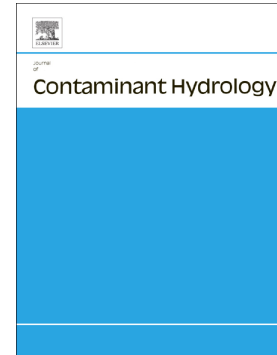


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Impact of heterogeneous properties of soil and LNAPL on surfactant-enhanced capillary desaturation

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## ABSTRACT

This paper investigates low-concentration ( $<1$  wt%) surfactant flushing when used as a follow-up technology for multiphase vacuum extraction on heterogeneous sites. Challenges posed by soil permeability, pore-size distribution, mineralogy, light non-aqueous phase liquid (LNAPL) weathering and groundwater hardness were quantified through batch and soil column tests. Compatibility issues between the mixed mineralogy soils, hard groundwater, mixed LNAPL and usual anionic surfactants were observed. The selected solution was a Winsor type I system promoting an interfacial tension of  $0.06$  mN/m between the site LNAPL and the amphoteric surfactant CAS in aqueous solution at pH 12. Surfactant losses to adsorption and pore media plugging were observed in the fine soil fraction. The capillary desaturation curves (CDC) obtained with the column tests suggested mixed-wettability behavior. The soil permeability strongly influenced LNAPL recovery, as expressed by the relationship obtained between capillary numbers ( $N_{Ca}$ ) and hydraulic gradients. In this case, the critical  $N_{Ca}$ , marking the onset of capillary desaturation, could only be obtained with realistic hydraulic gradients in the coarse soil fraction. At those gradients, potential LNAPL recovery was 30 % at the most. Unlike previously published CDCs, the relationship between  $N_{Ca}$  (log-scale) and LNAPL recovery was not linear but dependant on residual LNAPL saturation.

KEYWORDS : LNAPL, surfactant, in situ recovery, capillary number, soil properties

## 1 INTRODUCTION

Multiphase vacuum extraction (MVE) is an efficient *in situ* remediation technology at light non-aqueous phase liquids (LNAPL) impacted sites <sup>1</sup>. In the water-saturated zone, the MVE recovery efficiency reaches a limit when the LNAPL saturation becomes close to the residual oil saturation ( $S_{OR}$ ), and discontinuous LNAPL droplets are trapped in the soil pores by capillary forces <sup>2</sup>. Dewatering of the source zone coupled with LNAPL volatilization may increase LNAPL recovery, but this process is ineffective in the presence of heavier hydrocarbon products such as diesel <sup>3</sup>. In such cases, the injection of aqueous-based chemical reagents in the saturated part of the source zone are potential MVE follow-up technology <sup>4-5</sup>. In particular, low-concentration (<1 % on a weight basis (wt%)) surfactant flushing could offer advantages over high concentration solutions used for micellar solubilization (3 to 8 wt%) <sup>6</sup>, such as: cost savings on surfactants and other washing solution chemicals; the elimination of the need for reuse and recycling of surfactants; and simpler above-ground process effluent treatment. The technology could therefore be coupled with an existing MVE system and its process effluent treatment system.

The theory behind surfactant flushing applied to aquifer remediation has been studied at the laboratory scale <sup>7-11</sup> and also at the field scale <sup>6, 12-14</sup>. Dwarakanath *et al.* <sup>7</sup> produced CDCs in the laboratory for two non-aqueous phase liquids (NAPLs) with alluvial aquifer material. These CDCs showed the practical implications of mixed-wet to oil-wet characteristics on NAPL recovery. They highlighted that NAPLs displacement from soils by water is more difficult for mixed-wet or oil-wet soils than for water-wet or weakly water-wet soils. Martel *et al.* <sup>8</sup> used a large sand column to characterize the main NAPL recovery mechanisms (mobilization and solubilization) of organic contaminants recovery by a complex chemical solution. Pennell *et al.* <sup>9</sup>

performed column experiments to investigate the onset and extent of tetrachloroethylene (PCE) mobilization during surfactant flushing. Their results are used later in this paper for comparison purposes. In Sabatini *et al.*<sup>10</sup>, laboratory and field experiments are used to illustrate key technical and economic issues for surfactant flushing. They used a site-specific capillary curve to optimize the solubilization of denser-than-water NAPLs while avoiding mobilization and vertical migration. The laboratory research of Shiau *et al.*<sup>11</sup> identified surfactant systems capable of solubilizing and promoting microemulsions of chlorinated solvents.

In the field, Childs *et al.*<sup>12</sup> reported on a surfactant flushing for PCE removal at the Dover (DE) experimental site. The surfactant formulation achieved PCE micellar solubilization while avoiding downward migration. After 10 pore volumes of flushing, the overall PCE removal was 68%. Martel *et al.*<sup>13</sup> also demonstrated in the field the use of a surfactant solution to recover a dense NAPL in a five-spot injection/extraction pattern, while improving the sweep efficiency through the use of polymers. The relative importance of the recovery mechanisms, mobilization and solubilization was variable in the test cell. Finally, McCray *et al.*<sup>14</sup> summarizes remediation studies which were conducted Hill (UT) and Dover (DE) experimental sites, included technologies that mobilize, solubilize, and volatilize NAPL.

However, field applications of low-concentration surfactant flushing for LNAPL recovery are not widespread (Table ). For the study reported in this paper, based on the size of the LNAPL source zone covering more than 8000 m<sup>2</sup>, low-concentration surfactant flushing using concentrations below 1%-wt is the only economical alternative of surfactant flushing applicable to such a site. Low-surfactant concentrations do not favor micellar LNAPL dissolution or emulsion in the aqueous phase, and existing MVE effluent treatment systems such as air-liquid and oil-water separators, volatile organic compounds (VOC) catalytic oxidizer and granular

activated carbon water treatment units can be used without modification in combination with this type of surfactant flushing. Shiau *et al.*<sup>6</sup> demonstrated through 3 field tests the potential of this technology for residual LNAPL mass removal (Table 1).

