Effect of temperature on cosolvent flooding for the enhanced solubilization and mobilization of NAPLs in porous media

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ABSTRACT

This paper examines the potential for enhanced NAPL recovery from the subsurface through the combined application of hot water and cosolvent flushing. Batch experiments were conducted to determine the effect of temperature on fluid properties and the multiphase behavior of the ethanol-water-toluene system and to assess the impact of temperature on the capillary, Bond and total trapping numbers and on flooding stability. Column flooding experiments were also conducted to evaluate toluene NAPL recovery efficiency for different ethanol contents and flushing solution temperatures. The ethanol content considered ranged from 20 to 100% by mass, while the flushing solution temperatures were varied from 10 to 40 °C. It is shown that small variations in the system temperature can strongly influence the solubilization, mobilization and stability of the multiphase system, but that the impact of temperature on the enhanced NAPL recovery is also dependent on the ethanol content of the flushing solution. The impact of hot water on NAPL recovery was most pronounced at intermediate ethanol contents (40–60% by mass) where the increase in system temperature led to enhanced NAPL solubilization as well as NAPL mobilization. This study demonstrates that coupling of hot water with in situ cosolvent flooding is a potentially effective remedial alternative that can optimize NAPL recovery while reducing the amount of chemicals injected into the subsurface.

1. Introduction

Widespread production and use of organic compounds such as chlorinated solvents and BTEX compounds in various industrial applications have led to extensive contamination of the soil and groundwater. Because of the relatively low aqueous solubility of these compounds, they are often found in the field in the form of nonaqueous phase liquids (NAPLs). As it migrates through the subsurface, the NAPL mass can be retained in the pores in the form of discontinuous ganglia, or may accumulate in the form of pools if some hydraulic barrier is encountered. The low solubility, coupled with low biodegradability and high interfacial tension of many of these compounds means that they tend to persist in the subsurface for decades and perhaps centuries [1].

The remediation of soil and groundwater contaminated by NAPLs has proven to be one of the most challenging environmental problems. Although conventional pump and treat techniques are effective in containing the spread of dissolved contaminants, they are not efficient when the contamination is in the form of NAPLs, especially at geologically complex sites [2,3]. For this purpose, sig-

nificant efforts have been directed over the past two decades to develop effective means for the remediation of soils and groundwater that are contaminated by NAPLs. Among the promising techniques is in situ flooding for enhanced solubilization and mobilization of NAPLs (see for example recent review by Henry et al. [4], Soga et al. [5] and Oostrom et al. [6]). In situ flooding involves the injection of remedial agents into the NAPL source zone to increase the NAPLs' solubility and/or reduce their interfacial tension to render them more mobile [3,7–10]. The most commonly investigated remedial agents include surfactants [11–21] and cosolvents such as alcohols [10,22–25].

The alcohols most considered for groundwater remediation are low molecular-weight alcohols that are mutually miscible in both water and NAPLs, such as methanol, ethanol, 1-propanol and 2-propanol [3,6]. Laboratory studies have shown that cosolvent flooding consisting of low-concentration alcohol solutions (e.g., 1–5% by volume) can lead to enhanced NAPL solubilization, but that many pore volumes of the flushing solution are needed to remove a large percentage of the NAPL mass [23]. On the other hand, laboratory miscibility experiments have demonstrated that alcohol flooding comprising of high fractions of alcohols (70–90% or pure alcohol) can achieve near complete NAPL mass recovery within one pore volume [26]. Although the rapid recovery of large fractions of the NAPL mass is desirable, there is the risk, especially when

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DNAPLs are present, that mobilization may lead to the uncontrolled downward spreading of contamination to previously uncontaminated portions of the subsurface [22,26,27]. To reduce the risk of DNAPL downward migration, a number of studies examined the use of swelling alcohols that can reduce the DNAPL density through partition into the NAPL phase [26,28–31]. A multistep flooding process has also been proposed for the manipulation of the density and viscosity of the multiphase system in order to enhance flood efficiency sweep and limit DNAPL downward migration [8,10,21].

Field applications have demonstrated that in situ flooding can significantly reduce the contaminant mass from the NAPL source zone. At the same time, these applications point to several potential limitations and problems that are encountered when in situ flooding technologies are upscaled to the field (e.g., [3,32,33]). Even under the most favorable conditions, some residual NAPL mass will likely remain in the subsurface and continue to pose risks [34]. To overcome these limitations, some studies have proposed the coupling of physical–chemical treatment technologies with other remediation technologies [34–36]. These studies point to the potential synergistic effects of physiochemical and biological remediation technologies, with overall results that cannot be achieved when each technology is applied on its own. For example, Ramsburg et al. [37] describe a field application that involves the coupling of surfactant flooding followed by microbial reductive dechlorination. Ramakrishnan et al. [38] assess the impact of cosolvent flooding on TCE biodegradation. Amos et al. [39] evaluate the effect of Tween, a non-ionic surfactant, on dechlorination of chlorinated ethenes.

Heat-based technologies for the in situ remediation of contaminated soils and the groundwater are another set of technologies that have received considerable attention [6]. Thermal technologies take advantage of the temperature-dependency of the NAPL fluid properties to recover a larger fraction of the NAPL from the porous medium. By increasing the temperature in groundwater systems, the controls of several physical forces responsible for NAPL entrapment, primarily viscous forces, are minimized and NAPL removal becomes more efficient [23].

