixing model [Redman and DeRyck (1994)]. The most commonly used model for correlating dielectric permittivity to saturation levels in a soil made of a mixture of particles, water and air, is the Complex Refractive Index Model (CRIM) [Birchak et al. (1974); Roth et al. (1990); Endres and Knight (1992); Ajo-Franklin et al. (2004)]. Electrical resistivity is another parameter used as a means to estimate DNAPL saturation levels. Interpretation is performed using Archie's Law, which describes how resistivity depends on porosity if ionic conduction in the pore fluid dominates other conduction mechanisms in the rocks [Archie (1942)]. Resistivity is described as the sum of a bulk conductivity term and a surface conductivity term, both of which are saturation-dependent [Revil (2012)].

Finally, the Light Reflection Method (LRM) was used to calibrate NAPL saturation with optical density [Alazaiza et al. (2016)]. Schincariol and Schwartz (1990) and Schincariol *et al.* (1993) published the first studies showing a correlation between a reflected optical image and dyed NaCl concentrations during miscible experiments [Schincariol and Schwartz (1990); Schincariol et al. (1993)]. Flores *et al.* (2011) quantified the residual saturation of LNAPL using Sudan III dyed (synthetic organic compounds) with brilliant blue FCF and Simplified Image Analysis Method (SIAM). The difference between mass balance and image interpretation was only 4.7% [Flores et al. (2011)]. O'Carroll *et al.* (2004) used LRM to estimate the saturation of tetrachloroethylene (PCE) in a

flow chamber and observed a linear relationship between the hue and PCE saturation (with a correlation R^2 value of 0.91) [O'Carroll et al. (2004)]. Luciano *et al.* (2010) used mass balance calculations to validate the suitability of LRM, with a difference between mass balance and image interpretation of 6% [Luciano et al. (2010)]. Unlike previous authors, the approach adopted herein relied on a calibration based on a superior number (4) of water saturation calibration points ($S_w = 0\%$, 100%, $1-S_{rn}$, and S_{rw}).

The purpose of this study was to assess the potential of chemical and thermal enhancements for improving DNAPL recovery during pumping. Investigations were performed at lab scale with controlled 1D cells, a DNAPL mixture collected in the field and porous media made of glass beads. This experimental setup helped avoid potential artefact effects associated with porous medium heterogeneity, while focusing on primary mechanisms and parameters (*e.g.*, interfacial tension, micellar concentrations, ...) and on the indirect measurement of DNAPL saturation levels using three different methods (permittivity, electrical resistivity and optical density).

2. Materials and methods

The DNAPL used for the experiments was sampled at the Tavaux site (June 25, 2014) and stored in a cold room (at 4 °C). DNAPL was filtered just before its use (EMD Millipore, 0.45 μ m). The water used for all experiments was BRGM tap water degassed using an ultrasound tank (VWR Ultrasonic Cleaner - USC500D: 60 °C, 45 Hz, 60 min). This tap water is extracted from a groundwater well that shows very stable chemical characteristics.

The experiments with thermal enhancement were carried out in the 20-50 °C temperature range (in order to avoid DNAPL volatilization). Four surfactants were tested at their CMC: 2 non-ionic (Triton X-100: 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol and Tween 80: sorbitan mono-9-octadecenoate poly(oxy-1,2-ethanediyl)) and 2 anionic (Aerosol MA-80: sodium 1,4-dicyclohexyl sulphonatosuccinate and SDBS: sodium dodecyl benzene sulfonate). All surfactants were supplied by Sigma Aldrich (laboratory grade), except for the Aerosol MA-80, which was supplied by Cytec.

2.1 Characterization of fluid physical properties

All measurements presented herein were carried out in triplicate. Viscosity was first measured by Rheonova Laboratory (Grenoble, France) using a Discovery Hybrid Rheometer - DHR 3 (TA Instruments) and then at BRGM with a Haake Mars III rheometer from Thermo Fischer Scientific. Measurements were performed at atmospheric pressure and at 10, 15, 20, 30, 45 and 60 °C. Temperature was controlled through the Peltier effect. The temperature precision was 0.5 °C.

The IFT and contact angle between the DNAPL and water were measured at the Navier laboratory (Champs-sur-Marne, France) with a Tracker-S tensiometer (Teclis Scientific) and also at BRGM with a Drop Shape Analyser tensiometer DSA-100 (Krüss). The Tracker-S and the DSA-100 are automated drop tensiometers that can measure variations in IFT over time. The instrument can also be used to measure the contact angle between a liquid and a solid. Using optional lenses, the accuracy of IFT measurement can be increased to 0.1 mN.m⁻¹. The IFT and contact angle for DNAPL-water were measured at different temperatures (10 to 60 °C) and with surfactants at different concentrations. The temperature was stabilized with a thermostatically controlled water bath. Product densities were measured by first weighing three different 100 mL flasks and then weighing, for each temperature, the product was weighed in the closed vial while adjusting the volume required to fill the flasks.

2.2 Solubilization

DNAPL solubility measurements were performed using the experimental protocol of Rodrigues *et al.* (2017). The same protocol was applied for solubilization experiments in the presence of surfactants. Four surfactant concentrations were studied, according to their respective CMC value, from 0.25×CMC to 8×CMC. All measurements were performed in triplicate at 20 °C [Rodrigues *et al.* (2017)].

COC concentrations in water were analyzed by gas chromatography with flame ionization detector (Varian 3800) and head space injection (Agilent 7697A). The column used was an Agilent CP-SIL 5 CB (semi-capillary column, fused silica tube, length: 50 m, internal diameter: 0.53 mm, active phase: polydimethylsiloxane, carrier gas: helium).

2.3 Drainage-imbibition experiments in 1D cells

The main objective of the experimental study was to characterize the soil parameters in two-phase flow conditions (DNAPL and water) in a porous medium and under different conditions (thermal or chemical enhancement). To achieve this objective, the laboratory work was dedicated to performing drainage-imbibition experiments in 1D cells (filled with glass beads; GB) that were used to generate the capillary pressure-saturation curves in static flow conditions. The 1D cells had an internal diameter of 5.8 cm and a height of 5.56 cm (Figure 1). Two sizes of GB were used to fill the cells in order to reproduce the hydraulic conductivities measured at the site: 0.10 ± 0.02 mm and 0.5 ± 0.1 mm GB. The cells were carefully filled with GB and vibrated. The mass of GB porous medium inside the cells was kept constant in order to ensure similar porous medium compaction and porosity characteristics. The GB measured permeabilities were 1.30×10^{-10} m² and 6.73×10^{-12} m² for 0.5 mm GB and 0.1 mm GB, respectively. At both extremities, the main cells were connected via two tubes to two graduated “reservoir” columns (3.5 cm internal diameter and 41.8 cm high). These two reservoirs (containing respectively water and DNAPL) stored the fluids and allowed to control the pressure heads at the lower and upper parts of the cell. The cells and the columns were made of PolyVinylidene Fluoride (PVDF) and were connected by thermo-scientific Nalgene 8001-1014 | 180 metric clear PolyVinyl Chloride (PVC) tubes with 1 cm internal diameter. The volumes of DNAPL and water in the porous media were calculated by volume balance. The addition of surfactants and the heating up to 50 °C were carried out at the end of the drainage periods in order to start with the same values of S_{rw} as for the experiments without enhancement. The experimental set-up was also constantly monitored by geophysics and TDR probes. The number of drainage-imbibition experiments performed with 0.5 and 0.1 mm GB were respectively: 5 and 6 without enhancement and with membrane, 3 and 4 without enhancement and without membrane, 8 and 6 with surfactants, 2 and 2 with thermal enhancement.

The curves, which were afterwards calibrated using the van Genuchten-Mualem model (VGM), provide key parameters such as the irreducible water saturation (S_{rw}), the residual pollutant saturation (S_m), the entry pressure, and the calibration parameters α and n which characterize the capillary forces and the heterogeneity of the porous medium, respectively (Eq. 1 and Eq. 2) [Mualem (1976); van Genuchten (1980)].

$$S_{ew} = \frac{1}{[1 + (\alpha h_c)^n]^m} \quad \text{Eq. 1}$$

$$S_{ew} = \frac{S_w - S_{rw}}{1 - S_{rw} - S_{rn}} \quad \text{Eq. 2}$$

where $m = 1-1/n$, $S_{ew}(-)$ is the effective water saturation, h_c (m) is the capillary pressure head, α (m^{-1}) is a fitting parameter that is inversely proportional to the non-wetting fluid entry pressure value, and n (-) is the width of pore-size distribution.

The experimental data were fitted to the VGM capillary pressure-saturation function using the solver provided in Excel by minimizing the Sum of Squared Errors (SSE).

2.4 Monitoring of the drainage-imbibition experiments with dielectric permittivity

Dielectric permittivities were monitored using TDR probes (Decagon Devices 5TE 40567) with a 70 MHz frequency. Data acquisition frequency was 2 signals per minute. In addition to permittivity (-), these probes monitor volumetric water content-VWC ($\text{m}^3 \cdot \text{m}^{-3}$), temperature ($^{\circ}\text{C}$), and bulk electrical conductivity-EC ($\text{dS} \cdot \text{m}^{-1}$). They were connected to a Campbell Scientific CR1000 (4M) data logger to acquire temperature and permittivity data. The permittivity values were corrected relative to the reference values measured in air and water using the following equation (Eq. 3) [Kargas and Soulis (2012)]:

$$\varepsilon_{corrected} = \frac{\varepsilon_{w-theoretical}(\varepsilon_{measured} - \varepsilon_{air})}{(\varepsilon_w - \varepsilon_{air})} + \varepsilon_{air-theoretical} \quad \text{Eq. 3}$$

where $\varepsilon_{w-theoretical}$ (-) is the relative effective permittivity of pure water ($\varepsilon_{w-theoretical} = 80$ at 20°C), $\varepsilon_{measured}$ (-) is the relative effective permittivity of the medium measured with the TDR probe during the experiments, ε_{air} (-) is the relative effective permittivity of air measured at the beginning of the experiment, ε_w (-) is the relative effective permittivity of tap water measured at the beginning of the experiment, and $\varepsilon_{air-theoretical}$ (-) is the relative effective permittivity of pure air ($\varepsilon_{air-theoretical} = 1$).