**Table 1.** Documented case studies of low-concentration surfactant flushing.

Project/Site	NAPL	Surfactant mixture	Electrolyte	$\sigma_{ow}$	Recovery (PV)	Reference
Field test: Golden, OK	Gasoline fuel (LNAPL)	0.75% AOT + 0.19% Calfax 16L-35	1.2% NaCl	< 0.005 mN/m	65 – 99% (1 PV)	<sup>6</sup>
Field test: Bixby, OK	Unspecified LNAPL	0.75% AOT + 0.19% Calfax 16L-35	1.2% NaCl	< 0.005 mN/m	60 - 90% (1.4 PV)	<sup>6</sup>
Field test: Oklahoma City, OK	Gasoline and diesel fuels	0.75% AOT + 0.19% Calfax 16L-35	1.2% NaCl (gasoline pit) 1.4 – 1.6% NaCl (diesel fuel pit)	< 0.005 mN/m	80 – 91%	<sup>6</sup>

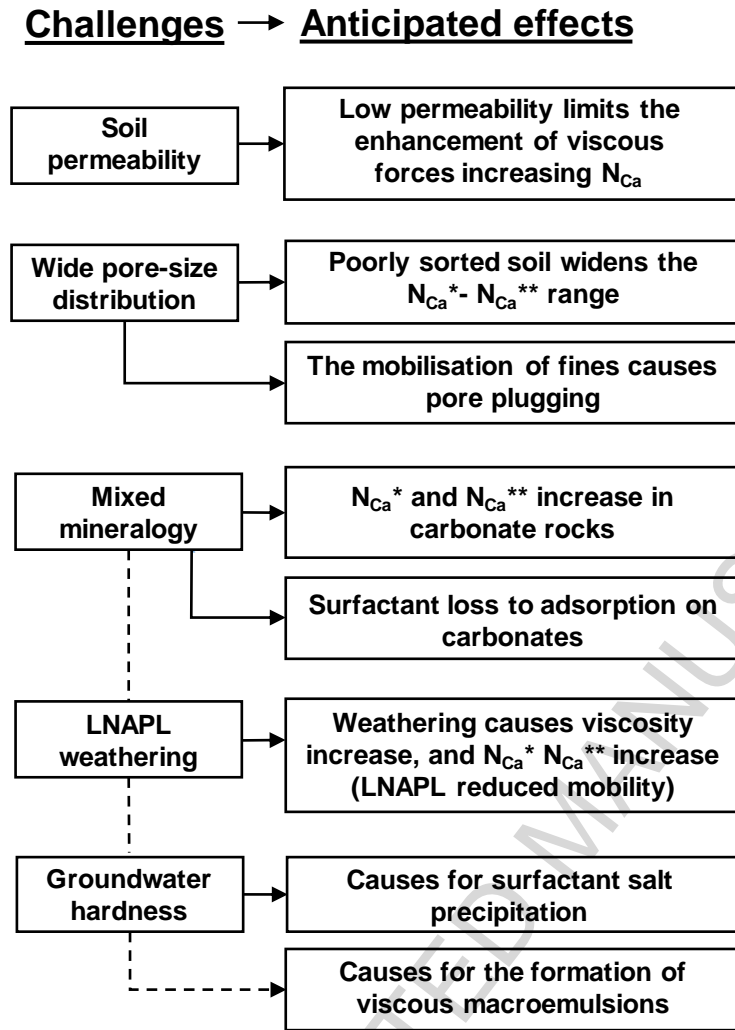
Low-concentration surfactant flushing acts to dislodge residual LNAPL droplets and ganglia trapped in a porous medium through a combination of two co-occurring mechanisms: (1) capillary force reduction, which is proportional to the LNAPL-water interfacial tension ( $\sigma_{ow}$ , units of N/m) reduction caused by the surfactant, and (2) viscous force increase, which is proportional to the surfactant solution viscosity ( $\mu_w$ , units of Pa·s) and specific flow rate ( $q_w$ , units of m/s). The relationship between  $N_{Ca}$  and the residual wetting or non-wetting phase saturations in soil is called the capillary desaturation curve (CDC)<sup>15</sup>. CDCs are presented on semi-log plots of percent residual saturation (normalized or not) versus capillary number. CDCs are characterized by a plateau at the initial residual saturation and low capillary numbers, a critical capillary number at which residual saturation starts to decrease ( $N_{Ca}^*$ ), and a total desaturation capillary number where residual saturation is zero ( $N_{Ca}^{**}$ ). CDCs were extensively

studied for enhanced oil recovery <sup>16</sup>. Among other factors, the impacts of pore size, pore size distribution, rock mineralogy and oil residual saturations on CDC shapes were studied. It was reported that carbonates having a mixed wettability relative to water and crude oil exhibited larger  $N_{Ca}^*$  ( $6 \times 10^{-5}$ ) values than water-wet sandstone ( $2 \times 10^{-5}$ ). Lake <sup>15</sup> mentions that the shape of the CDC depends on the width of the grain size distribution of the media, with wide distributions yielding a greater difference between  $N_{Ca}^*$  and  $N_{Ca}^{**}$  values.

Pennell *et al.* <sup>9</sup> demonstrated the use of the capillary number ( $N_{Ca}$ ) concept to quantify these forces acting during aquifer remediation. The relationship between  $N_{Ca}$  and the residual wetting or non-wetting phase saturations in soil is called the capillary desaturation curve (CDC) <sup>15</sup>. The  $N_{Ca}$  definition used in this study is from Dwarakanath *et al.* <sup>7</sup>:

$$N_{Ca} = \frac{q_w \mu_w}{\sigma_{ow}} \quad (1)$$

Previous studies on  $N_{Ca}$  and CDC <sup>10-11, 17</sup> highlighted the site-specific challenges of LNAPL capillary desaturation enhanced by surfactant flushing. Figure 1 summarizes these challenges when considering surfactant flushing for heterogeneous source-zone remediation. At heterogeneous sites such as the one considered for this research, such challenges are summarized in the left column of Figure 1. The right column of Figure 1 presents anticipated impacts of these challenges on LNAPL recovery by capillary desaturation, which is characterized by CDCs,  $N_{Ca}^*$  and  $N_{Ca}^{**}$  values.



**Figure 1.** Site-specific challenges associated with heterogeneous materials and anticipated effects on site-specific CDCs.

Another challenge related to the use of in-situ soil flushing is achieving contact between the surfactant solution and the LNAPL within a heterogeneous source zone. The use of shear-thinning polymers to promote horizontal flow uniformity in heterogeneous environments has been tested at various scales<sup>13, 18-21</sup>. For this project, the impact of heterogeneous stratigraphy on micellar flow uniformity was evaluated with a field tracer test published in a companion paper<sup>22</sup>.

