Journal of Contaminant Hydrology 100 (2008) 116–126

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Investigation of surfactant-enhanced mass removal and flux reduction in 3D correlated permeability fields using magnetic resonance imaging

Changyong Zhang [a,*], Charles J. Werth [a], Andrew G. Webb [b]

[a] Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, 205 N Mathews Ave, Urbana, IL 61801, United States
[b] Department of Bioengineering, Pennsylvania State University, 313 Hallowell Building, University Park, PA 16802, United States

ARTICLE INFO

Article history:
Received 25 January 2008
Received in revised form 27 May 2008
Accepted 6 June 2008
Available online 18 June 2008

Keywords:
NAPL
Surfactant flushing
Remediation
Heterogeneity
Mass transfer
MRI

ABSTRACT

Magnetic resonance imaging (MRI) was used to visualize the NAPL source zone architecture before and after surfactant-enhanced NAPL dissolution in three-dimensional (3D) heterogeneously packed flowcells characterized by different longitudinal correlation lengths: 2.1 cm (aquifer 1) and 1.1 cm (aquifer 2). Surfactant flowpaths were determined by imaging the breakthrough of a paramagnetic tracer ($MnCl_2$) analyzed by the method of moments. In both experimental aquifers, preferential flow occurred in high permeability materials with low NAPL saturations, and NAPL was preferentially removed from the top of the aquifers with low saturation. Alternate flushing with water and two surfactant pulses (5–6 pore volumes each) resulted in ~63% of NAPL mass removal from both aquifers. However, overall reduction in mass flux (Mass Flux 1) exiting the flowcell was lower in aquifer 2 (68%) than in aquifer 1 (81%), and local effluent concentrations were found to increase by as high as 120 times at local sampling ports from aquifer 2 after surfactant flushing. 3D MRI images of NAPL revealed that NAPL migrated downward and created additional NAPL source zones in previously uncontaminated areas at the bottom of the aquifers. The additional NAPL source zones were created in the direction transverse to flow in aquifer 2, which explains the higher mass flux relative to aquifer 1. Analysis using a total trapping number indicates that mobilization of NAPL trapped in the two coarsest sand fractions is possible when saturation is below 0.5 and 0.4, respectively. Results from this study highlight the potential impacts of porous media heterogeneity and NAPL source zone architecture on advanced in-situ flushing technologies.

1. Introduction

In the last two decades, various source zone treatment technologies have been used to cleanup nonaqueous phase liquids (NAPLs) from groundwater. Due to their low solubility in water and rate-limited mass transfer, traditional treatment technologies that rely solely on NAPL solubilization (e.g., pump-and-treat) are widely acknowledged as ineffective and costly (Mackay et al., 1985; Mackay and Cherry, 1989). As a result, more advanced in-situ flushing technologies have been developed to enhance NAPL recovery. Among these are cosolvent- and surfactant-enhanced aquifer remediation (Fountain et al., 1991; Pennell et al., 1993; Rao et al., 1997; Oostrom et al., 2006). The focus of this work is on the latter.

The use of a surfactant can significantly increase the aqueous phase solubility of NAPL components (>100 times) and decrease the interfacial tension (IFT) between NAPL and water (>3–5 times). As a result, the effects of surfactant flushing can be two-fold, i.e., enhanced NAPL solubilization and mobilization. The properties of several commonly used surfactants and the results of surfactant flushing on NAPL recovery in either one-dimensional (1D) column studies or two-dimensional (2D) sand box experiments are summarized in Table 1. Nonionic and anionic surfactants are commonly used due to their low toxicity and high solubilization capacity. Anionic surfactants typically result in lower IFT values between NAPL and water than nonionic surfactants, and greater NAPL mobilization.

* Corresponding author. Tel.: +1 217 333 6851; fax: +1 217 333 6968.
E-mail address: czhang@uiuc.edu (C. Zhang).

0169-7722/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jconhyd.2008.06.002

Table 1
Properties of commonly used surfactants

Surfactant	Type	CMC [wt.%]	C [wt.%]	NAPL	Solubility [mg/l]	IFT [dyn/cm]	Result
Tween 80[a, b, c]	Nonionic	0.0013	4	PCE	26,060	5.0	S, M
Tween 80[d]	Nonionic	0.0013	5	TCE	n/a	9.0	S, M
T-MAZ-80* [e]	Nonionic	0.012	1	TCE	15,890	11.7	S, M
Aerosol MA-80[c]	Anionic	n/a	8	PCE	76,360	0.16	M
Mix 1[a]	Anionic	n/a	4	PCE	n/a	0.09	M
Mix 1[f]	Anionic	0.233	1	TCE	n/a	1.4	M
Triton X-100[g, h]	Nonionic	0.00125	4	PCE	n/a	n/a	S, M
DOWFAX[i]	Nonionic	0.0150	1.35	TCE	4520	18	S

Notes: CMC = critical micelle concentration; *C* = surfactant concentration; IFT = interfacial tension between NAPL and surfactant solution; S = solubilization; M = mobilization; PCE = tetrachloroethene; TCE = trichloroethylene; Mix 1 = 1:1 mixture of Aerosol OT and Aerosol AY; n/a = not available.
*T-MAZ-80 is a POE (20) sorbitan monooleate.
References: [a] Pennell et al., (1994); [b] Taylor et al., (2001); [c] Ramsburg and Pennell (2001); [d] Conrad et al., (2002); [e] Oostrom et al., (1999); [f] Johnson et al., (2004); [g] Walker et al., (1998); [h] Edwards et al. (1991); [i] Field et al. (1999).