2.5 Monitoring of the drainage-imbibition experiments with electrical resistivity

Electrical resistivity was monitored using unpolarizable potential electrodes for voltage measurement, metallic current electrodes for current injection, a resistivity meter and data acquisition

software. To limit electrode polarization phenomena, which can add noise to the measurements, potential electrodes must be unpolarizable [Dahlin (2000)]. Cu/CuSO₄ electrodes were used and the method developed by Noel [Noel (2014)]. These electrodes were made by mixing milli-Q water 72.2%, CuSO₄ 26% and Gelatin 1.7% and heated the mixture to ≈ 80 °C for 45 minutes using a shaking heating plate. The resulting electrodes are unpolarizable, *i.e.*, they do not polarize the ground and therefore the electrode action on the potential measured can be considered negligible.

The metallic current electrodes were made of nickel-cobalt alloy (MP35N). The resistivity meter was SIP LAB IV and data acquisition software was SIP LAB IV. Resistivity was measured between 0.1 to 20 000 Hz but analysed at 1.4 Hz. This frequency was chosen because it is close to that used in the field [Chambers et al. (2004); Constable and Srnka (2007); Han et al. (2015); Deparis et al. (2019)]. The Wenner electrodes configuration was applied, as it well suited for cell experiments [Noel (2014)].

The values measured were resistance values, R_e , which were transformed into apparent electrical resistivity values, ρ_c , using the geometric coefficient, K_g (Eq. 4 and Eq. 5) [Reynolds (2011)] :

$$K_g = \frac{R_0}{R_e} \quad \text{Eq. 4}$$

$$\rho_c = R_e K_g \quad \text{Eq. 5}$$

where K_g (m) is the geometric coefficient, and R_0 ($\Omega \cdot m$) is the initial estimated resistance value.

The conductivity of the tap water, measured at the beginning of each experiment, made it possible to determine R_0 and to calculate K_g (using Eq. 4). The value of K_g was then used throughout the experiment to transform R_e into ρ_c .

Experiments were carried out to quantify the impact of chemical and thermal enhancements on permittivities and resistivities: drainage experiments were first performed with only tap water and GB by (i) introducing tap water with surfactants (at their CMC values) and (ii) increasing temperature. Experiments were then performed in order to quantify the effects of temperature on the permittivity and resistivity of DNAPL, water, DNAPL+GB, and water+GB systems. In these experiments, temperature was increased stepwise from 10 to 50 °C. Permittivity and resistivity were noted once the

temperature of each step had stabilized. The correlation curves helped to correct the permittivity and resistivity values with temperature variations.

2.6 *Monitoring of the drainage-imbibition experiments with image interpretation*

The optical imaging method used was the light reflection method (LRM), with a Nikon® D810 with NIKKOR LENS 105 (Nikon®) digital camera which has a high resolution of 34 Mega Pixels. The image resolution calculated from Fiji (open source image processing package based on ImageJ) for these experiments was approximately $0.003 \text{ mm}^2.\text{pixel}^{-1}$, depending on the image size [pixels×pixels] and the distance between the camera and the object of interest. The following camera set up was used: aperture = 1/200 s, ISO = 100 and the shutter = f/16. This set up remained the same during all experiments. The Capture One® software was used to take photographs without touching the camera. All pictures were acquired on RAW format (.raw) to save the full data information.

For the calibration, the drainage-imbibition experiments were conducted in the same way as with 1D cells but this time with a Hele-Shaw cell (to prevent light reflection). The dimensions of this cell were: height = 5.00 cm, length = 5.00 cm and width = 2.00 cm. The cell was made of PVDF (as with the 1D cells), to ensure high chemical resistance to the pure pollutant. The cell was composed of two transparent glass faces to allow photographing. The experiments were performed in a dark room and the light source was provided by two 2×300 W floodlights (Broncolor®). The camera was always placed in the same position for all experiments. A color scale was placed beside the cell to calibrate the differences, albeit small, between the lighting used for the various experiments.

First, a global Area Of Interest (AOI) was defined to obtain the mean grey value necessary to associate with S_w . Then each picture was converted into 8-bit format. Finally, the mean grey values were calculated using Fiji software, for different AOI centered in the middle of the picture. Fiji software was chosen because it is easy to apply a threshold that depends on the pixel intensity value. The threshold depends on the calibration curve fluid saturation versus intensity. Using Fiji, it is possible to determine the area associated with the threshold. From this information (DNAPL saturation and its own area), one can compute the DNAPL volumes present using the following expression (Eq. 6).

$$V_{DNAPL} = S_{DNAPL} A_{DNAPL} l \emptyset \quad \text{Eq. 6}$$

where $V_{DNAPL}(\text{m}^3)$ is the volume of DNAPL for a given saturation, S_{DNAPL} (-) is the DNAPL saturation for a given threshold on Fiji, $A_{DNAPL}(\text{m}^2)$ is the area associated of the given saturation, l (m) is the length between the front wall and the back wall of the cell, and \emptyset (-) is the porosity.

The image data analysis was performed according to the following main steps: a) convert the picture into 8 bit format to obtain 256 shades of gray; b) set up the scale; c) set up the I_0 (Initial luminous intensity), which was equal to white on the gray scale; d) define the AOI; e) set up the contrast to optimize the black pixels; f) compute the layers of DNAPL saturation present on the AOI, based on the linear relation derived from the calibration experiment.

3. Theory

The parameters presented in section 2 provide information regarding the potential for mobilizing DNAPL in a porous medium, using various relationships or models. For example, Pennell *et al.* (1996) used a method to estimate DNAPL mobilization in the porous medium with capillary number (N_{ca}), Bond number (N_B) and total trapping number (N_T) (Eq. 7 to Eq. 9).

$$N_{ca} = \frac{v_w \mu_w}{\sigma \cos \theta} \quad \text{Eq. 7}$$

$$N_B = \frac{g k k_{rw} \Delta \rho}{\sigma \cos \theta} \quad \text{Eq. 8}$$

$$N_T = \sqrt{N_{ca}^2 + 2 N_{ca} N_B \sin \alpha_{N_T} + N_B^2} \quad \text{Eq. 9}$$

where v_w (m.s^{-1}) is the Darcy velocity of the wetting phase (upward direction is considered positive), μ_w (Pa.s) is the dynamic viscosity of the wetting phase, $\Delta \rho$ (kg.m^{-3}) is the difference of densities between the wetting and non-wetting phase ($= \rho_w - \rho_n$), and α_{N_T} ($^\circ$) is the angle between the direction of flow and the horizontal direction.

The mobility ratio (m_r) can be calculated as follows (Eq. 10) [Lenormand *et al.* (1988); Dullien (1992)]:

$$m_r = \frac{k_{2r} \mu_1}{k_{1r} \mu_2} \quad \text{Eq. 10}$$

where m_r (-) is the mobility ratio, k_{1r} (-) is the relative permeability for the displaced phase, k_{2r} (-) is the relative permeability for the displacing phase, μ_1 (Pa.s) is the fluid dynamic viscosity for the displaced phase, and μ_2 (Pa.s) is the fluid dynamic viscosity for the displacing phase.

Regarding the monitoring of permittivities to characterize saturations, the CRIM model has been developed for multiphase systems (Eq. 11) [Birchak et al. (1974); Roth et al. (1990); Endres and Knight (1992)]:

$$\varepsilon = \left[\sum_{i=1}^N v_i \varepsilon_i^{\alpha_\varepsilon} \right]^{1/\alpha_\varepsilon} \quad \text{Eq. 11}$$

where ε (-) is the relative effective permittivity of the mixture, ε_i (-) is the relative effective permittivity of the i phase, v_i (-) is the volume of the i phase, and α_ε (-) is an empirical constant related to the geometry of the grains and their spatial distribution.

Ajo-Franklin *et al.* (2004) report correlations higher than 97% using the CRIM model with TCE in the saturated zone [Ajo-Franklin et al. (2004)]. For a three-phase mineral/water/NAPL mixture and assuming that $\alpha_\varepsilon = 0.5$, the CRIM equation becomes (Eq. 12):

$$\varepsilon = \left[\phi (S_w \sqrt{\varepsilon_w} + S_n \sqrt{\varepsilon_n}) + (1 - \phi) \sqrt{\varepsilon_s} \right]^2 \quad \text{Eq. 12}$$

where S_w (-) is the water (wetting fluid) saturation, ε_w (-) is the relative effective permittivity of water, S_n (-) is the DNAPL (non-wetting fluid) saturation, ε_n (-) is the relative effective permittivity of NAPL, and ε_s (-) is the relative effective permittivity of soil particles.

For electrical resistivity interpretation, Archie's Law is described as follows (Eq. 13) [Archie (1942)]:

$$\rho_c = \rho_{c,w} a_c \phi^{-m_c} \quad \text{Eq. 13}$$

where ρ_c ($\Omega.m$) is the real effective electrical resistivity of the bulk, $\rho_{c,w}$ ($\Omega.m$) is the real effective electrical resistivity of the fluid at temperature T , a_c (-) is an empirical parameter (typically equal to 1 but that can vary from <1 for intergranular porosity to > 1 for joint porosity), and m_c (-) is the cementing factor (also an empirical parameter usually approximately equal to 2, but that can vary from 1.2 for unconsolidated sediments to 3.5 for crystalline rocks).