The objective of this research is to assess the performance of a low-concentration surfactant solution in combination with an existing MVE system for the in-situ remediation in realistic



heterogeneous environments. In order to meet this objective, the challenges posed by soil permeability, pore-size distribution, mineralogy LNAPL weathering and groundwater hardness were quantified through batch and soil column tests. Laboratory batch experiments allowed to select an optimal surfactant solution considering soil-LNAPL-surfactant observed and measured interactions. Soil column experiments were conducted to construct site-specific capillary desaturation curves (CDCs) for grain size fractions representative of the stratigraphic layers encountered at the heterogeneous experimental site, using the surfactant solution.

The novelty of this experimental work is the quantification of the impacts of soil composition and heterogeneity on surfactant formulations, achievable capillary number ( $N_{Ca}$ ) and CDCs. The methodology presented in this paper is simple to implement and allows to measure the performance of low-concentration surfactant flooding under site-specific conditions, provided that the experiments are conducted with soil and LNAPL from that experimental site.

## 2 EXPERIMENTAL METHODS

A composite soil sample obtained from borehole drill cuttings was used for column experiments. Soil sieving was done on the composite sample in order to study the impact of 3 grain-size distributions on LNAPL residual saturations and recovery. Two columns were prepared for each grain size distribution so that each was tested in duplicates.

Grain size analysis was performed in-house with dry sieving down to 0.125 mm. Fractions finer than 0.125 mm were characterized with a Analysette 22 laser particle sizer (Fitsch, Germany) performed on humid samples. The grain size distribution was assessed by calculating the uniformity coefficient ( $C_U$ ) for each sample, which is dependent on the grain sizes corresponding to 90%-wt retained ( $d_{10}$ ) and 40%-wt retained ( $d_{60}$ ), as presented in Payne *et al.*<sup>23</sup>.

Mineralogy analysis was determined on the finer than 0.125 mm fraction of selected representative samples with X-ray diffraction mineralogy analysis using the semi-quantitative Rietveld method at the UQAT laboratories located in Rouyn-Noranda (Qc). Organic carbon content was measured in 3 composite soil samples by Maxxam Laboratories using a gravimetric method.

Methods presented by Martel and G  linas <sup>24</sup> were used for column packing and water saturation. Fifteen cm-long stainless steel columns with an inner diameter of 3.6 cm were used. Replicate groundwater was used by adding 0.6 mg/L of CaCl<sub>2</sub> to pure water, which corresponds to the water hardness measured on field groundwater samples. Hydraulic conductivity tests using a constant head apparatus were carried out with each water saturated column prior to contamination. Three different hydraulic gradients were applied for each test to correct for equipment-induced head-loss. To ensure that no preferential flow path existed inside each column, conservative tracer tests were done using a potassium bromide (KBr) solution at a concentration of 250 mg/L. Bromide measurements on 15 mL effluent samples were conducted with an ion-selective Orion electrode.

Soil columns were contaminated from the top down using 1 pore volume (PV) of LNAPL obtained at the experimental site and a high flow velocity was induced by a peristaltic pump, using the same methodology as Dwarakanath *et al.* <sup>17</sup>. LNAPL density was measured with a Anton Paar density meter (precision of 0.001 g/cm<sup>3</sup>), and the viscosity was measured by a Cannon Fenske Opaque viscometer, model 25 Y661. Excess LNAPL in the column was pushed out of the soil by injecting water at the same velocity as the LNAPL. Residual LNAPL saturations inside each column were determined based on a mass balance on injected and extracted LNAPL. Hydraulic conductivity tests were then carried out using the same constant

head apparatus as previously used on the uncontaminated columns in order to measure the impact of the residual LNAPL saturation on the aqueous phase relative permeability.

A list of 11 environmentally-friendly surfactant candidates was defined based on a literature survey (Table 2). The following surfactant selection criteria were then sequentially applied to all listed surfactants: (1) commercial availability; (2) LNAPL-surfactant solution compatibility; (3) LNAPL-surfactant solution-soil compatibility; and (4)  $\sigma_{ow}$  measurements.

**Table 2.** Surfactant candidates

Commercial Name	Chemical Name	Reference	Charge
Aerosol AY (AAY)	Sodium diamyl sulfosuccinate	17	Anionic
Aerosol MA (AMA)	Sodium dihexyl sulfosuccinate + isopropyl alcohol	25	Anionic
Aerosol OT (AOT)	Sodium dioctyl sulfosuccinate	6	Anionic
Calfax (CFX)	C16 (Linear) Sodium Diphenyl Oxide Disulfonate	6	Anionic
Chembetaine CAS (CAS)	Cocamidopropyl hydroxysultaine	26	Amphoteric
			Cationic (pH 1)
			Anionic (pH 12)
Dowfax 8390 (DOW)	Mono- and di-hexadecyl diphenyloxide di-sulfonate	10	Anionic
HostapurSAS (SAS)	Sodium C14-17 sec-Alkyl sulphonate	13	Anionic
Polysorbate 80 (P-80)	Polyoxyethylene (20) sorbitan monooleate ou ethoxylated sorbitan fatty ester	20	Nonionic
SDBS	Sodium dodecylbenzenesulfonate	27	Anionic
SDS	Sodium dodecylsulfate	28	Anionic
Tomadol 900 (T900)	Ethoxylated alcohol (nonylphenol substitute)	Internal	Nonionic

Commercial availability was checked with local distributors. LNAPL-surfactants compatibility was then checked by mixing 5 mL of washing solution at 1%-wt with 5 mL of LNAPL obtained at the site. Following a 20-min centrifugation, the resulting phase viscosity was visually assessed. LNAPL-surfactant solution-soil compatibility was assessed through a qualitative bottle test using the methodology proposed by Powers *et al.* <sup>29</sup>. All LNAPL-aqueous phase interfacial

tension measurements ( $\sigma_{ow}$ ) were carried out using the pendant drop technique with a First Ten Angstrom dynamic FTA analyzer<sup>30</sup>. Adjustments of the amphoteric surfactant solution pH was performed with laboratory grade NaOH.

Surfactant flushing of soil columns was performed using a constant head injection apparatus. The apparatus allowed the sequential application of three fixed-gradient steps for surfactant flushing. The impacts of surfactant-LNAPL-soil-groundwater interactions on the effective aqueous phase permeability were measured during the first fixed-gradient step. During this first step, the surfactant solution was injected in the column until pH and air-water surface tension ( $\sigma_{aw}$ ) values at the column outlet reached those of the injected solution, and until free-phase LNAPL was no longer produced. The flow rate was measured by weighing the effluent at every 20-mL intervals. The pH was measured in each 20-ml effluent sample using pH color strips. The  $\sigma_{aw}$  values were measured using the pendant drop technique with a First Ten Angstrom dynamic FTA analyzer. Experiments using gradients increased in steps were then carried out to determine the CDCs for each soil column following the methodology presented by Sabatini *et al.*<sup>10</sup>. Produced LNAPL at the end of each step was measured gravimetrically. The CDC was constructed using the  $N_{Ca}$  equation (1).