One variation of heat-based remediation technologies involves the injection of hot water for the enhanced recovery of NAPLs. Hot water flooding was first developed within the petroleum industry for the enhanced recovery of petroleum (e.g., [40–42]). More recently, it has been demonstrated that hot water flooding may also lead to enhanced in situ remediation of the soil and groundwater contaminated with NAPLs [43–45]. Davis [44] reported that hot water injection is most effective when NAPL content is greater than residual saturation with mobilization being the dominant recovery mechanism. Davis and Lien [46] conducted laboratory displacement experiments using water with temperature in the range of 10–50 °C to recover oil wastes from sands and showed that hot water led to higher oil recovery primarily due to enhanced mobilization as a result of reduction of NAPL viscosity. EPA [47] showed in a field application that the injection of heated water can lead to enhanced recovery of coal tar from the subsurface, but the remaining coal tar concentration remained above residual immobile levels. More recently, O'Carroll and Sleep [48] conducted bench scale sandbox experiments for the enhanced recovery of Voltesso – a light NAPL whose density and viscosity are strongly temperature-dependent – by hot water flooding. The study reports that hot water flooding resulted in greater NAPL mass removal, but did not yield lower NAPL residual saturation.

For surfactant or cosolvent in situ flooding, the temperature of the water–NAPL-agent system is an important operational parameter that influences the phase behavior and relative mobility of the ternary system. An increase in the temperature of a liquid will generally cause its density and viscosity to decrease due to reduction in the interaction between molecules [44]. Interfacial tension is also expected to decrease as the temperature increases. Temperature also influences the liquid solubility which increases for some compounds, while it decreases for others [49]. Although temperature is recognized to have significant impact on the fundamental parameters influencing surfactant/cosolvent in situ flooding, the impact of temperature on NAPL mass recovery has not been systematically evaluated in the literature.

The purpose of this study is to assess the effects of coupling hot water and cosolvent flooding on NAPL recovery from porous media. For demonstration purposes the NAPL and cosolvent considered in this study are toluene and ethanol, respectively. Toluene is a petroleum product that ranks among the most commonly encountered organic contaminants at hazardous waste sites [50]. Ethanol is a cosolvent that is widely considered in in situ NAPL remediation because of its low cost and intoxicity. However, these compounds serve as examples because temperature influences a number of parameters that control the entrapment, mobilization and solubility of practically all NAPLs. Specifically, we first examine the influence of temperature on the physical properties of the toluene–ethanol–water system and how that relates to the non-dimensional capillary, Bond and total trapping numbers [27,51]. One factor that can impact the effectiveness of cosolvent flooding is the development of displacement instabilities and fingering which occur when the resistance to flow of the displacing fluid is less than that of the displaced fluid [25,48,52–54]. The change of the fluid properties of the multiphase system with temperatures is used to assess the impact of temperature on the alcohol flood stability. Laboratory scale flushing experiments are also performed to evaluate the potential for enhanced NAPL toluene recovery through the variation of the flushing solution composition and temperature.

2. Experimental procedure

2.1. Fluid properties

Batch experiments were performed to evaluate the dependence of the ternary phase diagrams, solubility and interfacial tension of the ethanol–toluene–water system on temperature. The ternary phase diagrams describe the solubilization potential of the components within the various phases present in the system [55]. A titration procedure was used to determine the turnover points between the one-phase and two-phase regions which define the location of the miscibility curve on the ternary phase diagrams [56,57]. A solution of known composition was placed in a glass vial capped with a Teflon minivalve to minimize evaporation. The components of the ternary phase diagram (toluene, water and ethanol) were gradually added to the solution using gastight macrosyringes. The turning point was observed directly from the change in transparency. The titration method was performed at 20 °C and 40 °C. A water bath was used to maintain a constant temperature.

The solubility of toluene as a function of ethanol content and temperature was measured by contacting known amounts of toluene and water–ethanol solution for 24 h to reach equilibrium. A water bath was used to maintain a constant temperature of the multiphase system throughout the 24-h period. Samples from the aqueous phase were then extracted by a gas tight syringe and analyzed using Hewlett-Packard 5890 Gas Chromatography equipped with flame ionization detector (detection limit = 2 mg/L). Toluene solubility experiments were conducted at 20 °C and 40 °C. For each ethanol content and temperature considered, duplicate solubility measurements were performed.

The interfacial tension (IFT) between the NAPL and aqueous phases was measured with a KSV 703 Digital Tensiometer using the Du Nouy Ring method. The IFT measurements were conducted at 20 °C and 40 °C and for ethanol contents ranging from 0 to 35% (by

mass). For ethanol contents greater than 35%, reliable estimates of the IFT were not measured due to the miscibility of the multiphase system. For quality control, the IFT measurements were collected in triplicates.

2.2. Column flooding experiments

The in situ flooding experiments were performed in a vertically oriented Kontes glass column (inner diameter: 4.8 cm, length: 30 cm). The column was closed at both ends using a perforated Teflon® cap and a stainless steel screen was placed inside the caps to prevent the loss of fines. The caps contained a built-in small reservoir to allow the uniform distribution of injected liquids. The columns were filled progressively in layers of about 2 cm of dry clean sand with mean grain diameter of 0.2 mm. The sand consisted of 98.6% SiO_2 with no clay, silt size particles and organic content.

The same compaction procedure was applied to all column flooding experiments to produce similar conditions. After soil compaction, the columns were saturated by injecting distilled water upwards for at least 24 h at a low flow rate (1 mL/min) to minimize air entrapment. This corresponds to more than 8 pore volumes of water flushing prior to the toluene injection and ethanol flushing. The average porosity within the sandpack was about 0.36, which corresponds to a column pore volume of about 195 mL.

Contamination of the water saturated sandpack was achieved by introducing 10 g of toluene (Merck, Gas Chromatography grade) into the column through a gastight syringe connected to a vial equipped with a Mininert valve to minimize losses by evaporation. The toluene was colored with Oil red O to visually observe the initial distribution of the NAPL and its subsequent flushing. The toluene was injected upwards with specific discharge of 0.003 cm/s. It was visually observed that upon termination of NAPL injection, the toluene was limited to approximately the lower most 10 cm of the column (NAPL source zone) for all experiments. The resulting average NAPL-phase saturation in the source zone was about 0.18. The non-uniform initial distribution of the NAPL within the source zone which is limited to a portion of the column was selected to resemble field settings where hydraulic gradients are rarely sufficient to promote the development of more uniform distributions of NAPL [22].