Glover (2010) proposed, on the basis of Archie's law, the following equations to calculate S_w for a two-phase system, where neglecting the conductivity of GB is neglected as it is very low ($\sigma_{c,GB} = 10^{-20} \text{ S.m}^{-1}$) (Eq. 14 to Eq. 17) [Glover (2010)]:

$$\sigma_{c,bulk} = \sigma_{c,DNAPL}[\phi(1 - S_w)]^{m_1} + \sigma_{c,water}[\phi(S_w)]^{m_2} \quad \text{Eq. 14}$$

$$\left(-\frac{\phi_1^2}{2}\right)m_2^2 + \left(\phi_1 + \frac{\phi_1^2}{2}\right)m_2 - \phi_1^{m_1} = 0 \quad \text{Eq. 15}$$

$$m_2 = \frac{-\left(\phi_1 + \frac{\phi_1^2}{2}\right) \pm \left[\left(\phi_1 + \frac{\phi_1^2}{2}\right)^2 - 4\left(-\frac{\phi_1^2}{2}\right)(-\phi_1^{m_1})\right]^{\frac{1}{2}}}{-\phi_1^2} \quad \text{Eq. 16}$$

$$m_2 = \frac{-(4\phi_1 + 2\phi_1^2) \pm (4\phi_1^2 + 4\phi_1^3 + \phi_1^4 - 8\phi_1^2\phi_1^{m_1})^{\frac{1}{2}}}{-4\phi_1^2} \quad \text{Eq. 17}$$

where $\sigma_{c,bulk} = \sigma_c \text{ (S.m}^{-1}\text{)}$ is the real effective electrical conductivity of the bulk, $\sigma_{c,DNAPL} \text{ (S.m}^{-1}\text{)}$ is the real effective electrical conductivity of DNAPL, $m_1 \text{ (-)}$ is the cementation exponent of DNAPL phase, $\sigma_{c,water} \text{ (S.m}^{-1}\text{)}$ is the real effective electrical conductivity of water, $m_2 \text{ (-)}$ is the cementation exponent of water phase, and $\phi_1 = \phi(1 - S_w)$; $\phi_2 = \phi(S_w)$.

For image analysis, the optical density of reflected light, D_r , can be defined as (Eq. 18 and Eq. 19) [Stimson (1974); Schincariol et al. (1993); Flores et al. (2011)]:

$$D_r = -\lg(\rho_t) \quad \text{Eq. 18}$$

$$\rho_t = \frac{I_r}{I_0} \quad \text{Eq. 19}$$

where: $D_r = \text{OD (-)}$ is the optical density of reflected light, $\rho_t \text{ (-)}$ is the ratio of reflected/initial luminous intensity, $I_r \text{ (-)}$ is the reflected luminous intensity, and $I_0 \text{ (-)}$ is the initial luminous intensity.

4. Results and discussion

4.1 Fluids characterization

4.1.1 Dynamic viscosity

While chlorinated solvents are typically more fluid than water (with viscosities less than 1 mPa.s) [Sleep and Ma (1997)], the dynamic viscosity of the DNAPL studied herein was much higher (5 mPa.s

at groundwater temperature, *i.e.* 12 °C). The viscosity of a chlorinated solvent is generally reduced by 1% per degree Celsius [Davis (1997)]. The dynamic viscosity of the DNAPL studied here reduced by 57% when the temperature rose from 10 to 60 °C, which is in agreement with the literature (Supplementary materials, Figure A-1). As shown in this figure, the change in dynamic viscosity as a function of temperature fitted a second order polynomial curve. For water, the reduction in dynamic viscosity was 54% for the same temperatures. The μ_w/μ_{nw} ratio ranged from 0.23 to 0.19 for temperatures of 10 °C and 60 °C, respectively. This 15% reduction in viscosity ratios may contribute to improve DNAPL mobility.

4.1.2 *Interfacial tension and contact angle between DNAPL and water*

The IFT, σ , was measured as 11.15 ± 0.05 mN.m⁻¹ at 20°C (Supplementary materials, Figure A-2). This value was lower than that of pure TCE or PCE in distilled water (respectively 36.9 and 45.9 mN.m⁻¹) [Andersson et al. (2014)]. The results for reduced interfacial tensions with added surfactants were very contrasted. Three trends were observed: a moderate effect for Tween 80, a substantial effect for relatively high CMC of Triton X-100 and Aerosol MA-80, and a very substantial beneficial effect for low surfactant concentrations of SDBS. More precisely, we found that the reduction in IFT for Tween 80 was 52% with the concentration of 64×CMC ($\sigma_{\text{final}} = 5.28$ mN.m⁻¹). As for Triton X-100 and Aerosol MA-80, the reductions were respectively 96% and 90% for a concentration of 64×CMC ($\sigma_{\text{final}} = 0.48$ mN.m⁻¹ and 1.10 mN.m⁻¹). Finally, SDBS seemed to be the most advantageous surfactant as it could reduce the IFT by 99% at a lower surfactant concentration ($\sigma_{\text{final}} = 0.10$ mN.m⁻¹). Experimental results showed that thermal enhancement had only limited influence on DNAPL/water IFT. This parameter decreased by only 2.3% between 10 and 60 °C (respectively 12.17 to 11.89 mN.m⁻¹).

The DNAPL-water-glass contact angle without surfactant was 119.33 ± 4.16 ° at 20 °C (Supplementary materials, Figure A-3), which is typical of such a non-wetting fluid and close in order of magnitude to values reported in the literature (*e.g.*, 129° for TCE in pure water) [Orphius and Kibbey (2005)]. The reduction in contact angles with chemical enhancement were consistent with previous work [Amirpour et al. (2015)]. The contact angle was significantly reduced by adding SDBS; it reached 30.33° (*i.e.* a 75% drop) for SDBS concentrations far below the CMC and therefore DNAPL

became wetting, as the angle was less than 90°. Regarding the other anionic surfactant, adding Aerosol MA-80 reduced the contact angle by 23% for a concentration equivalent to 16×CMC ($\theta_{\text{final}} = 91.33^\circ$). The two nonionic surfactants gave similar curves. Triton X-100 and Tween 80 only reduced the contact angles by 5.6 and 4.9% ($\theta_{\text{final}} = 112.70^\circ$ and 113.50°), respectively. The temperature increase only moderately reduced the contact angle. Increasing the temperature from 10 to 60 °C decreased the contact angle from 126.33 to 108.00° (*i.e.* a 14% reduction).

Based on these results, we can estimate the effect of chemical and thermal enhancements on capillary pressure, P_c . As a first approximation, we considered DNAPL and water in a tube (pore throat) with a circular cross section (Eq. 20).

$$P_c = \frac{2\sigma\cos\theta}{r} \quad \text{Eq. 20}$$

where P_c (Pa) is the capillary pressure, $\sigma = \sigma_{\text{nw}}$ (mN.m⁻¹) is the interfacial tension, θ (°) is the pore contact angle, and r (cm) is the mean radius of interface ($r = r_{\text{tube}}/\cos\theta$)

The nonionic surfactants reduced P_c less than the anionic surfactants. Triton X-100 and Tween 80 only reduced the capillary pressure by 77.3% and 62.5%, respectively, while the anionic surfactants were far more effective in reducing capillary pressure (respectively, 98.9% and 99.7% for Aerosol MA-80 and SDBS). Thermal enhancement had only a minor effect on P_c (49.4% reduction).

4.1.3 Density

The studied DNAPL was denser (1.66 kg.L⁻¹ at 20 °C) than well-known chlorinated solvents such as TCE and PCE (respective densities at 20 °C: 1.46 and 1.62 kg.L⁻¹). PCE density variations as a function of temperature are moderate; with decreases on the order of 0.1 kg.L⁻¹ for a temperature increase from 20 to 90 °C [Sleep and Ma (1997)]. The Tavaux site DNAPL also displayed a moderate density decrease as a function of temperature; as the density decreased only by 3% for temperatures ranging from 10 to 60 °C (Supplementary materials, Figure A-4).

4.2 Solubilization

The DNAPL solubility was low: 40.00 mg.L⁻¹ (at 20 °C) (Supplementary materials, Figure A-5). The two non-ionic surfactants generated a global solubility increase ($\Sigma[\text{COC}]$) of a factor of 20 for Triton X-100 (for a concentration of $8 \times \text{CMC}_{\text{theoretical}}$) whereas it was only 1.45 for Tween 80 for the same concentration ratio. The addition of MA-80 aerosol at $8 \times \text{CMC}$ increased the solubilization yielded by a factor of 18; but only by a factor of 1.3 for SDBS with the same CMC ratios. Usually, as surfactant concentration increases, the volume of core micelles increases, leading to a linear increase in the apparent solubility [Pennell et al. (2014)]. A linear change in apparent solubility has also been demonstrated for surfactant concentrations greater than their CMC for several chlorinated compounds (*e.g.*, PCE, TCE, HCBd and HCEa) [Jafvert (1994); Kommalapati et al. (1997); Harendra and Vipulanandan (2011); Rodrigues et al. (2017)].

The CMC_{real} of the surfactants that correspond to the $\text{IFT} = f([\text{surfactant}])$ and $[\Sigma\text{COC}] = f([\text{surfactants}])$ curves' inflection points are (Supplementary materials, Figure A-5): 1200.00 mg.L⁻¹ for Triton X-100, 503.04 mg.L⁻¹ for Tween 80, 11640.00 mg.L⁻¹ for Aerosol MA-80 and 65.34 mg.L⁻¹ for SDBS. Increasing the temperature from 12 °C (temperature of the groundwater) to 60 °C increased the solubility by 13% (44.16 versus 50.00 mg.L⁻¹), which is relatively small change.