### 3 RESULTS

#### 3.1 Soil characterization

Studied soil grain size distributions were labelled as a function of their silt mass fractions: the coarse soil columns (0.5-2.0 mm) contain less than 10% silt. The intermediate soil columns

(0.01-2.0 mm) contain 20% of silt material and 1.2% of clay. The fine soil columns ( $< 2.0$  mm) contain 40% silt and 5% clay. In the USDA soil classification system, these coarse, intermediate and fine soil respectively correspond to a fine sand, a loamy fine sand and a sandy loam. Coefficients of uniformity ( $C_u$ ) were respectively 2, 10 and 60 for fine, intermediate and coarse soils, all indicative of poorly sorted soil. Dry soil density after packing was  $1751 \text{ kg/m}^3$  ( $\pm 44 \text{ kg/m}^3$ ), and pore volumes were 48 mL ( $\pm 5 \text{ mL}$ ).

Quartz, feldspars and amphibolites were the most common minerals present in the soil (45% to 75% on a mass basis). However, significant proportions of clay (2% to 30% on a mass basis) and carbonate minerals (12% to 25% on a mass basis) were also present. The organic carbon content of the soil was measured at  $2.3 \pm 0.1 \text{ \%wt}$ , which is not considered high.

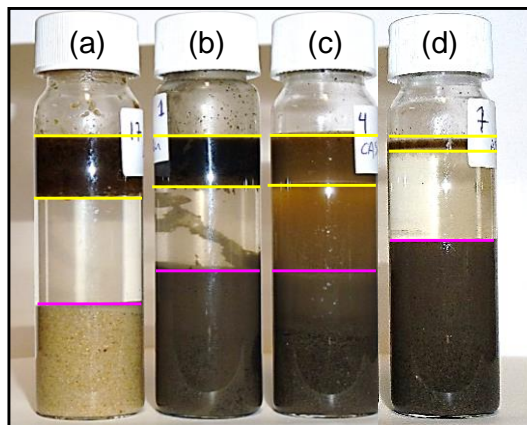
### 3.2 LNAPL characterization

The LNAPL present at the experimental site is the result of pure paraxylene solvent migrating into a soil previously contaminated by heavier diesel fuel. For that reason, the proportions of xylene and diesel are unknown. The density and kinematic viscosity of the LNAPL collected at the site and used for the experiments is  $860 \text{ kg/m}^3$  and  $1.00 \times 10^{-6} \text{ m}^2/\text{s}$  (1.00 cSt) respectively. As a comparison, the density and kinematic viscosity of the pure paraxylene solvent is  $860 \text{ kg/m}^3$  and  $0.76 \times 10^{-6} \text{ m}^2/\text{s}$  (0.76 cSt).

### 3.3 Surfactant screening

Results from the surfactant screening process are as follow. DOW was excluded from the list after the producer indicated the non-availability of this product for aquifer remediation purposes.

Commonly used branched anionic surfactants (AOT, SDS, SDBS and SAS) produced a viscous organic phase when 1%-mass surfactant solutions were mixed the LNAPL. In addition, qualitative bottle tests showed a strong interaction between soil and other anionic candidates, AMA and AAY, as well as with the CAS (pH 1) solution (Figure 2).



**Figure 2.** Qualitative bottle tests: (a) silica sand - water- LNAPL system; (b) Site soil - water- LNAPL system; (c) Site soil – CAS (pH 12) – LNAPL system; (d) Site soil – AMA – LNAPL system

The possibility of creating locally a viscous organic phase or strong interactions between the soil, LNAPL and surfactant was not desirable for this project targeting a heterogeneous environment including low-permeability soil layers prone to plugging. For that reason, further use of anionic surfactants including salinity scans was excluded.

As a corollary to the exclusion of all anionic candidates based on potential adversary effects observed during these screening tests (with the exception of CFX), the option of forming a middle-phase microemulsion achieving ultra-low interfacial tensions with the LNAPL was no longer considered. The screening process was therefore refocused on achieving the greatest

possible interfacial tension reduction within a Winsor Type I system. The final surfactant formulation selection was based on the  $\sigma_{ow}$  measurements. The formulation 1.5%-wt CAS ( pH 12) achieved  $\sigma_{ow}$  values of 0.06 mN/m, which was satisfactory compared with other published data, considering that this selected formulation was compatible with the site soil and LNAPL. Preconditioning of the porous media with NaOH is, however, required with this formulation in order to reduce adsorption and enhance the interfacial reduction with the LNAPL. The analysis of previous exploratory soil column experiments (not reported here) indicated that the NaOH mass required to precondition the site soil to a pH of 12 was in a realistic range (between 1.3 and 2.1 g NaOH per kg of soil).

### 3.4 Soil column experiments

Table 3 presents a summary of the soil column experiments initial conditions. Table 4 and Figure 3 present the step tests results.



**Table 3.** Initial conditions of the soil column experiments

Column No.*	Grain size	$k$	$K_{SAT}$ ( $S_{OR}=0$ )	$C_U$	$S_{OR}$	$K_w$ ( $S_{OR}$ )
	(mm)	( $m^2$ )	(m/s)	(-)	(-)	(m/s)
Coarse-A	0.5-2.0	$1.8 \times 10^{-11}$	$1.3 \times 10^{-4}$	2	0.21	$3.5 \times 10^{-5}$
Coarse-B		$1.7 \times 10^{-11}$	$1.3 \times 10^{-4}$	2	0.16	$3.6 \times 10^{-5}$
Intermediate-A	0.01-2.0	$9.2 \times 10^{-13}$	$6.9 \times 10^{-6}$	11	0.32	$1.3 \times 10^{-6}$
Intermediate-B		$7.5 \times 10^{-13}$	$5.6 \times 10^{-6}$	11	0.30	$1.4 \times 10^{-6}$
Fine-A	<2.0	$7.8 \times 10^{-14}$	$5.9 \times 10^{-7}$	59	0.20	$7.2 \times 10^{-8}$
Fine-B		$6.7 \times 10^{-14}$	$5.1 \times 10^{-7}$	59	0.20	$8.0 \times 10^{-8}$