All flooding experiments were conducted with an upwards specific discharge of about 0.003 cm/s. The ethanol contents considered in the flooding experiments ranged from 20 to 100% by mass, while the temperatures ranged from 10 to 40 °C. This range of temperatures is consistent with other in situ groundwater remediation studies involving hot water flooding (e.g., [46,48]). The lower end temperature is representative of temperatures encountered in the field. In each experiment, about 4 pore volumes of remedial solution were injected through the column.

To achieve an average temperature of about 40 °C in the column, the inflow reservoir was immersed in a constant temperature water bath. To maintain a steady-state temperature of the effluent at about 40 °C, the system was heated using a band heater with an insulation tape wrapped around the column. To achieve steady effluent temperatures of about 10 °C, cooling bands were wrapped around the length of the column. During the flushing experiments, the temperature was monitored continuously at the inlet and exit of the column and along the outer surface of the column.

3. Results

3.1. Dependence of fluid properties on temperature

Available data on the expansion of organic chemicals with temperature shows that these chemicals typically expand about 0.1%
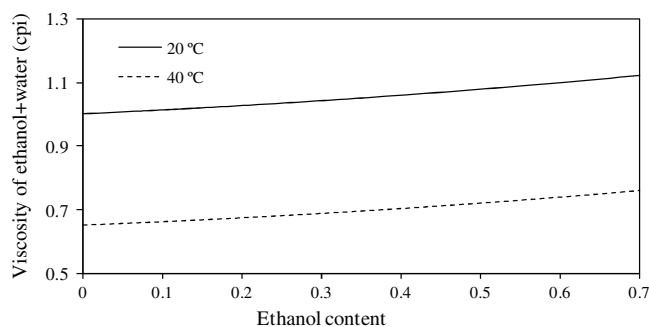

Fig. 1. Viscosity of the flushing solution as a function of ethanol content (mass fraction) at 20 and 40 °C (computed using the Refutas method [64]).

per degree Celsius [44]. For an increase in temperature from 20 to 40 °C, the toluene density decreases from 0.86 to 0.85 g/mL while the ethanol density decreases from 0.78 to 0.77 g/mL [58,59]. The density of water varies by less than 1% as the temperature increases from 20 to 40 °C. Therefore, the density of the multiphase system comprising of water, ethanol and toluene would vary by less than 2% over the range of temperatures considered in this study. These variations are minor compared to variations in the other fluid properties, unless a change from LNAPL to DNAPL or vice versa occurs.

Temperature has a strong influence on flushing solution – such as water and alcohol – and NAPL viscosities (e.g., [60,61]). For an increase in temperature from 20 to 40 °C, the toluene viscosity decreases from 0.59 to 0.47 cp [62]. The viscosity of water decreases from 1 to 0.66 cp, while the ethanol viscosity decreases from 1.2 to 0.84 cp [63]. The viscosity of the flushing solution as a function of ethanol content and for different temperatures is shown in Fig. 1. These viscosities were computed using the Refutas method [64] which gives the viscosity of a mixture as a function of the viscosity of its components. While the flushing solution viscosity increases slightly with increase in ethanol content, a change in temperature from 20 to 40 °C yields a 40% reduction in viscosity.

Fig. 2 shows the measured IFT of a water–ethanol–toluene system as a function of ethanol content and for different temperatures. The standard error computed from the triplicate IFT measurements was less than 0.1 dyn/cm for all ethanol contents. For a temperature increase from 20 to 40 °C, the absolute drop in IFT is small, about 1–4 dyn/cm depending on ethanol content. However, the relative decrease in IFT with temperature becomes significant at ethanol contents in the range of 30–40% by mass and this could induce NAPL mobility. At lower ethanol contents, the IFT remains high and NAPL mobilization is not expected to occur at both temperatures. On the other hand, at alcohol contents near unity, the liquids are fully miscible and an increase in the system temperature will have minimal impact on NAPL mobility. This suggests that the impact of combining hot water to in situ alcohol flooding would be most significant at intermediate alcohol contents.
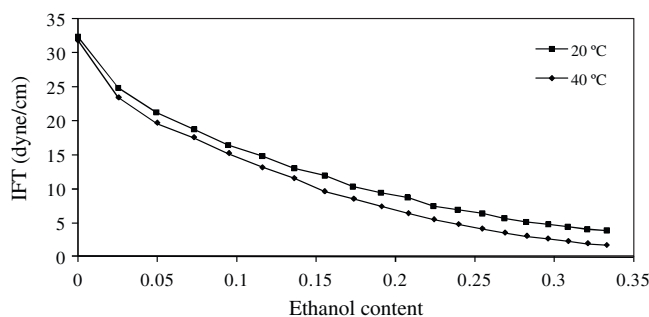