4.3 Drainage-imbibition experiments

4.3.1 Drainage-imbibition experiments without enhancement

The P_c - S_w curves for 0.5 and 0.1 mm GB are compared in Figure 2a. Table 1 shows the results of these experiments and the van Genuchten-Mualem (VGM) fitting parameters. The experimental data were fit to the VGM capillary pressure-saturation function (Eq. 1 and Eq. 2) using sum of squared errors (SSE) minimization. The SSE were low ($\text{SSE} < 0.0014$), which demonstrated that the VGM model can be used to describe the experimental results. The experimental results are mainly focused on residual DNAPL saturation and irreducible water saturation. It is clear from the graph that the parameters differed slightly for each size of glass bead. For 0.5 mm GB, S_{rn} was approximately 10.9% vs. 12.7% for 0.1 mm GB. According to the results, S_{rw} was around 24.8% for 0.5 mm GB and 30.9% for 0.1 mm GB. This is explained by capillary forces as the mean pore radius was higher for 0.5 mm

GB and therefore the influence of capillary forces was lower. Therefore, during drainage, less DNAPL could be incorporated into the 0.5 mm GB medium (S_m was 23.0% higher than for 0.1 mm GB) while during imbibition, more DNAPL trapped in the 0.5 mm GB medium could be extracted (S_m was 16.0% higher than for 0.1 mm GB). The curve for 0.1 mm GB has a lower S_w amplitude. These results are in agreement with the data reported in the literature [Mualem (1976); van Genuchten (1980); Gerhard and Kueper (2003a)].

The parameter α value, characteristic of the reverse of the suction effects, was higher for the 0.5 mm GB, which was expected, since capillary effects were higher for the 0.1 mm GB. The slope of the median portion of the curves was relatively flat, which confirms that the GB were indeed homogeneous [Ouchiyama and Tanaka (1984); Likos and Jaafar (2013); Chapuis et al. (2015); Chiapponi (2017)]. The interpretation of parameter n values variations is more complex: sensitivity tests show that for high α values and n values greater than 4 (in a homogeneous medium), as in our case, the variations of n had a minor influence on the shape of the retention curves.

4.3.2 Drainage-imbibition experiments with enhancements

The remediation enhancement yield was calculated as follows (Eq. 21):

$$\text{Remediation yield} = 100 - 100 \left(\frac{S_{rn, \text{chemical enhancement}}}{S_{rn, \text{without enhancement}}} \right) \quad \text{Eq. 21}$$

Adding SDBS had the highest impact on reducing the IFT. Therefore, the best remediation enhancement yield was obtained with SDBS (27.6% i.e. $S_m = 0.079$), for 0.5 mm GB. Aerosol MA-80 and Triton X-100 had similar remediation enhancement yields (24.0 and 22.5% respectively, i.e. $S_m = 0.083$ and 0.085). Tween 80 had a remediation enhancement yield close to zero ($S_m = 0.11$). For 0.1 mm GB, the best remediation enhancement yield was with SDBS (46.3% i.e. $S_m = 0.068$). Aerosol MA-80 performed better than Triton X-100: the remediation enhancement yields were respectively 35.56 and 38.1% ($S_m = 0.082$ and 0.078). Tween 80 had a remediation enhancement yield of 7.0% ($S_m = 0.118$).

The remediation enhancement yields for 0.1 mm GB were higher than those observed with the 0.5 mm GB. This is because the capillary forces were higher for 0.1 mm GB and the effect of the

surfactants, whose purpose is to reduce the IFT, is improved. The best results were obtained with SDBS. Figure 2b shows the average of the experimental results for P_c - S_w curves with SDBS (imbibition) for the 0.5 mm GB and 0.1 mm GB (fitted with the VGM model). At the end of drainage, adding surfactant influences the slope of the line, which is slightly more horizontal, demonstrating that the capillary effects, and therefore the capillary fringes (thickness of the migration front), were weaker.

Capillary number (N_{ca}), Bond number (N_B), and Total trapping number (N_T) were calculated using Eq. 7 to Eq. 9 on the basis of the experimental and rheological data (Figure 3). As expected, increasing the grain size increases all three numbers. Here, viscosity forces predominate over gravitational forces, while capillary forces predominated over other forces. Adding surfactants increased N_{ca} and consequently N_T . Increasing N_{ca} decreases the residual saturations [Lake (1989); Pennell et al. (1996); Sheng (2015)]. It was found that the thermal enhancement had no effect on S_m or on the shape of the P_c - S_w curve during the imbibition stage of these static drainage-imbibition experiments. The thermal enhancement only affected the viscosity.

4.4 Monitoring of the drainage-imbibition experiments with dielectric permittivity

4.4.1 Drainage-imbibition experiments without enhancement

Permittivity calibration curves were plotted as a function of water saturation for 0.5 and 0.1 mm GB (Figure 4). Permittivity could be related to water saturation by a second order polynomial relationship. The scatter plot was less dispersed for the 0.5 mm GB than for the 0.1 mm GB and therefore R^2 was lower for the 0.1 mm GB ($R^2 = 0.79$ vs 0.90 for 0.5 mm GB). This can be explained by the difference between capillary effects.

The resulting trends were very similar for 0.5 and for 0.1 mm GB. The calibration curves were also very similar: the ratios of polynomial curves for 0.5 mm GB/polynomial curves for 0.1 mm GB vary between 0.97 and 1.20. For homogeneous porous media, grain size has little influence on permittivity. These results were consistent with previous research on permittivities measured in a water-air system. The small differences can be attributed to the less regular GB, the spherical shape of GB and the pore connectivity [Robinson and Friedman (2001); Robinson and Friedman (2002); Robinson et al. (2005); Brovelli and Cassiani (2010)].

Experimental data was fitted to the CRIM model (see Eq. 12), using the following values: $\emptyset = 0.38$ (experimental values), $\epsilon_w = 80$ (experimental value), $\epsilon_n = 3.11$ (experimental value for 100% DNAPL), $\epsilon_m = 7.5$ (literature review for GB material [von Hippel (1954); Robinson and Friedman (2002)]).

We see that a value $\alpha_e = 0.5$ (cited in the literature) does not fit our experiments. The α_e values calculated by the least-square method were respectively 0.70 and 0.75 for 0.5 mm and 0.1 mm GB (with respective R^2 of 0.89 and 0.78). Therefore, for our experiments the CRIM model can be applied using the following equations (Eq. 22 to Eq. 23):

$$\text{For 0.5 mm GB} \quad \epsilon' = [\emptyset(S_w \epsilon_w'^{0.7} + S_n \epsilon_n'^{0.7}) + (1 - \emptyset) \epsilon_m'^{0.7}]^{\frac{1}{0.7}} \quad \text{Eq. 22}$$

$$\text{For 0.1 mm GB} \quad \epsilon' = [\emptyset(S_w \epsilon_w'^{0.75} + S_n \epsilon_n'^{0.75}) + (1 - \emptyset) \epsilon_m'^{0.75}]^{\frac{1}{0.75}} \quad \text{Eq. 23}$$

Figure 4 shows a satisfactory match between the experimental data and the CRIM model for higher saturations than S_{rw} (less than 8% difference). The CRIM model fitted the data better for 0.5 mm GB. For lower water saturation, the ratios between the values estimated and the experimental values increased. The estimated values were overestimated by a factor of 1.14 for 0.5 mm GB and were underestimated by a factor of 0.92 for 0.1 mm GB. Persson and Berndtsson (2002) also obtained a better match to their data by introducing an extra degree of freedom in the mixing equations [Persson and Berndtsson (2002)].

Figure 5 illustrates permittivity variations as a function of different drainage-imbibition cycles. The drainage-imbibition experiments could be closely correlated with permittivities but after the end of the second cycle (end of imbibition 2), the correlation no longer held. This is probably because the DNAPL and water ganglions that remain trapped during the experiments influenced the dielectric response.

Some authors have shown that the CRIM model based on the relative permittivity of free water, air (or non-wetting fluid) and solids may not be suitable in all situations, especially in the transition phases (when S_w are between S_m and S_{rw}). These authors have proposed to consider a 4th constituent, the bound water. Indeed, the dielectric constant of bound water is very different from that of free water (due to the electrical bonds limiting the freedom of polarization of water molecules) [Dasberg and Hopmans (1992); Capparelli et al. (2018)]. An equation derived from the CRIM model incorporating

the bound water has been proposed [Dobson et al. (1985); Dirksen and Dasberg (1993)]. Capparelli et al. (2018) carried out monitoring of S_w variations with TDR probes in unsaturated soils. They showed, as in our experimental results, a difference between the values estimated with the CRIM model and the experimental values. The experimental results were compared to the classical CRIM model, to the four-phase dielectric mixing model (with bound water), and to the classical CRIM model with a variable exponent. The best results were obtained with the three-phase dielectric mixing model with a variable exponent (α_e) [Capparelli et al. (2018)].