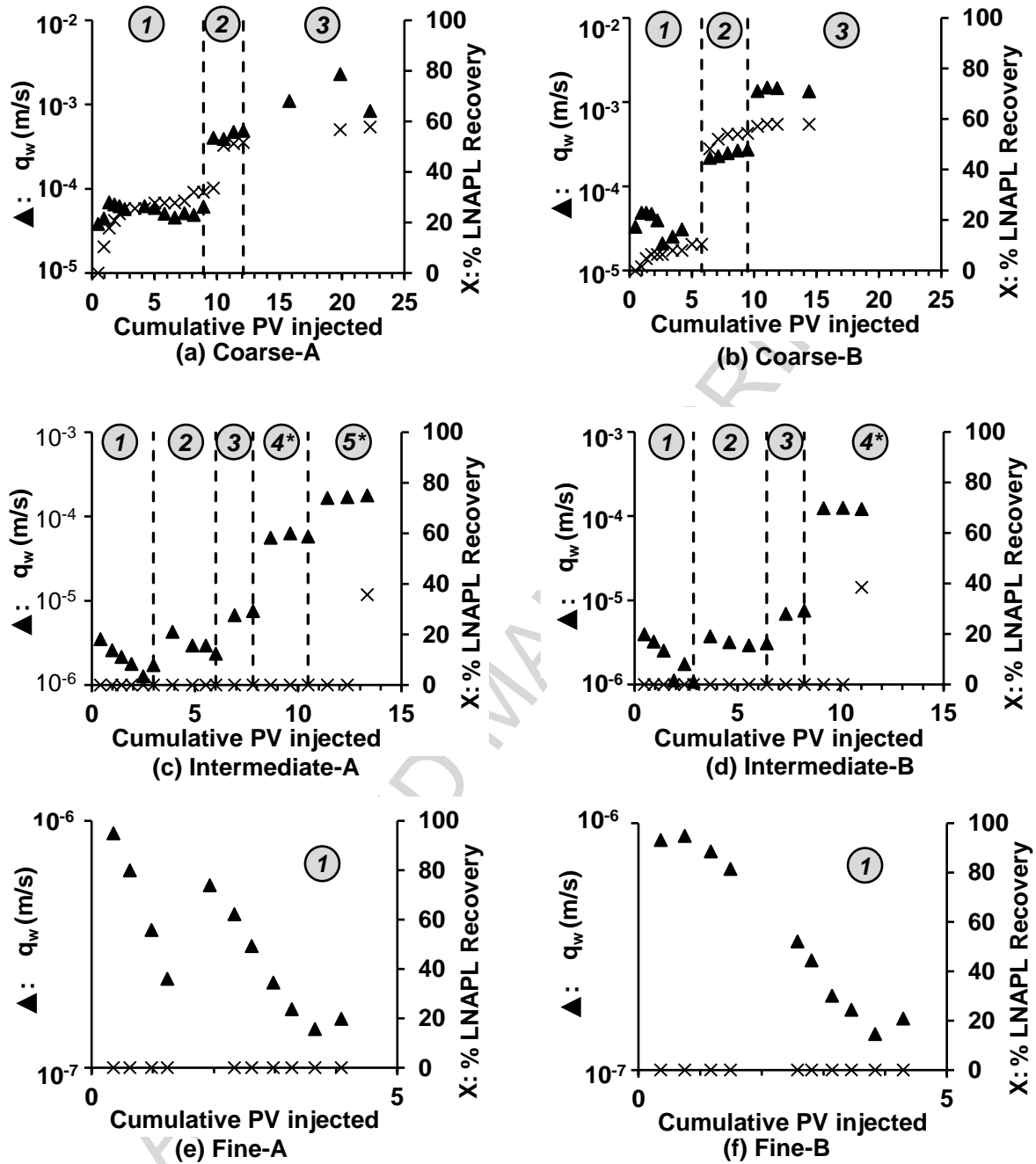
\*Soil column experiments were conducted in duplicates (A and B);  $k$  is the soil intrinsic permeability,  $K_{SAT}$  ( $S_{OR}=0$ ) is the soil hydraulic conductivity to water at zero LNAPL saturation,  $C_U$  is the uniformity coefficient,  $S_{OR}$  is the residual LNAPL saturation and  $K_w$  ( $S_{OR}$ ) is the soil hydraulic conductivity to water at the residual oil saturation.

**Table 4.** Capillary desaturation step tests of the soil column experiments

Column No.	Step no.	dh/dl **	q <sub>w</sub>	N <sub>Ca</sub>	S <sub>oR</sub>	LNAPL Recovery <sup>(2)</sup>
		(m/m)	(m/s)	(-)	(-)	(%)
Coarse-A	1	0.71	$5.4 \times 10^{-5}$	$1.3 \times 10^{-3}$	14.6	32
	2	7.1	$4.5 \times 10^{-4}$	$1.1 \times 10^{-2}$	9.7	55
	3	15	$1.4 \times 10^{-3}$	$3.3 \times 10^{-2}$	9.0	58
Coarse-B	1	0.71	$3.7 \times 10^{-5}$	$8.6 \times 10^{-4}$	14.2	10
	2	7.1	$2.5 \times 10^{-4}$	$5.8 \times 10^{-3}$	7.2	54
	3	15	$1.4 \times 10^{-3}$	$3.3 \times 10^{-2}$	6.2	58
Intermediate-A	1	3.6	$1.9 \times 10^{-6}$	$4.5 \times 10^{-5}$	32.1	0
	2	7.1	$3.1 \times 10^{-6}$	$7.3 \times 10^{-5}$	32.1	0
	3	15	$7.5 \times 10^{-6}$	$1.8 \times 10^{-4}$	32.1	0
	4 <sup>(3)</sup>	n.m.	$5.8 \times 10^{-5}$	$1.4 \times 10^{-3}$	31.9	0
	5 <sup>(3)</sup>	n.m.	$1.8 \times 10^{-4}$	$4.2 \times 10^{-3}$	20.7	36
Intermediate-B	1	3.6	$1.8 \times 10^{-6}$	$4.2 \times 10^{-5}$	29.8	0
	2	7.1	$3.2 \times 10^{-6}$	$7.4 \times 10^{-5}$	29.8	0
	3	15	$7.5 \times 10^{-6}$	$1.8 \times 10^{-4}$	29.6	0
	4 <sup>(3)</sup>	n.m.	$1.2 \times 10^{-4}$	$2.8 \times 10^{-3}$	18.4	38
Fine-A	1	15	$2.8 \times 10^{-7}$	$6.6 \times 10^{-6}$	19.9	0
Fine-B	1	15	$4.5 \times 10^{-7}$	$1.0 \times 10^{-5}$	19.6	0

\*\* Applied over a column length of 0.14 m; <sup>(2)</sup> Cumulative; <sup>(3)</sup> Additional pressure steps

performed under pump pressure



**Figure 3.** Effluent flux ( $q_w$ , m/s) and LNAPL mass produced (% LNAPL recovery on a mass basis) as a function of PV injected during the soil column fixed-gradient step tests. Steps are marked by the vertical dashed lines and circled numbers. Steps 1 to 3 are constant head tests.