Fig. 2. Interfacial tension of the flushing solution and toluene as a function of ethanol content (mass fraction) at 20 and 40 °C.
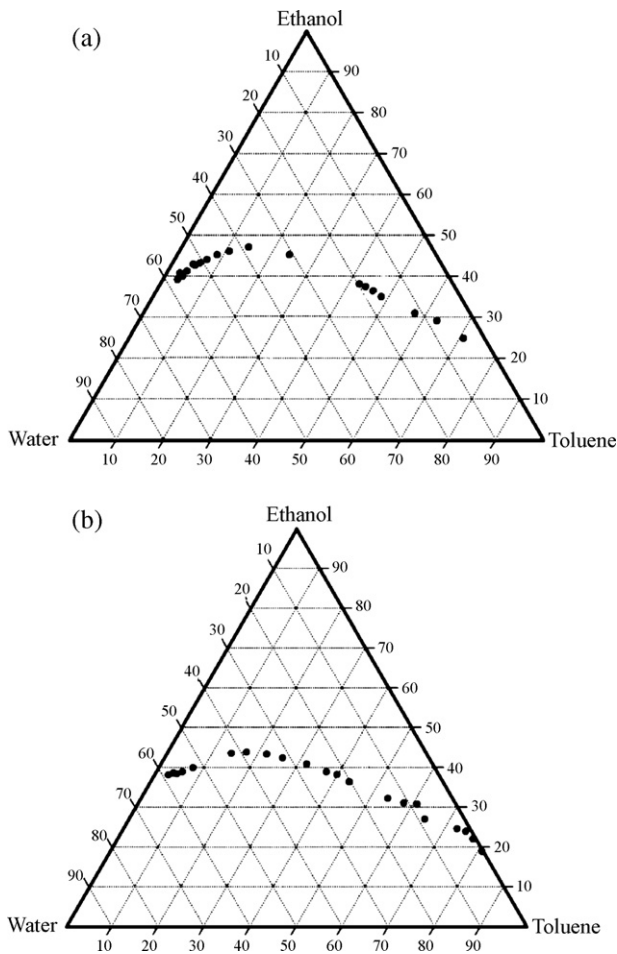
Fig. 5. Solubility of toluene in the flushing solution as a function of ethanol content (mass fraction) at 20 and 40 °C.

Fig. 5 shows the measured solubility of toluene in the flushing solution as a function of ethanol content at 20 and 40 °C. The error bars represent the mean standard error of the replicate data. The solubility of toluene is strongly influenced by ethanol content and temperature. The data are consistent with the log-linear cosolvency model which predicts the log transform of the solubility to be a linear function of ethanol content (e.g., [49]):

$$\log C_m = \log C_w + \sigma_c f_c \tag{1}$$

where C_m and C_w are the solubilities in ethanol–water mixture and water, respectively; σ_c is the cosolvency power; f_c is the volume fraction of ethanol in the mixture. The cosolvency power correlates to log K_{ow} where K_{ow} is the octanol–water partition coefficient of the solute [49]. The cosolvency power at 20 and 40 °C are determined from linear regression as 2.4 ($r^2 = 0.96$) and 3.0 ($r^2 = 0.97$), respectively. Yalkowsky [49] estimates that the cosolvency power at a temperature of 25 °C is about 2.8 which falls within the computed cosolvency power values.

3.2. Impact of temperature on the capillary, Bond and total trapping numbers

The combined effect of temperature on the mobility of the NAPL can be evaluated through the total trapping number which is a ratio of the viscous and buoyancy forces to capillary forces. The trapping number for two immiscible liquids is defined in terms of the capillary and Bond numbers [51]:

$$N_{Ca} = \frac{q_w \mu_w}{\sigma_{ow} \cos \theta} \tag{2}$$

$$N_B = \frac{\Delta \rho g k k_{rw}}{\sigma_{ow} \cos \theta} \tag{3}$$

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin \alpha + N_B^2} \tag{4}$$

where N_{Ca}, N_B and N_T refer to capillary number, Bond number and total trapping number, respectively; q_w is specific discharge of the aqueous phase; μ_w is viscosity of aqueous phase; σ_{ow} is interfacial tension between the NAPL and aqueous phase; θ is the contact angle; $\Delta \rho$ is the density difference of the NAPL and aqueous phase; g is gravitational acceleration; k is intrinsic permeability; k_{rw} is the relative permeability of the aqueous phase; and α is the angle of flow to horizontal axis.

In the case of vertical flow ($\alpha = 90$), the total trapping number reduces to:

$$N_T = \left| N_{Ca} + N_B \right| \tag{5}$$

The onset of residual NAPL mobilization has been observed to occur for total trapping number values in the range of 2×10^{-5} to 5×10^{-5} [27,51].

The effect of temperature on the total trapping number is shown in Fig. 6. The total trapping number was computed at 20 and 40 °C

Fig. 3. Water–ethanol–toluene miscibility curve at (a) 20 °C and (b) 40 °C.

The reduction in IFT of the system can also be seen from the miscibility curve shown in Fig. 3 for temperatures of 20 and 40 °C. At the higher temperature the miscibility curve approaches the water–toluene axis, enabling the two phases to become fully miscible at lower amounts of ethanol. The increase of the miscibility of the ethanol–water–toluene with temperature is also depicted in Fig. 4 which shows the ethanol content of the plait point (point where the compositions of the two-phase system approach each other) and the peak point on the miscibility curve as a function of temperature. The data plotted on these two curves were compiled by Skrecz et al. [65] from previous published studies. They also include the data collected in the present study at 20 and 40 °C.
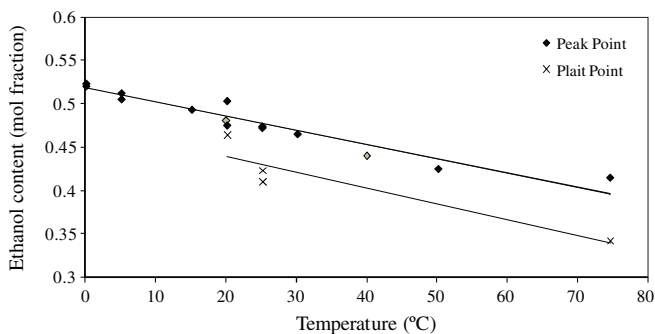