4.4.2 Drainage-imbibition experiments with enhancements

Relative to the response considered as the blank test (water + GB), the mean measured permittivities were impacted by +1.4% (SDBS), +0.5% (Aerosol MA-80), -1.6% (Triton X-100), and -2.1% (Tween 80), respectively. It was observed, therefore, that the permittivity was slightly increased for nonionic surfactants and slightly decreased for anionic surfactants. But such deviations can be considered as negligible. Figure 5 shows the averages of S_m with permittivity averages corresponding to the experiments with and without surfactants (with 0.1 and 0.5 mm GB). Even though the standard deviations sometimes overlap, we can assess the recovery yields from the permittivity measurements: the average permittivities for 0.5 and 0.1 mm GB without surfactants were respectively 27.77 and 25.32 (for S_w at the end of imbibition = 0.89 and 0.87). In presence of surfactants, the average permittivities for 0.5 mm GB and 0.1 mm GB were respectively 29.07 and 30.81 (for S_w at the end of imbibition of 0.915 and 0.917). Figure 5 also shows the permittivity variations that correspond to the different remediation yields (for different surfactants): for the 0.5 mm GB, the final permittivities are, in increasing order: $\rho_{c,SDBS} > \rho_{c,Aerosol\ MA-80} > \rho_{c,Triton\ X-100} > \rho_{c,Tween\ 80}$. The averages overestimations for S_m with chemical enhancement were by a factor of 1.06 ± 0.02 (for 0.5 mm GB) and 1.09 ± 0.01 (for 0.1 mm GB).

Experiments were conducted to estimate the influence of temperature on measured permittivities for DNAPL and water with 0.5 mm GB (Supplementary materials, Figure A-6). The permittivity values were influenced by temperature variations. Increasing the temperature from 20 to 50 °C caused an average permittivity increase for DNAPL with GB of 19.0% (from 5.45 to 6.49). The variation in

$\epsilon_{\text{DNAPL+GB}}$ as a function of temperature, estimated from the slopes of the linear correlations, is + 0.034 $\text{m}^3\cdot\text{m}^{-3}\cdot^\circ\text{C}^{-1}$. Results from various authors show that the permittivity of light chlorinated solvents fall slightly as temperature rises. A linear relation has been established, with coefficients ranging between -0.003 and -0.051 $\text{m}^3\cdot\text{m}^{-3}\cdot^\circ\text{C}^{-1}$ [Morgan and Lowry (1930); Loon et al. (1967); Nath and Narain (1982); Nath (1995); Corradini et al. (1996); Ajo-Franklin et al. (2006)]. In our case, the DNAPL is essentially composed of a mixture of heavy chlorinated compounds, which may explain the difference in behavior.

Permittivities for water with GB decreased linearly as temperature rose ($0.023 \text{ m}^3\cdot\text{m}^{-3}\cdot^\circ\text{C}^{-1}$), with values that were consistent with the literature [Weast (1986); Persson and Berndtsson (1998); Logsdon (2000); Logsdon (2005); Seyfried and Grant (2007)]. The variations in $\epsilon_{\text{DNAPL+GB}}$ and $\epsilon_{\text{water+GB}}$ as a function of temperature were quantified and can be interpreted with the CRIM model. At the end of imbibition, the measured permittivities were 28.50 and 25.58 for 0.5 and 0.1 mm GB, respectively (vs estimated permittivities of 26.89 and 27.12, respectively). The experiments with surfactants and thermal enhancement showed that the reductions in residual saturations can be quantified with permittivity measurements.

4.5 *Monitoring of the drainage-imbibition experiments with electrical resistivity*

4.5.1 *Drainage-imbibition experiments without enhancement*

Calibration curves ($\rho_c = f(S_w)$) were plotted for 0.5 and 0.1 mm GB (Figure 6). Experiments with DNAPL alone in GB were performed to determine the experimental values corresponding to $S_w = 0\%$ and $S_w = 100\%$. Resistivity data were found to be more dispersed than permittivity data. Resistivity can be correlated to water saturation via a power relationship. The correlation factor, considering all the measured data, was satisfactory for 0.5 mm GB: $R^2 = 0.81$. The results were more dispersed with the 0.1 mm GB than with the 0.5 mm GB. Resistivity was related to S_w via a power law for 0.1 mm GB; with a correlation factor $R^2 = 0.74$. The results were different for 0.5 and 0.1 mm GB: the features of the trend curves are similar but are shifted. For homogeneous beads, and for identical S_w , the resistivity was higher for the 0.1 mm GB. This can be explained by the difference in DNAPL distributions in pores.

On the basis of Eq. 14 to Eq. 17 and by applying the least-squares method, we obtained the following equations (Eq. 24 and Eq. 25):

$$\text{for 0.5 mm GB} \quad \rho_{c,bulk} = \frac{1}{\sigma_{c,bulk}} = \frac{1}{\sigma_{c,DNAPL}[\emptyset(1 - S_w)]^{1.752} + \sigma_{c,water}[\emptyset(S_w)]^{1.9}} \quad \text{Eq. 24}$$

$$\text{for 0.1 mm GB} \quad \rho_{c,bulk} = \frac{1}{\sigma_{c,bulk}} = \frac{1}{\sigma_{c,DNAPL}[\emptyset(1 - S_w)]^{1.678} + \sigma_{c,water}[\emptyset(S_w)]^{2.4}} \quad \text{Eq. 25}$$

where $\rho_{c,bulk}$ ($\Omega.m$) is the real effective electrical resistivity of the bulk, and $\rho_{c,DNAPL}$ ($\Omega.m$) is the real effective electrical resistivity of DNAPL.

The conductivity values measured for DNAPL and water used to fit the model were: $\sigma_{c,DNAPL} = 3.1807 \times 10^{-8} \text{ S.m}^{-1}$ and $\sigma_{c,water} = 0.04 \text{ S.m}^{-1}$.

A correction factor was used in order to better estimate the experimental data. The correction factors were as follows (Eq. 26 and Eq. 27):

$$\text{for 0.5 mm GB} \quad \frac{\rho_{c,measured}}{\rho_{c,estimated}} = 1.34S_w^{0.40} \quad \text{Eq. 26}$$

$$\text{for 0.1 mm GB} \quad \frac{\rho_{c,measured}}{\rho_{c,estimated}} = 2.00S_w - 0.011 \quad \text{Eq. 27}$$

Figure 7 illustrates the resistivity variations (measured and estimated) as a function of different drainage-imbibition cycles. The model overestimated the values at the start and under-estimated the values in most other cases. For the 0.5 mm GB, the average ratios of measured resistivity/estimated resistivity were 0.64 for $S_w = 100\%$ (start), 3.14 at the end of the drainage 1 and 0.99 at the end of the imbibition 1. For the 0.1 mm GB, these ratios were 0.72 at the start, 12.84 at the end of drainage 1 and 5.22 at the end of imbibition 1. As for permittivity, it reminded that the resistivity measurement is very local while the water saturation measurement is more global. Uncertainty is higher for large resistivity values because the measured potential difference is smaller.

These resistivity overestimations have been discussed by previous authors. Byun et al. (2019) showed that in a porous medium with water and gas, a cementation factor that considers the saturation condition improves resistivity modeling with Archie's law [Byun et al. (2019)]. Other authors also demonstrated that at pore scale, the resistivity indices did not generally obey Archie's law in the non-homogeneous zones (for example in a transition zone with values close to S_{rn} and S_{rw}). It is therefore

possible to over or underestimate resistivity depending on the thickness of the water films surrounding sand grains or GB [Li et al. (2015)]. These water films play a role not only on the pore space connectivity but also on resistivity [Bernabé et al. (2011); Li et al. (2015); Bernabé et al. (2016)]. Finally, previous authors have shown that many other parameters could be taken into account at different scales in electrical conductivity models in porous media: tortuosity, pore size distribution, pore-conductance distributions, interconnectivity, and universal power laws of percolation [Glover (2010); Cai et al. (2017); Ghanbarian and Sahimi (2017)].

4.5.2 Drainage-imbibition experiments with enhancements

The experimental results show that adding surfactants generated a greater impact on resistivity measurements than on permittivity measurements. For mean reference values of $132 \pm 17 \text{ } \Omega \cdot \text{m}$ (for water+GB), the mean values measured for nonionic surfactants were respectively $123 \pm 21 \text{ } \Omega \cdot \text{m}$ for SDBS and $30 \pm 9 \text{ } \Omega \cdot \text{m}$ for Aerosol MA-80 (*i.e.* a factor of 0.92 and 0.22). Conversely, adding anionic surfactants increased resistivity: $216 \pm 25 \text{ } \Omega \cdot \text{m}$ for Triton X-100 and $140 \pm 19 \text{ } \Omega \cdot \text{m}$ for Tween 80, *i.e.* respective increased of a factor of 1.62 and 1.05. However, these relative variations were small in comparison with the resistivity of the DNAPL and GB ($\rho_{c, \text{DNAPL}} = 2730063$ and $3413632 \text{ } \Omega \cdot \text{m}$ respectively for 0.5 and 0.1 mm GB) and considering the high sensitivity and low accuracy of these geophysical measurements at very low frequencies. Such variations can therefore be considered as negligible.

Figure 7 shows the averages of S_m with averaged resistivity corresponding to the experiments with and without surfactants (with the 0.1 and 0.5 mm GB). As shown, the residual saturations can be approached by the resistivity measurements. The correlations were less clear with resistivities than with permittivities. Decreasing trends for S_m are seen in the resistivity measurements. For the 0.5 mm GB, for example, the resistivities at the end of the imbibition with and without surfactant were respectively 150 and 84 $\Omega \cdot \text{m}$ (for S_m of 0.109 and 0.085). For 0.1 mm GB, the differences were

greater: 1061 $\Omega\cdot\text{m}$ (without surfactants with $S_{rn} = 0.131$) vs. 79 $\Omega\cdot\text{m}$ (with surfactant with $S_{rn} = 0.082$).

The reported standard deviations were quite high for imbibition without surfactant.