Steps 4 and 5 (marked with \*) indicate increased pressure steps performed in order to produce LNAPL for the construction of the capillary desaturation curve.

## 4 INTERPRETATION AND DISCUSSION

### 4.1 Soil clogging due to surfactant-NAPL-soil interactions

Effects of surfactant-NAPL-soil interactions were evaluated globally by quantifying their impact on the column aqueous discharge flux ( $q_w$ ) under a fixed hydraulic gradient as a function of cumulative pore volume (PV) injected (Figure 3). For all column experiments, an initial drop by a factor of 1.4 was expected as the more viscous washing solution ( $\mu = 1.4$  mPa.s) displaces the resident water ( $\mu = 1.0$  mPa.s).

For the coarse soil column experiments (Coarse-A and Coarse-B), a  $q_w$  drop was only observed during the first fixed-gradient step. Both coarse soil column experiments showed an initial  $q_w$  increase from 0 to 1.7 PV injected (Coarse-A) and from 0 to 1.4 VP injected (Coarse-B). This initial increase corresponds to the production of LNAPL at the effluent and corresponding aqueous phase relative permeability increase. This increase, however, is not sufficient to overcome a subsequent  $q_w$  drop in both experiments, from 1.7 to 6.6 PV injected (Coarse-A) and from 1.4 to 2.6 VP injected (Coarse-B). The amplitude of these drops corresponds respectively to factors of 1.4 and 2.3, which is exactly in the range of the  $q_w$  drop anticipated due to the viscosity of the solution ( $\mu = 1.4$  mPa.s) or slightly above it. Subsequent steps did not show any  $q_w$  decrease due to surfactant-NAPL-soil-groundwater interactions. Results suggest surfactant-NAPL-soil-groundwater interactions such as viscous phase production or soil particle migration were not significant for the coarse soil.

Both intermediate soil column experiments (Intermediate-A and Intermediate-B) showed a  $q_w$  drop occurring during the first two fixed-gradient steps. During those 2 steps, no LNAPL was produced at the effluent. During the first step,  $q_w$  dropped by factors of 2.0 (Intermediate-A) and 3.6 (Intermediate-B). During the second step,  $q_w$  dropped by an additional factor of 1.8 (Intermediate-A) and 1.2 (Intermediate-B). The combined amplitude of these 2 drops, which are higher than the range of the  $q_w$  drop anticipated due to the viscosity of the solution, are potentially linked to the presence of the 0.01-0.5 mm grain size fraction or surfactant-NAPL-soil interactions. This phenomenon stabilized, however, after the injection of 6.0 and 6.4 PV for Intermediate-A and Intermediate-B, respectively. The fact that  $q_w$  is either decreasing during the first two steps or stable during the latter steps, even after LNAPL was produced (Figure 3 (c) and 3 (d)) suggests that the permeability loss observed is permanent in nature and that permeability was not recovered during flushing. Gabr *et al.*<sup>31</sup> also observed clogging during column tests in which naphthalene was recovered with an anionic surfactant solution. Although their soil was slightly coarser than the Intermediate soil of this experiment, a similar permeability reduction of one half order of magnitude was observed in a soil containing 95% of silica sand and 5 % of kaolinite. However, in their experiment, the hydraulic conductivity loss showed to be reversible. Although full recovery occurred after a large number of pore volume circulated (>50), it was clearly initiated at 5 PV. This reversible nature of the permeability loss excluded fines migration as the cause of clogging (which would be unrecoverable), and pointed towards phase behavior related clogging. These phase behaviors include the formation of liquid crystal, gels, phase conversions and microemulsions. This further supports the hypothesis that since the permeability reduction we observed does not appear to be reversible, it is linked to a permanent phenomenon such as fines migration and settling.

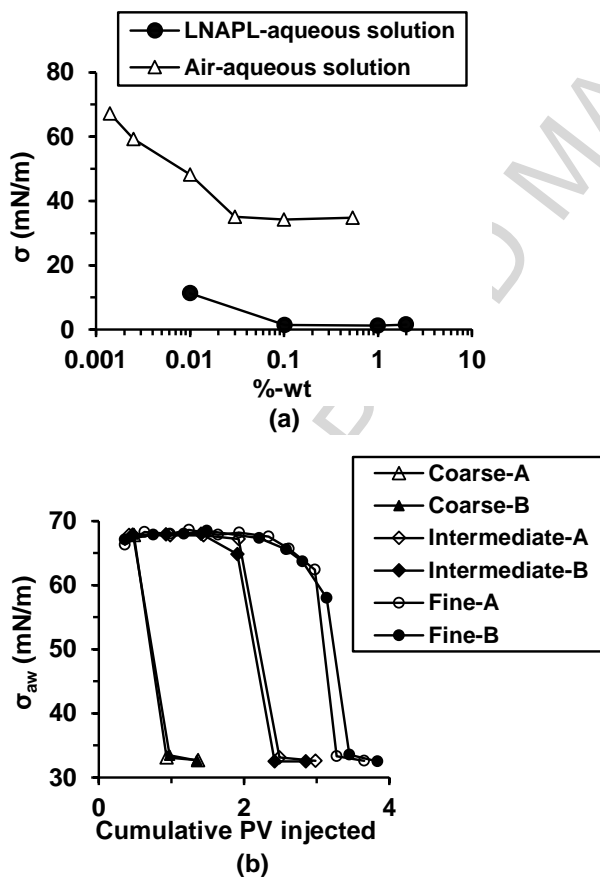
Results from the fine soil experiments (Fine-A and Fine-B) confirm the link between the presence of fine grains and the amplitude of the  $q_w$  drop. Drops of factors of 5.6 and 5.3 were measured respectively for Fine-A and Fine-B, resulting in clogging at the end of the first fixed-gradient steps (4.1 and 4.3 VP injected, respectively). These columns did not produce any LNAPL. The presence of clay particles (5%-wt) within this soil fraction is most likely responsible for this behavior.