Fig. 4. Ethanol content (mole fraction) of the plait point and peak point of the miscibility curve as a function of temperature (based on data compiled by Skrecz et al. [65]). Data from current study are marked in grey.
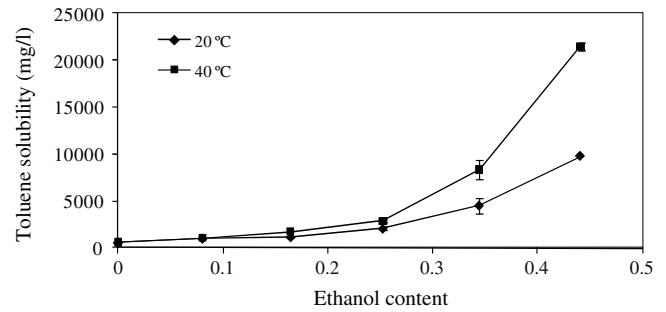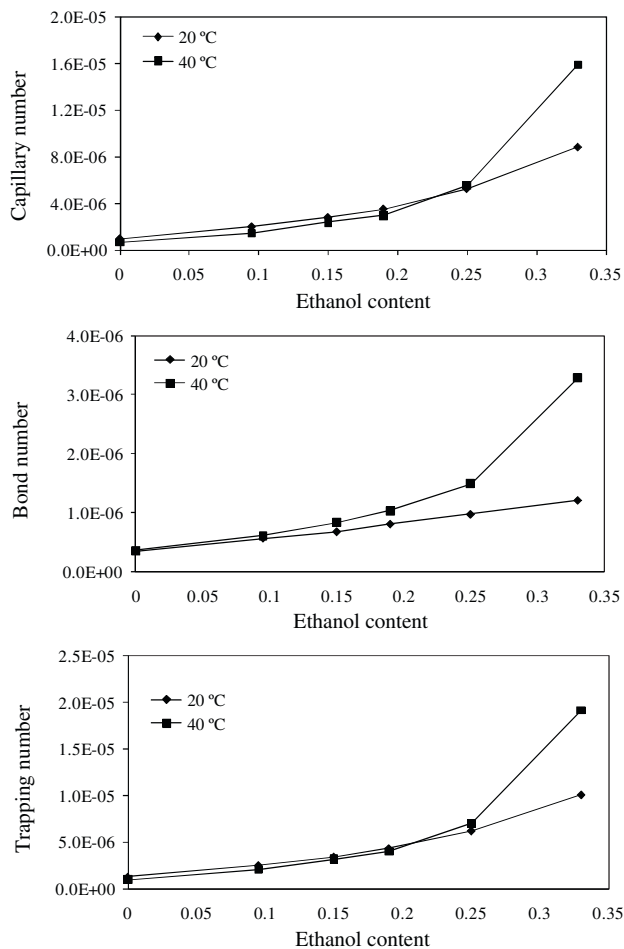
Fig. 6. Capillary, Bond and total trapping number as a function of ethanol content (mass fraction) at 20 and 40 °C.

using the viscosity, IFT, and density relationships presented above and assuming a Darcy velocity $q_w = 0.003$ cm/s, intrinsic permeability (clean sand) $k = 10^{-7}$ cm^2, a relative permeability $k_{rw} = 0.9$, $\alpha = 90$, and $\theta = 0$. These parameters correspond to the column flushing experiments that will be discussed in the following section. For ethanol contents of up to 25% by mass, the total trapping number exhibits a slight decrease as the temperature increases, with the decrease in the viscosity of the flushing solution and the decrease in IFT almost offsetting each other. For these ethanol content levels and the considered range of temperatures, mobilization of the NAPL is not expected to occur. The net increase in the recovered NAPL mass when the system temperature is increased would be primarily due to the increase in solubilization.

For ethanol contents of 30% or greater, the total trapping number is expected to increase rapidly with increase in temperature (Fig. 6). This increase in the total trapping number results from the reduction of the IFT which appears in the denominator of the capillary and Bond numbers (Eqs. (2) and (3)). For ethanol contents of about 35–40% and temperature of 40 °C, the total trapping number is estimated to exceed the critical threshold of 2×10^{-5}. On the other hand, the total trapping number at 20 °C and 40% ethanol content remains below this critical threshold suggesting little mobility would occur at the lower temperature. Consequently, the increase in temperature at this ethanol content is predicted to instigate NAPL mobility, and that can lead to a substantial increase in NAPL recovery. For higher ethanol contents, increasing the temperature would still yield lower IFT (Fig. 2) and higher solubility (Fig. 5), but the impact on NAPL recovery would be less dramatic because NAPL

mobility occurs at both temperatures. Under such low IFT conditions, the definition of the total trapping number becomes invalid because the two fluids are miscible.

3.3. Impact of temperature on the alcohol flooding stability

In stable displacement, small perturbations as a result of microscopic heterogeneities along the interface separating two fluids are dampened out and a sharp planar wetting front is maintained between the fluids [54]. Displacement is classified as unstable when these minute perturbations expand into larger fingering. One criterion that predicts the onset of instabilities along the interface between two miscible fluids is given by [25,52]:

$$v_{crit} = \frac{kk_{r1}(\rho_1 - \rho_2)g \sin \beta}{\mu_1(M - 1)} \tag{6}$$

where the subscripts 1 and 2 refer to the displacing and displaced fluids, respectively; v_{crit} is the critical Darcy velocity that delineates stable from instable displacement; k is the intrinsic permeability; k_{r1} is the relative permeability of the displacing fluid; μ_1 is the absolute viscosity of the displacing fluid; ρ_1 and ρ_2 are densities of the two fluids; β is the angle between the direction of flow and the horizontal; $M = k_{r1}\mu_2/k_{r2}\mu_1$ is the mobility ratio. In miscible displacement a gradual change in composition exists near the interphase [66]. Instabilities develop due to unfavorable contrasts in gravitational forces and/or viscous forces. Gravitational instability occurs when the numerator of Eq. (6) is negative, while viscous instabilities occur when the mobility ratio which appears in the denominator is less than one (i.e., the mobility of the displacing fluid is less than that of the displaced fluid). If both types of instabilities are present, the displacement is always unstable. On the other hand, the flow is unconditionally stable when neither instabilities are present. The flow is conditionally stable when either viscous displacement or gravitational instability is present. Viscous forces balance out gravitational instabilities (negative numerator) provided the actual Darcy velocity of the alcohol flood exceeds the critical velocity given by Eq. (6). Gravitational forces balance out viscous instabilities (negative denominator) when the actual Darcy velocity is lower than the critical velocity.