Experiments were conducted to estimate the influence of temperature on measured resistivities of water and DNAPL. The resistivity of DNAPL at 50 °C only represented 25.3% of the resistivity at 20 °C (5.88×10^5 vs. 2.32×10^6 $\Omega\cdot\text{m}$, respectively at 50 and 20 °C). The resistivity values of water were very low compared to those of DNAPL. Resistivity values were 31 $\Omega\cdot\text{m}$ at 20 °C, and 17 $\Omega\cdot\text{m}$ at 20 °C (*i.e.* 57% of the value at 20 °C). The decrease in water resistivity as a function of temperature increase was due to the increase in ionic mobility [Dakhnov (1962); Hayashi (2004); Light et al. (2005); Grellier et al. (2008)]. Dakhnov (1962) established the following relationship (for ionic fluids) (Eq. 28):

$$\rho_{c,w} = \frac{\rho_{c,w_0}}{1 + \alpha_{c,w}(T - T_0)} \quad \text{Eq. 28}$$

where $\rho_{c,w}$ ($\Omega\cdot\text{m}$) is the electrical resistivity of the fluid at temperature T (°C), ρ_{c,w_0} ($\Omega\cdot\text{m}$) is the resistivity of the fluid at temperature T_0 , $\alpha_{c,w}$ is the temperature coefficient of resistivity ($\alpha_{c,w} \approx 0.023$ °C⁻¹ for $T_0 = 23$ °C, and 0.025 °C⁻¹ for $T_0 = 0$ °C)

The slopes of the linear relationships in the graphs $(\rho_{c,0}/\rho_c) - 1 = f(T - T_0)$ determine the values of the coefficient α_c for the Dakhnov equation (Supplementary materials, Figure A-7).

With respect to the drainage-imbibition experiments with thermal enhancement, the residual saturations were almost identical with and without thermal enhancement. $\rho_{c,\text{measured}}$ values measured at the end of imbibition without enhancement were lower than during the thermal enhancement experiments: 63 $\Omega\cdot\text{m}$ (vs. 150 $\Omega\cdot\text{m}$ without thermal enhancement) for the 0.5 mm GB and 87 $\Omega\cdot\text{m}$ (vs. 1061 $\Omega\cdot\text{m}$ without thermal enhancement) for the 0.1 mm GB. At the end of imbibition 1, the $\rho_{c,\text{estimated}}$ were respectively 84 $\Omega\cdot\text{m}$ for 0.5 mm GB (vs. 152 $\Omega\cdot\text{m}$ at 20 °C) and 112 $\Omega\cdot\text{m}$ for 0.1 mm GB (vs. 203 $\Omega\cdot\text{m}$ at 20 °C). In theory, the $\rho_{c,\text{measured}}$ therefore decreased by 45% in both cases.

4.6 Monitoring of the drainage-imbibition experiments with image interpretation

Figure 8 shows an experiment with 0.5 mm GB. The pollutant was dark brown-black. Note that during the drainage, the migration front was relatively sharp (which corresponded to curve $P_c = f(S_w)$

for drainage 1 with a relatively horizontal plateau – Figure 2). At the end of drainage, the cell was filled with DNAPL but filling was not totally homogeneous (due to wall effects). During the imbibition, the migration front was more diffuse, which was expected considering the $P_c = f(S_w)$ curve for imbibition (which shows a less horizontal pseudo-plateau).

Figure A-8 (Supplementary materials) describes the variations of mean grey values for an increasing AOI that begins at the centre of the picture, as detailed below. Increasing the AOI length increased the number of contained pixels. This curve was calculated with a Fiji macro which served to associate a mean grey value with the S_w value, as the grey value was sensitive to the number of pixels inside the selected AOI. However, for AOI between 500 pixels and 1000 pixels, the computed mean grey values were stable, implying that between 2.5×10^5 and 1.0×10^6 pixels were necessary. This interval length was chosen to compute all mean grey values for the calibration curve shown in Figure 9.

The calibration curve could only be made for the points corresponding to $S_w = 1, 0, S_m$ and S_{rw} . The curve shows a good correlation ($R^2 = 0.98$). The size of the GB did not influence the calibration curve. Also, no differences were observed in Optical Density (OD) measured for $S_w = 1$ and $S_w = 0$. S_m (with respective means of 0.24 and 0.32 for 0.5 and 0.1 mm GB) and S_{rw} values (with respective means of 0.89 and 0.84 for 0.5 and 0.1 mm GB) were very close to those measured with the circular 1D cells (less than 3% difference). Variations in S_m and S_{rw} follow a linear regression which is in agreement with the literature [Schincariol et al. (1993); Flores et al. (2011); Watson et al. (2019)]. The optical density experiments show that residual saturations can be estimated accurately ($R^2 = 0.98$) even with surfactants and thermal enhancement. The OD was found to vary linearly as a function of S_w .

5. Conclusions

Drainage-imbibition experiments were performed in 1D cells with the aim of comparing the efficiency of thermal and chemical enhancements on the DNAPL recovery performance. Four different surfactants (SDBS, Aerosol MA-80, Triton X-100 and Tween 80) were tested at concentrations well below their respective CMC (in order to avoid DNAPL dissolution). The best remediation enhancement yield was obtained with SDBS: 27.6% for the 0.5 mm GB and 46.3% for 0.1

mm GB. Experiments with thermal enhancement were also conducted at 50 °C (in order to avoid DNAPL volatilization). However, no significant improvement in the remediation enhancement yield was observed.

The drainage-imbibition experiments were monitored by electrical resistivity, permittivity and optical density. The goal was to confirm whether the residual saturations could be estimated indirectly. Regarding the permittivity measurements, the estimation of residual saturations fits well with the CRIM model in most cases. The experiments with surfactants and thermal enhancement showed that the variations in residual saturations could also be quantified with permittivity measurements. An adapted version of Archie's Law was used to model resistivity variations as a function of residual saturation variations. The estimated electrical resistivity data showed less correlation with the measurements than the permittivity data. Also, it was not possible to accurately quantify water saturations with electrical resistivity monitoring. However, the accuracy is sufficient (especially for high values of water saturation) for highlighting differences between the treatment technologies. The optical density experiments showed that residual saturations can be accurately estimated even with surfactant and thermal enhancement.

Future work will focus on multiphase flow modeling and pumping experiments in a 2 D tank at the laboratory scale, for the purpose of process up-scaling. The permittivity and resistivity measurements as well as the optical densities during the pumping test over time shall provide information regarding how chemical enhancement affects DNAPL recovery yields (at different flow rates). At field scale, the combined monitoring of electrical resistivities (which provide a global picture) and permittivities (which provide accurate but spatially limited information) is expected to improve the reliability of residual saturation data.

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1019 Figure 1: Schematic of 1D cell

1020 Figure 2: Pressure-water saturation curves for 0.5 and 0.1 mm GB: a) drainage-imbibition without

1021 enhancement and b) imbibition without surfactant and with SDBS

1022 Figure 3: Comparison of a) Capillary number (N_{ca}), b) Bond number (N_B), and c) Total trapping

1023 number (N_T) for 0.5 and 0.1 mm GB

1024 Figure 4: Fitting the experimental permittivity values as function of water saturation with the CRIM

1025 model: a) 0.5 mm GB and b) 0.1 mm GB

1026 Figure 5: Change of water saturation and permittivity (measured and estimated) as a function of

1027 drainage-imbibition cycle for 0.5 and 0.1 mm GB in 1D cells (with and without enhancements)

1028 Figure 6: Fitting the experimental resistivity values as a function of water saturation with Archie's

1029 law: a) 0.5 mm GB and b) 0.1 mm GB

1030 Figure 7: Change of water saturation and resistivity (measured and estimated) as a function of

1031 drainage-imbibition cycle for 0.5 and 0.1 mm GB in 1D cells (with and without enhancements)

1032 Figure 8: Drainage-imbibition experiments in the Hele-Shaw cell (example with 0.5 mm GB)

1033 Figure 9: Fitting the experimental optical density values as a function of water saturation (without

1034 enhancement, with chemical and thermal enhancements)

1035 Table 1: Results of drainage-imbibition experiments for 0.5 and 0.1 mm GB

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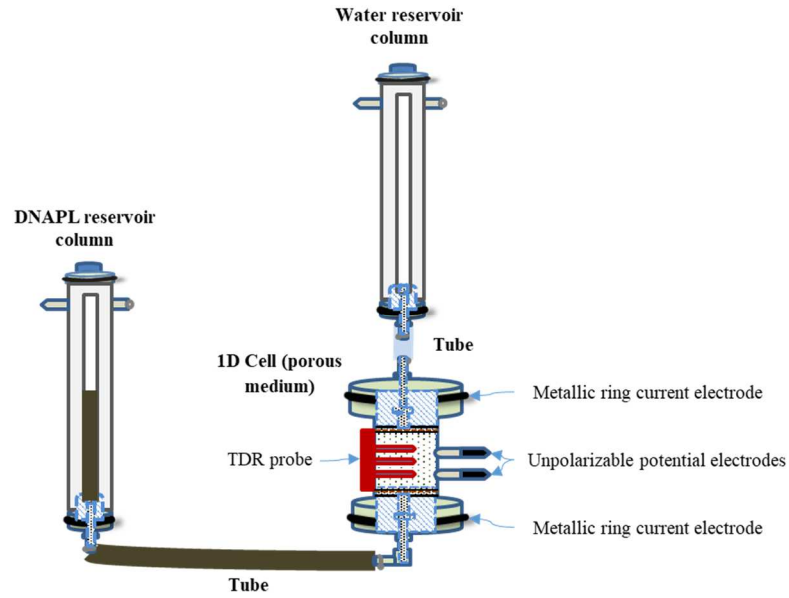
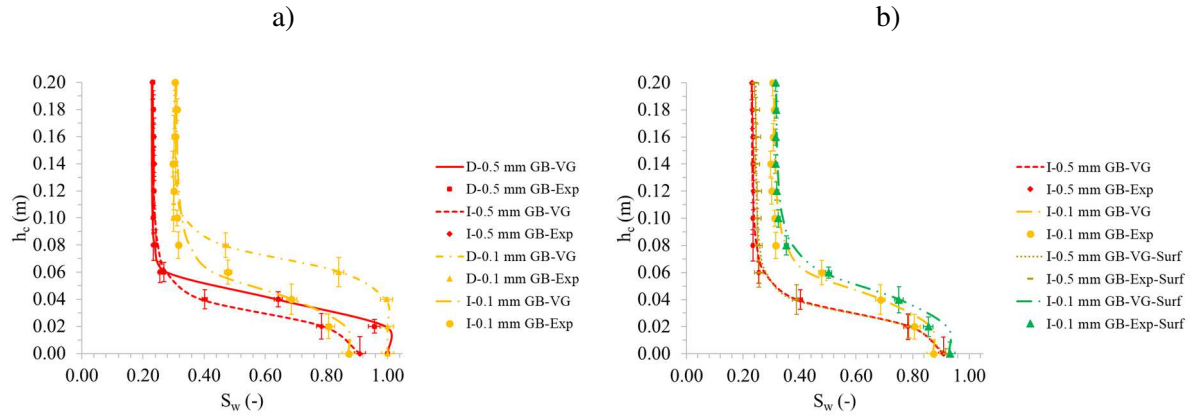