In experiments conducted in 1D columns, Pennell et al. (1994) showed 90% of residual tetrachloroethylene (PCE) was removed from a column packed with coarse sand (mean grain diameter d_{50} ~ 0.71 mm) after flushing 15.5 pore volumes (PV) of a 4% Tween 80 solution; solubilization accounted for 77% mass removal, and mobilization accounted for only 13%. In a separate column experiment, Pennell et al. (1994) showed that 99% of residual PCE could be removed from a column packed with graded sand (40–270 mesh, d_{50} ~ 0.17 mm) using a 4% 1:1 mixture of Aerosol AY and Aerosol OT (Mix 1 in Table 1); the majority of NAPL removed was attributed to mobilization (82%) due to the significant reduction in IFT (i.e., 0.09 dyn/cm). These 1D column experiments provided valuable information on the selection criteria of surfactants according to the goals of remediation, i.e., solubilization *vs.* mobilization. However, issues associated with heterogeneous permeability distribution were not considered.

Both experimental investigations (Walker et al., 1998; Oostrom et al., 1999; Saba et al., 2001; Taylor et al., 2001) and modeling studies (Dekker and Abriola, 2000; Rathfelder et al., 2001; Saenton et al., 2002; Lemke et al., 2004; Lemke and Abriola, 2006; Christ et al., 2006; Jin et al., 2007) have shown that surfactant-enhanced NAPL remediation is affected by NAPL source zone architecture (e.g., NAPL ganglia to pool mass ratios), which, among other factors, depends to a large extent on porous media heterogeneity. Several experimental studies were performed in 2D heterogeneous flowcells containing one or several horizontal fine-grained lenses surrounded by a coarse sand matrix (Taylor et al., 2001; Walker et al., 1998; Oostrom et al., 1999). Taylor et al. (2001) found surfactant flushing with a 4% Tween 80 solution was more effective in removing residual NAPL than NAPL pools via enhanced solubilization. For example, when the majority of NAPL was entrapped as residual ganglia in a coarse sand matrix (d_{50} ~ 0.71 mm), greater than 80% of NAPL mass was recovered with 5 PV of surfactant solution; however, when a large portion of NAPL was present as pools above fine-grained lenses (d_{50} ~ 0.17–0.3 mm), only 70% of NAPL mass was recovered with 8 PV of surfactant solution. No mobilization was observed in these experiments. In contrast, Walker et al. (1998) observed NAPL mobilization in a coarse sand matrix (d_{50} ~ 0.5 mm) and pooling on top of a fine sand lens (d_{50} ~ 0.2 mm) during flushing with a 4% Triton-X100 solution. Oostrom et al. (1999) also reported NAPL mobilization in a coarse sand matrix (d_{50} ~ 0.7 mm) as well as penetration into a fine-grained barrier (d_{50} ~ 0.2 mm) during flushing with a 1% T-MAZ-80 solution. The IFT of the 1% T-MAZ-80 (11.7 dyn/cm) is greater than that for the 4% Tween 80 (5.0 dyn/cm). Hence, it is not clear why Oostrom et al. (1999) observed NAPL mobilization but Taylor et al. (2001) did not, given that the d_{50} of porous media used in both studies were similar.

Only a limited number of studies have evaluated the effectiveness of surfactant-enhanced remediation in more realistic heterogeneous 2D (Conrad et al., 2002; Robert et al., 2006; Suchomel and Pennell, 2006) or 3D permeability fields (Johnson et al., 2004). In a 2D flowcell packed with a heterogeneous distribution of sands representative of fluvial lithologies, Conrad et al. (2002) demonstrated that approximately 90% of a denser-than-water NAPL (DNAPL) was recovered with 8.6 PV of a 5% Tween 80 solution, and NAPL mobilization was observed only inside the coarse materials (d_{50} ~ 0.71–1.1 mm). These authors also observed mobilization into low permeability regions (d_{50} ~ 0.26 mm) when flushing with a 1.5% Aerosol MA-80 solution due to the lower IFT (0.62 dyn/cm). In a more realistic 3D correlated random permeability field, Johnson et al. (2004) found that a combined dense brine barrier and a surfactant mixture (1% 1:1 mixture of Aerosol AY and Aerosol OT, Mix 1 in Table 1) induced mobilization and resulted in 85% NAPL mass recovery. Results from these studies indicate that excellent NAPL recovery (>85%) is possible in a layered heterogeneous system, and when a brine barrier is used in a correlated random permeability field. However, NAPL recovery in a 3D correlated random permeability field in the absence of brine was not explored.

A limited number of field tests (Jawitz et al., 1998; Ramsburg et al., 2005) and modeling studies (Sale and McWhorter, 2001; Jawitz et al., 2005) have explored the impacts of mass removal on aqueous mass flux and/or concentration reduction. Ramsburg et al. (2005) demonstrated in a pilot-scale field test that surfactant flushing effectively reduced DNAPL concentrations at many locations within the treatment zone by as much as 2 orders of magnitude. Modeling results from Sale and McWhorter (2001) suggest that almost complete removal of NAPL mass from a uniform permeability field is necessary to achieve significant reductions in mass flux across a down-gradient control plane. In contrast, Jawitz et al. (2005) developed a stream-tube model and demonstrated that less mass removal is required to achieve a given mass flux reduction as aquifer and NAPL source zone heterogeneity increase. Controlled laboratory studies are needed to characterize the relationship between mass removal and mass flux reduction in 3D heterogeneous permeability fields.

The objective of this study is to determine the combined effects of surfactant-enhanced solubilization and mobilization on NAPL mass removal and mass flux reduction from 3D heterogeneous correlated permeability fields. Specifically, we