As indicated above the viscosity and density of the flooding fluid and NAPL decrease as temperature increases. The impact of temperature on miscible displacement stability must take into consideration the combined effect of these factors. Fig. 7 is a plot of the critical Darcy velocity for the ethanol–toluene–water system considered in this study. The flow is assumed upwards, similar to the column experiments. The critical velocity is given as a function of ethanol content and for different values of, k_{rw}/k_{rn}, the ratio of the relative permeability of the ethanol solution and the NAPL, and k_{r1}/k_{r2} for different temperatures. Gravitational instabilities occur at ethanol content of about 0.63 (by mass) or greater, which correspond to flooding solutions that are less dense than toluene. Depending on the ratio of the relative permeabilities of the NAPL and aqueous solutions, which are function of the porous medium, the fluids and the phase saturations, viscous instabilities may also occur. For k_{rw}/k_{rn} greater than 2, the mobility ratio is greater than 1 and viscous instabilities would not be present. On the other hand, for lower k_{rw}/k_{rn} values, the mobility ratio would be less than one and hence, viscous instabilities would develop. The overall stability of the system takes into account both gravitational and viscous forces, as shown in Fig. 7.

Temperature can enhance/diminish the stability of the system, depending on ethanol content and the ratio k_{rw}/k_{rn}. For k_{rw}/k_{rn} values near unity, the unstable zone at ethanol contents greater than 0.63 is slightly larger with increase in temperature. On the other hand, for larger k_{rw}/k_{rn} values, the possibility of stable miscible displacement at low ethanol contents is enhanced at 40 °C.
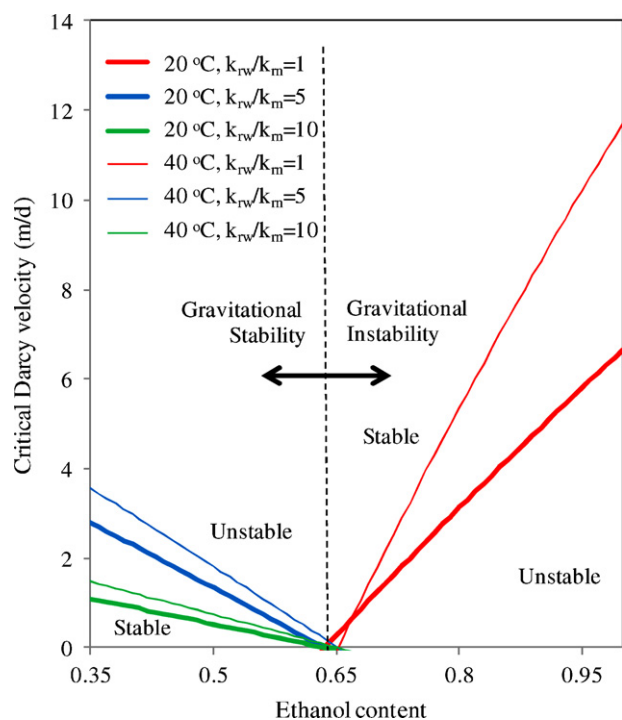
Fig. 7. Critical Darcy velocity distinguishing stable from unstable miscible displacement as a function of ethanol content (mass fraction) and ratio of relative permeabilities at 20 and 40 °C.

As the column experiments will show (Section 3.4), significantly enhanced toluene mobilization may be achieved using less ethanol in the flushing solution when the system temperature is increased from 20 to 40 °C. Using less ethanol in the flooding solution would likely lead to more stable displacement by reducing the chance of gravitational instabilities.

3.4. Column experiments

The toluene effluent concentration and mass removal from the sand-packed column for different ethanol content are shown in Fig. 8. These experiments were conducted at a temperature of 20 °C. Only a small fraction of the toluene was recovered when 20 and 40% ethanol solution were injected through the column. On the other hand, significantly higher toluene recoveries were observed with 60% and 100% ethanol solutions. The sharp increase in the effluent toluene concentration at these higher ethanol contents (Fig. 8a) was due to enhanced dissolution and to mobilization of NAPL-phase toluene which was confirmed visually from the dyed NAPL in the collected effluent samples. This is consistent with total trapping number calculations (Fig. 6) which does not predict significant mobilization for ethanol contents of 40% or less and at 20 °C. The asymmetry in the breakthrough curves is a result of NAPL mobilization which leads to the transport of a NAPL bank just ahead of the cosolvent flushing front [55]. The tail of the breakthrough curves may be due to some less accessible toluene mass trapped within the soil.

The ethanol flooding experiments were also repeated at temperatures of 10 and 40 °C. Fig. 9 shows the effluent concentration and toluene mass removal for 40% ethanol content at 20 °C and 40 °C. Fig. 10 shows corresponding plots for 60% ethanol content and temperatures of 10, 20 and 40 °C. A comparison of the mass removal for all cases considered is shown in Fig. 11.