Figure 1: Schematic of 1D cell



(D: drainage, I: imbibition, VG: Van Genuchten Mualem fitting values; Exp : raw values; Surf: addition of SDBS)

Figure 2: Pressure-water saturation curves for 0.5 and 0.1 mm GB: a) drainage-imbibition without enhancement and b) imbibition without surfactant and with SDBS

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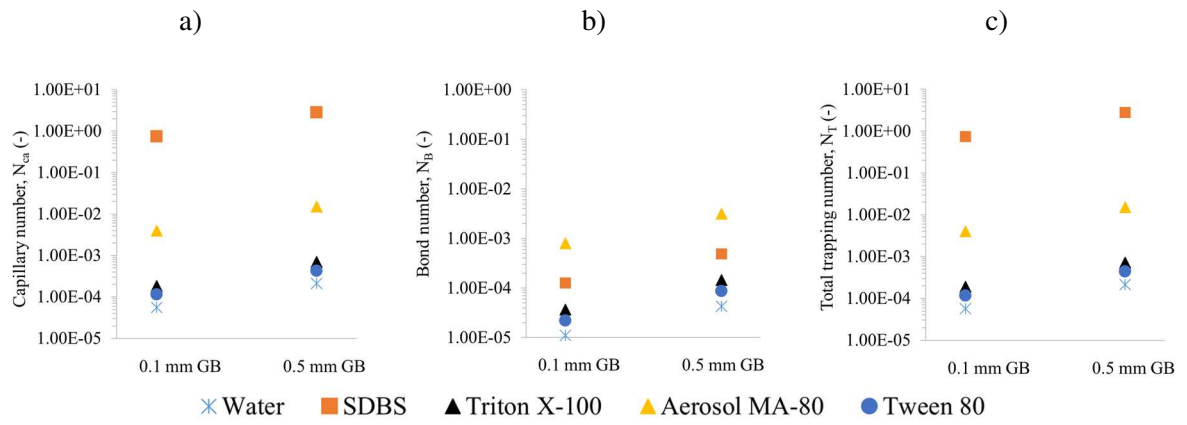


Figure 3: Comparison of a) Capillary number (N_{ca}), b) Bond number (N_B), and c) Total trapping number (N_T) for 0.5 and 0.1 mm GB

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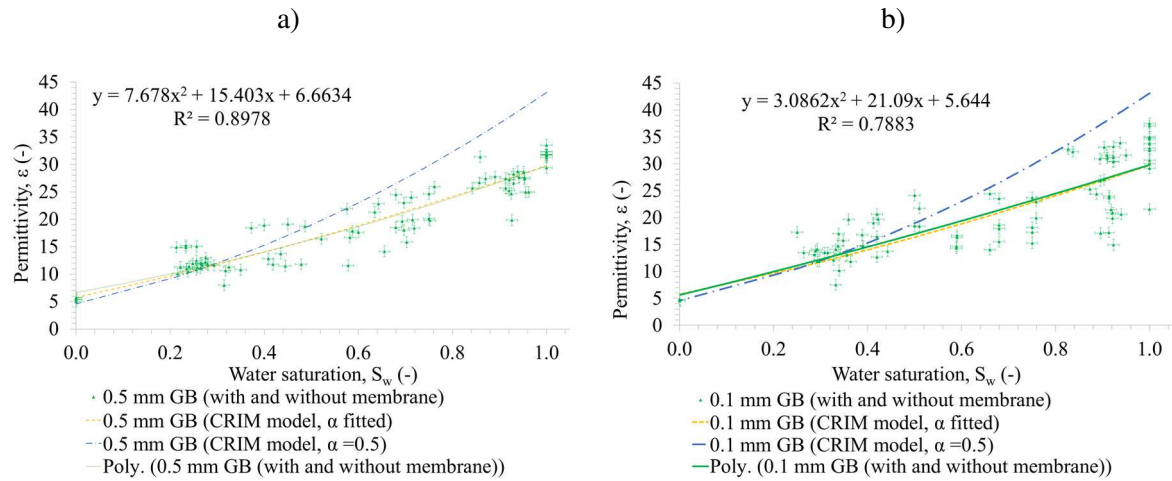


Figure 4: Fitting the experimental permittivity values as function of water saturation with the CRIM model: a) 0.5 mm GB and b) 0.1 mm GB

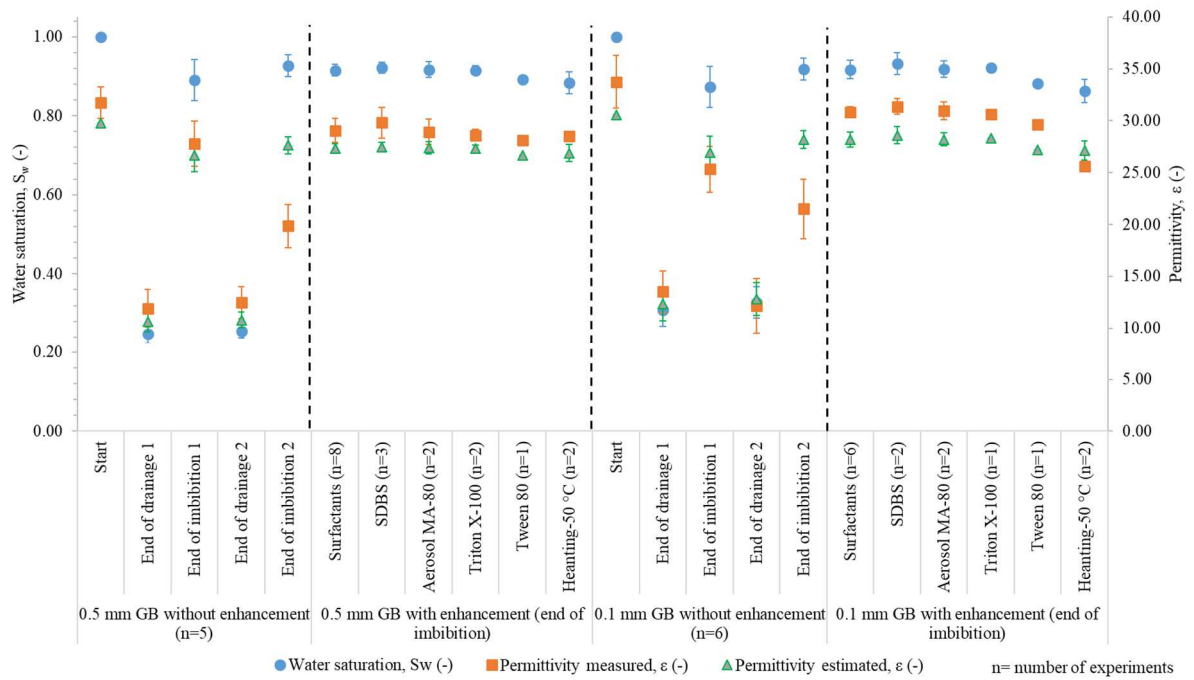


Figure 5: Change of water saturation and permittivity (measured and estimated) as a function of drainage-imbibition cycle for 0.5 and 0.1 mm GB in 1D cells (with and without enhancements)