These results indicate that the fine soil is not suitable for surfactant-enhanced capillary desaturation. For the other two grain size fractions (intermediate and coarse soil, Figure 3 (a) to (d)), they suggest that pore plugging would not be a major issue for these grain-size distributions. These results also show that fixed-gradient step tests are an appropriate methodology to assess the global effect of surfactant-LNAPL-soil-groundwater interactions and that such tests should be used routinely during the selection of surfactant solution formulations.

## 4.2 Surfactant loss due to adsorption

Surfactant loss due to adsorption as a function of soil grain size fractions is presented in Figure 4. An equilibrium between adsorbed surfactant monomers and their aqueous concentration throughout the soil column is assumed to be reached when  $\sigma_{aw}$  measured at the column effluent corresponds to the  $\sigma_{aw}$  of the solution prior to injection. This is based on the strong correlation between interfacial and surface tensions (Figure 4 (a), measured at neutral pH). Other researchers already used surface tension to quantify surfactant adsorption onto soil for aqueous phase surfactant concentrations less than the critical micelle concentration<sup>32</sup>. As the link between surfactant adsorption and the clay content in soil was already demonstrated by Rodriguez-Cruz et al.<sup>33</sup>, adsorption was anticipated.

Figure 4 (b) shows that such equilibrium was obtained after the injection of 0.9 and 1.0 PV for the coarse soil (i.e. no adsorption occurred), after 2.5 and 2.4 PVs for the intermediate soil, and after 3.3 and 3.5 PVs for the fine soil. These results can be used to calculate the CAS mass adsorbed to soil in equilibrium with the 1.5%-wt aqueous CAS concentration. The ratio of adsorbed surfactant mass over dry soil mass for each column, expressed in g of surfactant per g of dry soil, is 0.0026 and 0.0028 for the coarse soil, 0.0060 and 0.0058 for the intermediate soil and 0.10 and 0.11 for the fine soil. Adsorption being a surface-related phenomenon, this evaluation confirms that surfactant losses to adsorption on soil particles is greatly dependent on grain size distribution.



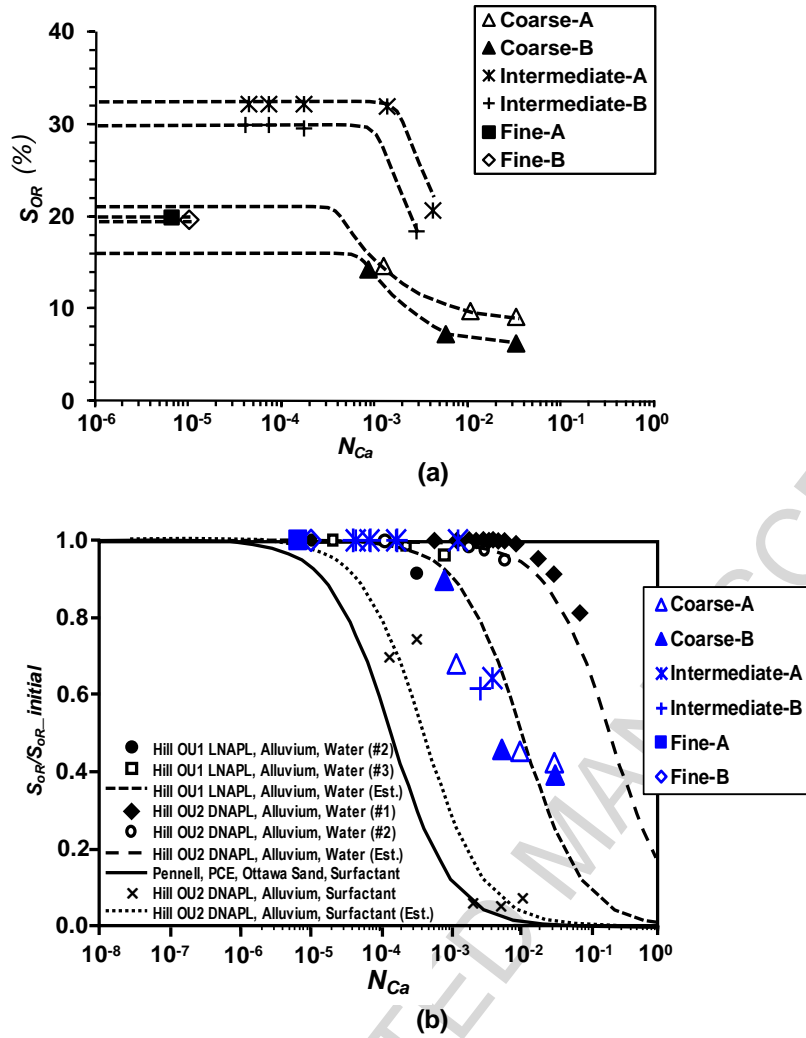
**Figure 4. (a)** Surface and interfacial tension measurements as a function of surfactant concentration for the same CAS solution; **(b)** Surface tension of column effluents as a function of cumulative pore volume (PV) injected used for surfactant (CAS) adsorption calculations.

These results show that soil column tests and surface tension measurements on column effluents are an appropriate methodology to assess surfactant losses due to adsorption on soil particles, and that these should be used routinely for the design of surfactant flushes at any scale to ensure that the targeted  $\sigma_{ow}$  reduction is effectively reached.

### 4.3 Capillary desaturation curves

Figure 5 (a) presents the CDCs obtained for each column experiment as well as a combined normalized CDC encompassing all experimental results.





**Figure 5.** (a) Capillary desaturation curves obtained for the 6 soil column experiments. Experimental points as well as information from duplicate columns were used to draw the dashed curves; (b) Global capillary desaturation curve representative of sites conditions <sup>7, 9, 17</sup>.

The wettability of the tested system is assessed by comparing the global site-specific CDC data with published CDCs (Figure 5 (b)). In aquifer remediation studies,  $N_{Ca}^*$  values in the range of  $10^{-5}$  to  $10^{-4}$  were reported by Pennell *et al.* <sup>9</sup> for Ottawa sand columns contaminated with laboratory-grade PCE, representative of strongly water-wet systems.  $N_{Ca}^*$  values in the  $10^{-3}$ - $10^{-1}$  range were reported by Dwarakanath *et al.* <sup>7</sup> for aluminosilicate alluvium columns contaminated by weathered DNAPLs, representative of mixed wettability systems. Their study highlighted the

fact that CDCs are an interesting tool to measure the practical implications for NAPL recovery of the system wettability. They also showed that anionic surfactants lowered the  $N_{Ca}^*$  by 2 to 3 orders of magnitude, indicating a wettability shift toward water-wet. Sabatini *et al.*<sup>10</sup> also observed water-wet conditions for laboratory grade PCE and clean soil (Dover AFB site) resulting from the use of surfactant solutions. Applying incremental  $\sigma_{ow}$  reductions from 4 mN/m to less than 0.005 mN/m, they reported a  $N_{Ca}^*$  value of  $5 \times 10^{-6}$ .