For the case with 40% ethanol content, increasing the system temperature from 20 °C to 40 °C resulted in an increase in toluene mass recovery from 6% to 47%, a factor of about 8. The solubility
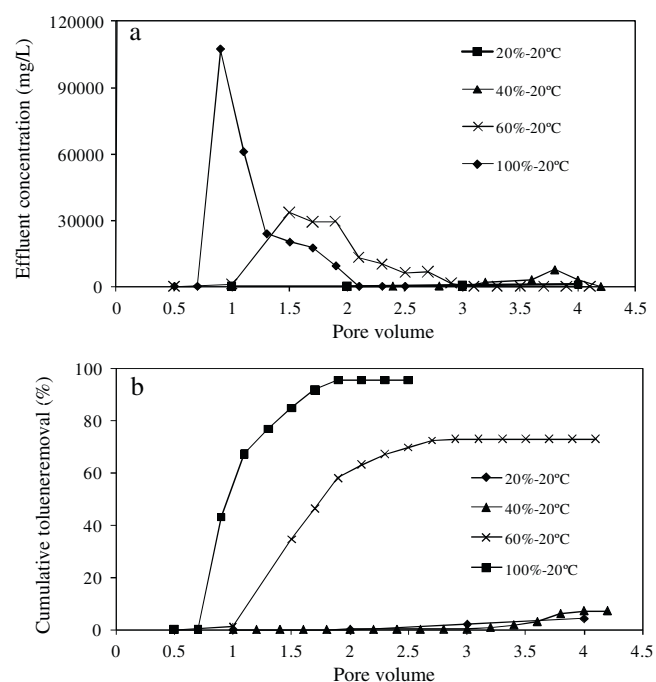

Fig. 8. (a) Effluent toluene concentration and (b) toluene mass removal for different ethanol contents (by mass) in the flushing solution at 20 °C.
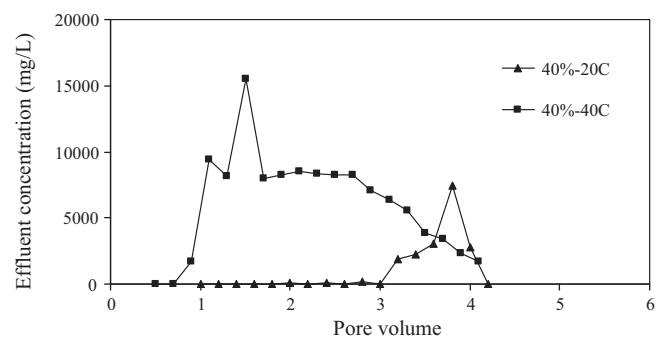

Fig. 9. Effluent toluene concentration for 40% ethanol content in the flushing solution at 20 and 40 °C.

of toluene for 40% ethanol content on the other hand increased by a factor of 2.1 from 7200 mg/L to 15,000 mg/L, for temperatures of 20 and 40 °C, respectively (Fig. 5). Moreover, the peak toluene concentration in the effluent for the case of 40 °C was close to 16,000 mg/L, which exceeds the solubility limit. The sharp increase in mass recovery for the case of 40% ethanol and 40 °C and the
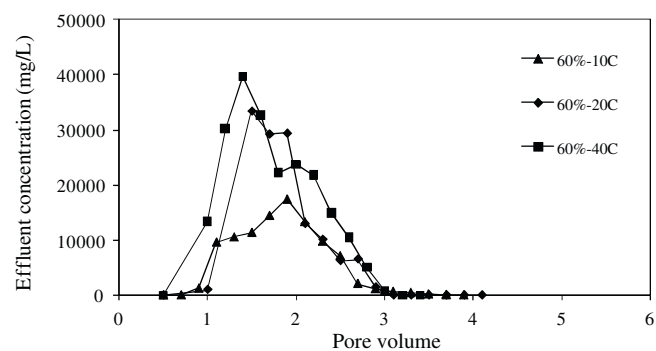

Fig. 10. Effluent toluene concentration for 60% ethanol content in the flushing solution at 10, 20 and 40 °C.
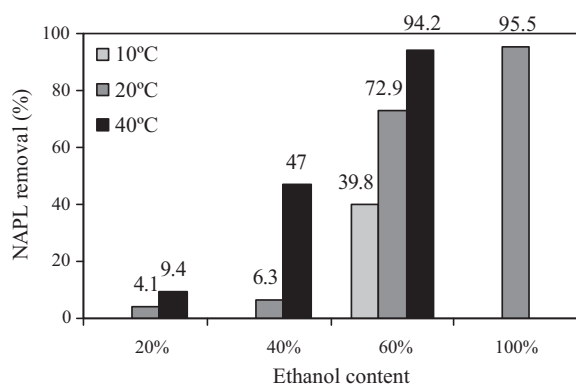
Fig. 11. Cumulative toluene removal for different ethanol contents and temperatures.

increase in effluent concentration beyond solubility indicate that NAPL mobilization has occurred. Inspection of the effluent also showed free product at 40% ethanol and 40 °C but practically no free phase toluene at 40% ethanol and 20 °C. NAPL mobility at 40 °C and 40% ethanol content is also consistent with the total trapping number calculation (Fig. 6).

A significant increase in recovered toluene with increase in temperature was also observed in the case with 60% ethanol content. For temperatures of 10, 20 and 40 °C, the recovered toluene mass were 40%, 73% and 94%, respectively. The increase in mass recovery with temperature was due to both enhanced solubility (Fig. 5) and mobilization. It is important to note that although the flushing solution at this high ethanol content and the NAPL are miscible (i.e., can fully mix under equilibrium batch conditions), in the column these two liquids may be present in two phases due to non-equilibrium conditions even at 100% ethanol flushing (as also observed by Palomino and Grubb [53]). The relative impact of temperature on toluene NAPL recovery is relatively smaller than the case with 40% ethanol content because at the higher ethanol content (60%), some NAPL mobilization occurred at all 3 temperatures.

Because subsurface temperatures are often closer to 10 °C, the difference in mass recoveries at 10 and 20 °C (40% vs. 73% mass recovery) point to the importance of maintaining the temperature in any laboratory scale evaluation close to what would be encountered in the field for more consistent evaluation of the real system.