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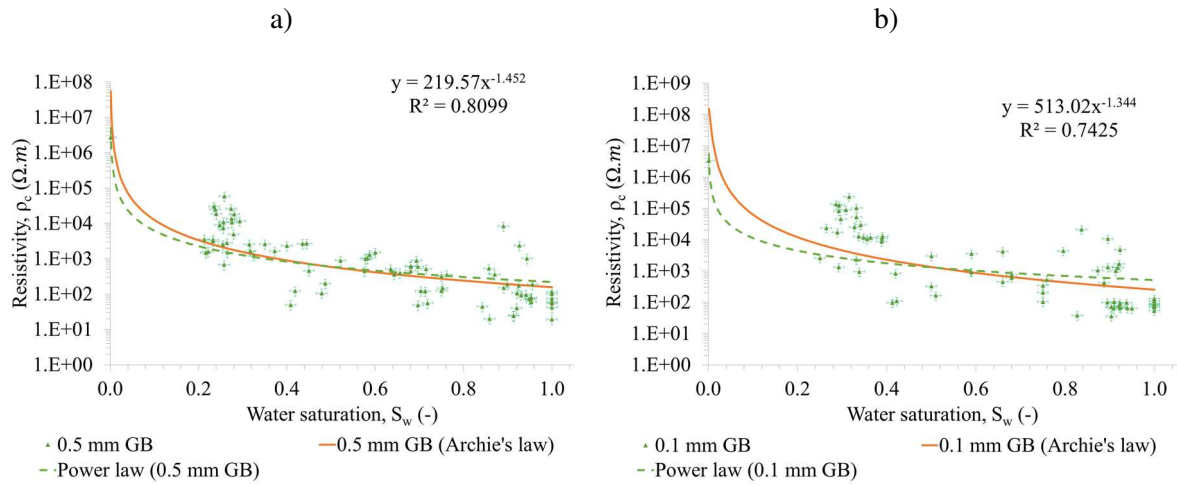
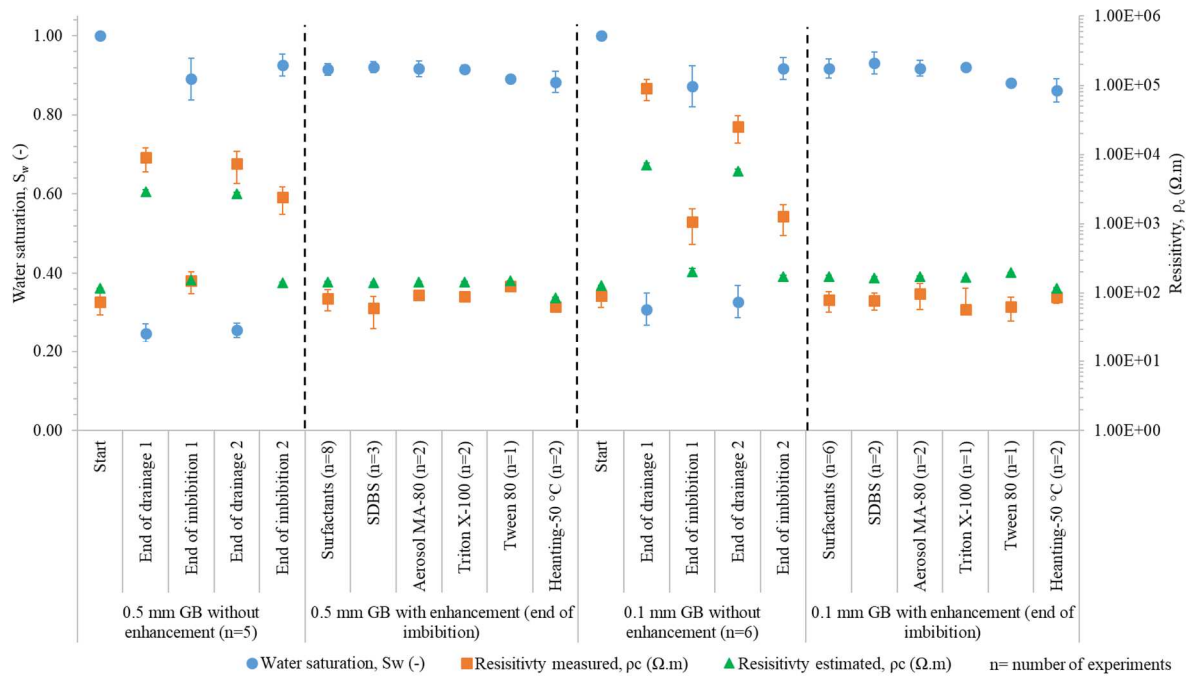


Figure 6: Fitting the experimental resistivity values as a function of water saturation with Archie's law: a) 0.5 mm GB and b) 0.1 mm GB



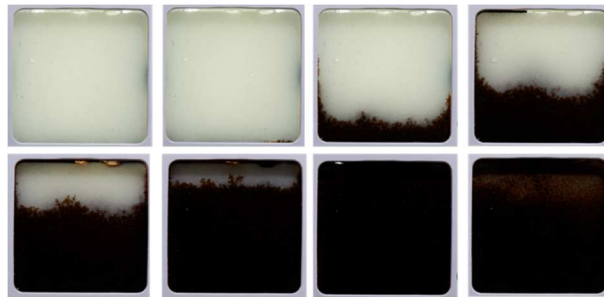
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Figure 7: Change of water saturation and resistivity (measured and estimated) as a function of drainage-imbibition cycle for 0.5 and 0.1 mm GB in 1D cells (with and without enhancements)

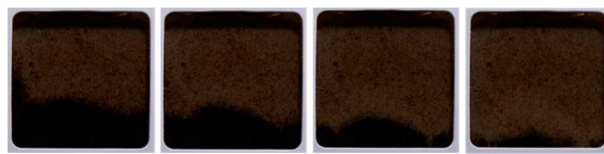
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Drainage 1



Imbibition 1



Drainage 2

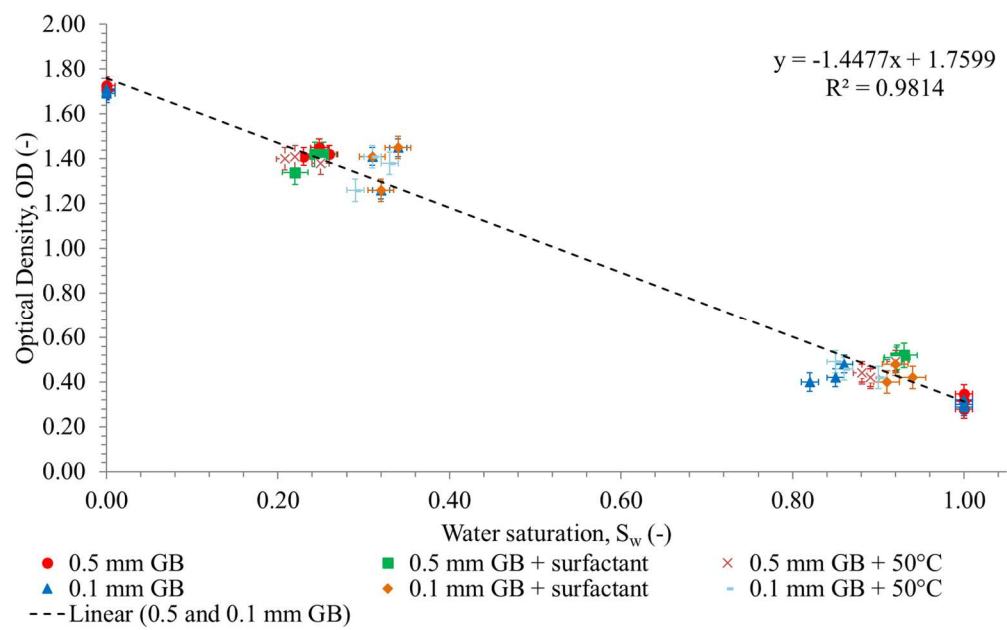


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Figure 8: Drainage-imbibition experiments in the Hele-Shaw cell (example with 0.5 mm GB)

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Figure 9: Fitting the experimental optical density values as a function of water saturation (without enhancement, with chemical and thermal enhancements)

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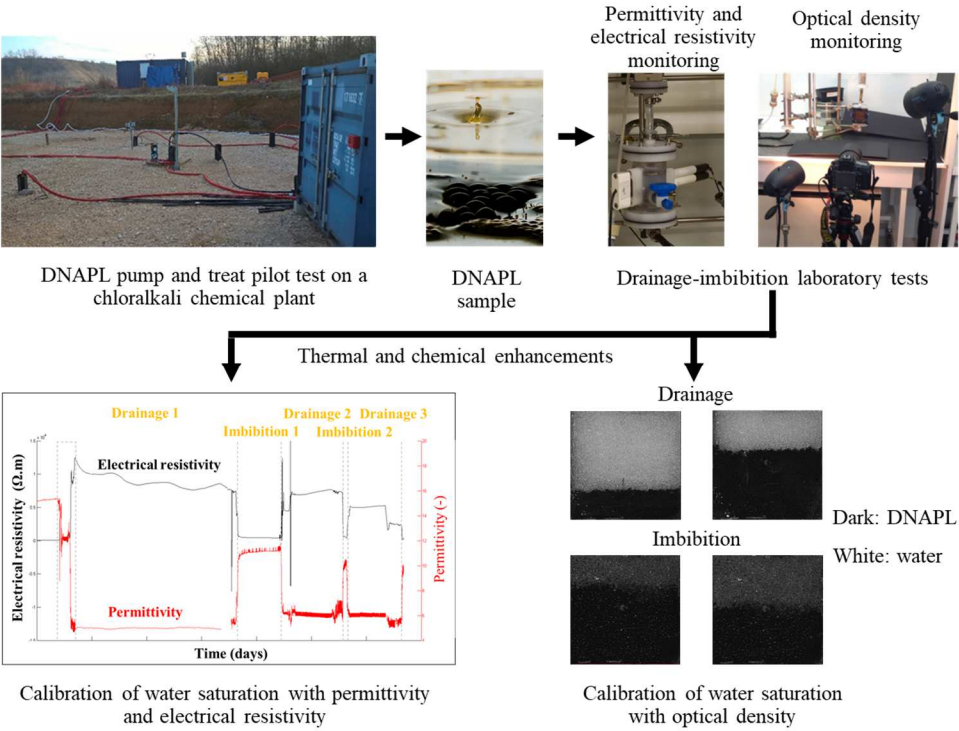
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Table 1: Results of drainage-imbibition experiments for 0.5 and 0.1 mm GB

Parameters	0.5 mm GB		0.1 mm GB	
	Drainage D	Imbibition I	Drainage D	Imbibition I
α (m ⁻¹)	26.06	38.36	14.72	23.29
n (-)	15.35	5.15	9.49	16.98
SSE	0.0038	0.0025	0.0056	0.0214
S _{rn} (-)	0.000	0.109	0.000	0.127
S _{rw} (-)	0.248	0.248	0.309	0.309

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1 **Graphical abstract**



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