The CDC data obtained for this project is close to the estimated CDC for Hill OU1 LNAPL and OU2 soil (a mixed-wettability system), and both show a  $N_{Ca}^*$  of  $10^{-3}$ . The OU2 soil consists of a >90% alumino-silicate alluvium, and the OU1 LNAPL consists of weathered jet fuel obtained from a contaminated fire-training area. The CDC data are positioned to the right of the CDC obtained by Pennell *et al.*<sup>9</sup> for a water-wet system (Ottawa sand and laboratory grade DNAPL). The CDC data therefore suggest that: (1) The system tested exhibits a mixed-wettability; and (2) the Winsor Type I system optimized for site conditions and based on the use of an amphoteric surfactant at pH 12 did not reverse the wettability towards water-wetness, as observed by Dwarakanath *et al.*<sup>7</sup> with Hill OU2 alluvium and DNAPL.

The impact of the mixed-wettability and the high  $N_{Ca}^*$  value measured for the site is related to the range of capillary numbers achievable under realistic hydraulic gradients. In the coarse soil columns where  $K_w(S_{oR}) = 3.5 \times 10^{-5}$  m/s, LNAPL capillary desaturation was first observed at  $N_{Ca}$  values of  $1.3 \times 10^{-3}$  (Coarse-A) and  $8.6 \times 10^{-4}$  (Coarse-B), obtained with a hydraulic gradient corresponding to 0.7 m/m (Figure 5 and Table 4), and resulting in LNAPL recoveries of 32 and 10% respectively. This hydraulic gradient is considered high but realistic within a 5-spot injection/extraction well pattern. However, any further increase of  $N_{Ca}$  and LNAPL recovery in the coarse soil layer would result in unrealistically high hydraulic gradients. For example, the

second point on the Coarse-A and Coarse-B curves, representing >50% LNAPL cumulative recovery, were obtained with a  $N_{Ca}$  close to  $10^{-2}$  requiring an unrealistic hydraulic gradient of 7.1 m/m. Based on these findings, capillary desaturation has a low potential for LNAPL recovery (<30%) in the coarse soil.

In the intermediate soil columns where  $K_w (S_{oR}) = 1.4 \times 10^{-6}$  m/s, LNAPL capillary desaturation was first observed at  $N_{Ca}^*$  values of  $4.2 \times 10^{-3}$  (Intermediate-A) and  $2.8 \times 10^{-3}$  (Intermediate-B), obtained with a hydraulic gradient of 15 m/m (Figure 5 and Table 4). This gradient is considered unrealistic within a 5-spot injection/extraction well pattern. In the fine soil columns, LNAPL capillary displacement could not be triggered at all due to low  $K_w (S_{oR})$  and pore plugging. Based on the intermediate and fine soil permeabilities, LNAPL capillary desaturation is not a suitable LNAPL recovery mechanism in these types of soil.

The similarities of the CDC obtained from the coarse and intermediate soil columns (Figure 5 (b)) suggest that parameters such as the larger spreading of the grain size distribution or the initial  $S_{oR}$  value did not influence the overall shape of the CDC.

Finally, the CDC obtained for the coarse soil exhibits tailing as  $S_{oR}$  is lowered. The relationship between the  $N_{Ca}$  (log-scale) and LNAPL recovery is not linear but is also dependant on  $S_{oR}$ . LNAPL trapping in the porous media through mechanisms such as capillary by-passing and snap-off are responsible for this phenomenon. As  $S_{oR}$  decreases, the LNAPL mobility is reduced due to the decrease of the relative permeability to the LNAPL<sup>15</sup>. This phenomenon was not reported on other published CDCs.

## 5 CONCLUSION

The injection of low-concentration (<1 wt%) surfactant solutions in the saturated part of a heterogeneous source zone at an experimental site was investigated as a multiphase vacuum extraction follow-up technology. The impacts of soil permeability, wide pore-size distribution, mixed mineralogy, weathered LNAPL and groundwater hardness on surfactant formulations, achievable capillary number ( $N_{Ca}$ ) and resulting site-specific capillary desaturation curves were quantified in soil columns representative of the main stratigraphic layers encountered on site. Results show that fixed-gradient step tests are an appropriate methodology to assess the global effect of surfactant-LNAPL-soil-groundwater interactions and that such tests should be used routinely during the selection process of surfactant solution formulations. The main findings of this research are the following:

- Compatibility issues between the mixed mineralogy soils, hard groundwater, mixed LNAPL and usual anionic surfactants were observed during the screening process. The optimized solution was a Winsor type I system promoting an interfacial tension of 0.06 mN/m between the site LNAPL and the amphoteric surfactant CAS in aqueous solution at pH 12;
- Surfactant losses to adsorption and pore media plugging due to the mobilization of fine soil particles were the most significant in soil where the < 0.01 mm fraction was present, and were not observed in the coarse soil (0.05-2.0 mm);
- The site-specific capillary curves suggest that the system tested exhibits a mixed-wettability and that the Winsor Type I system optimized for site conditions and based on the use of an amphoteric surfactant at pH 12 did not reverse the wettability towards water-wetness;
- The soil permeability strongly influences LNAPL recovery potential through the relationship between  $N_{Ca}$  and hydraulic gradients. In this case, the critical capillary number could only be obtained with realistic hydraulic gradients in the coarse soil layers.

At those gradients, potential LNAPL recovery was 30 % at the most. The critical capillary number could not be achieved in the intermediate and fine soil fractions under realistic hydraulic gradients.

- Unlike previously published CDCs, the relationship between  $N_{Ca}$  (log-scale) and LNAPL recovery was not linear but dependant on  $S_{OR}$ .
- The findings suggest that heterogeneous soil properties and weathered LNAPL at the site made the injection of low-concentration (<1 wt%) surfactant solutions not applicable to the studied site.

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### Author Contributions

This manuscript was written with contributions from all authors. All authors have given their approval to the final version of the manuscript. T. Robert conducted the laboratory experiments, performed the data interpretation and wrote the first draft of the paper. The other authors equally contributed to the experimental protocol and data interpretation, and reviewed the draft.

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