For the case with 20% ethanol content, increasing the temperature of the injected solution from 20 to 40 °C led to an increase in mass recovery from 4.1% to 9.4% (Fig. 11). The small absolute increase in toluene recovery is attributed to the increase in solubility with temperature at the 20% ethanol content (Fig. 5) and absence of NAPL phase in the effluent at both temperatures. The absence of NAPL mobilization is consistent with the relatively high measured IFT (Fig. 2) and with total trapping numbers that are less than the critical value at the 20 and 40 °C.

Overall, the flushing experiments presented above show that a relatively small change in the temperature of the multiphase system may potentially have a significant impact on the recovery of NAPLs from porous media. Alternatively, these experiments also show that the same performance can be achieved but with a significant reduction of the ethanol content in the flushing solution when the system temperature is slightly elevated (Fig. 11, 60% ethanol content at 40 °C compared to 100% ethanol at 20 °C). This reduction in the amount of injected chemicals is desirable, particularly when these chemicals are not always completely recovered and their impact on the environment is not always benign.

While uncontrolled downward migration of NAPL is a potential risk when NAPL mobilization is instigated, the injection of ethanol solutions at moderately elevated temperatures may lead to a lower

risk of downward movement. The reduced ethanol content that would be used in these applications would lead to higher flushing solutions densities (i.e., closer to that of water) and, hence, is likely to lead to less uncontrolled downward spreading of the NAPL. Palomino and Grubb [53], based on a two-dimensional laboratory scale study, observed similarly that a reduction in the ethanol content from 100% to 50% led to a substantial decrease in the NAPL downward migration.

Another potential advantage of injecting the flushing solution at elevated temperatures is the possible reduction in operating costs for the same NAPL mass recovery. Although the costs of NAPL source remediation technologies are highly dependent on site-conditions, it is recognized that the costs of chemicals and residue disposal encountered in surfactant/cosolvent flushing generally constitute a significant portion of total costs [3,67,68]. For example, results of cost analyses conducted by Lowe et al. [3] show that the cost of chemicals, which includes surfactants and alcohols used in flooding solution, may be as high as 60% of total costs at large sites. At smaller sites, the treatment of the produced fluids can be a significant component of the cost. Hence, the reduction in the use of chemicals and in the production of fluids requiring treatment when hot water is coupled with cosolvent flushing may lead to important cost savings. The use of hot water would involve additional expenditures such as increased utility costs and the costs of purchasing additional equipment (e.g., water boiler). However, these costs will generally constitute a small fraction of total costs [3,47].

4. Conclusions

Batch and column experiments were conducted to assess the phase behavior of an ethanol–water–toluene multiphase system and the impact of system temperature on the flushing stability and NAPL recovery mechanisms from saturated porous media. The temperatures considered in this study ranged from 10 °C to 40 °C, with ethanol contents ranging from 20% to 100%.

The main findings of this study are:

- The viscosity, solubility and IFT of the multiphase (water–ethanol–toluene) are strongly dependent on temperature. The magnitude of the temperature dependence is function of the ethanol content of the system.
- Calculation of the total trapping number as a function of ethanol content and for different temperatures shows that, as expected, the total trapping number increases when the ethanol content of the flushing solution is increased. The effect of temperature on the other hand is more complex. For low ethanol contents (up to 25% by mass), the total trapping number is slightly reduced due to reduced viscosity of the flushing solution and a slight decrease of the IFT. For these conditions, the increase in NAPL recovery would be primarily due to increase in solubility. On the other hand, a large increase in the total trapping number is observed at ethanol contents in excess of 30% by mass due to the decrease in the IFT. Under these conditions, increasing the system temperature would lead to enhanced NAPL mobility.
- The results of the flushing experiments indicate that the impact of temperature on NAPL recovery is most pronounced at intermediate ethanol contents (about 40–60% by mass). The increase in temperature from 20 to 40 °C with 40% ethanol content resulted in an increase from 6% to nearly 47% mass recovery. A large increase was also observed at 60% ethanol content (NAPL mass recovery of 73% vs. 94%). These large increases are primarily attributed to mobilization due to reduced IFT and, to enhanced solubilization. In contrast, the NAPL recovery for 20% ethanol and at 20 °C was limited (about 4%) due to the low toluene solubil-

ity and high IFT of the system. Even at 40 °C, the recovered NAPL mass did not exceed 10%.

- Increasing the temperature of the system can lead to similar NAPL mass recoveries, but using less chemicals. The decrease in injected chemical agents is desirable because some of these chemicals can have adverse impacts on the environment. Moreover, because the cost of chemicals and residue disposal constitute a significant portion of operational costs, the reduction in the use of chemicals through the coupling of hot water and cosolvent flushing may yield to lower overall costs.
- While laboratory experiments are often conducted at room temperatures, temperatures in the field are typically lower (10 °C or lower). The difference in temperature, though small, can lead to potentially significant difference in system performance.
- The decrease in the viscosity of the flushing solution with increase in temperature may lead to unstable displacement conditions. However, operating at higher temperatures may allow the use of lesser ethanol contents, while yielding comparable NAPL recovery, which in turn would lead to higher densities of the flushing solution, reduced gravitational instabilities and lower risk of downward NAPL migration.

Overall, the performed batch and flooding experiments and ensuing analysis show that temperature can have an important impact on NAPL recovery. In field applications, the benefits of coupling hot water and cosolvent flushing are strongly dependent on site-specific conditions including NAPL composition, its spatial distribution and subsurface properties. Prior to implementation, further analysis would be needed to assess the feasibility and practicality of this technology and to determine the flushing solution composition and temperature for the optimal enhanced NAPL recovery.

Acknowledgments

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