AN EXPERIMENTAL INVESTIGATION OF HOT WATER AND COSOLVENT FLUSHING FOR REMEDIATION OF NAPL-CONTAMINATED AQUIFERS

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Abstract

Pump-and-treat is the most commonly used method for removing contaminants from groundwater but has proven ineffective in the case of nonaqueous phase liquids (NAPLs). Two methods that have been used to enhance recovery of crude oil, hot water and alcohol flooding, were investigated in the laboratory as a means of enhancing the dissolution and recovery of NAPLs in groundwater. A ubiquitous NAPL, tetrachloroethylene (PCE), was chosen for recovery in this investigation.

In investigating hot water flooding, the temperature-dependence of several fluid properties was first evaluated over the range from 5°C to 40°C. Among fluid properties, the most substantial variations with temperature were seen in PCE diffusivity and aqueous and PCE phase viscosity: PCE diffusivity increased by 162%, while the aqueous and PCE phase viscosities increased by 51% and 31% respectively. PCE solubility was shown experimentally to have a minimum value near 20°C (225 mg/l), which is substantially higher than the majority of published values. Steady-state dissolution experiments were then conducted in a jacketed, 2.5-cm internal diameter by 1-cm long column, with both glass beads and a natural coastal sand as packing material. Mass transfer rate coefficients increased with temperature and with NAPL saturation; the mass transfer rate coefficient increased by a factor of two as temperatures rose from 5°C to 40°C. A comparison of the results with existing dimensionless correlations for mass transfer in porous media elucidated the role of diffusivity and the Schmidt Number (Sc) in such models. Overall, the data suggest that addition of heated water to a pump-and-treat system could yield greater recoveries of dissolved PCE than with conventional methods,
although the improvement is not dramatic over the temperature range studied. However, heated water is expected to be much more beneficial for NAPLs with lower boiling points.

A second promising approach for enhanced remediation of NAPL-contaminated aquifers is the use of chemical cosolvents to enhance the efficiency of conventional pump-and-treat remediation. Miscible cosolvents such as alcohol promote dissolution of NAPLs into the aqueous phase; reduce interfacial tension between NAPLs and water, thus enhancing NAPL mobilization; and may alter physical properties that control or influence subsurface contaminant transport and fate processes. Methanol is an attractive cosolvent because it is readily available, inexpensive, and mutually miscible with water and many NAPLs. For these reasons it was selected for study for the remediation of PCE-contaminated porous media.

The PCE/methanol/water system was studied to evaluate the effect of methanol concentration on interfacial tension, equilibrium phase composition, and phase density. When volumetric methanol concentrations in the aqueous phase increased from 0% to 60%, interfacial tension between the NAPL and aqueous phases decreased by 73%, aqueous phase PCE solubility increased from 225 mg/l to 9140 mg/l in an approximately log-linear fashion, and the equilibrium NAPL phase densities changed by less than 1%. Methanol predominately partitions into the aqueous phase and does not promote NAPL swelling and uncontrolled mobilization of free-phase NAPL. A subsequent experiment evaluated the effectiveness of a 60% methanol/40%water mixture on the removal of residual PCE from a glass bead medium. Because of the reduction in interfacial tension, this mixture resulted in the mobilization of 12% of the PCE from the column. Subsequent removal of PCE with the methanol/water mixture was by dissolution, and measured mass transfer rate coefficients for a portion of the medium were within a factor of
five of predictions from existing correlations. The data suggest that flooding with methanol/water mixtures significantly decreases the number of pore volumes required to remove NAPLs from contaminated aquifers.
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Summary and Conclusions

1. A laboratory study was performed to investigate the utility of hot water and alcohol flooding on the enhanced remediation of NAPL-contaminated aquifers. A ubiquitous NAPL, tetrachloroethylene (PCE), was chosen as a representative contaminant.

2. Among fluid properties, the most substantial variations with temperature were seen in PCE diffusivity and aqueous and PCE phase viscosity: PCE diffusivity increased by 162%, while the aqueous and PCE phase viscosities decreased by 51% and 31% respectively, for temperatures between 5°C to 40°C. PCE solubility was shown experimentally to have a minimum value near 20°C (225 mg/l), which is substantially higher than the majority of published values.

3. Mass transfer rate coefficients were measured for the PCE/water system as a function of temperature, and increased by less than a factor of two as temperatures increased from 5°C to 40°C. The mass transfer rate coefficient was found to vary with approximately the square root of diffusivity, which is attained by the inclusion of $Sc^{0.5}$ in the mass transfer model. The best-fit value for the exponent of $Sc$ was 0.48. The dependency of $Sh$ on $Sc$ has not been previously demonstrated for the dissolution of NAPL ganglia, although it was postulated by previous investigators.

4. The addition of heated water increased the maximum potential mass flux for PCE dissolution by a factor of two as the temperature increased from 5°C to 60°C. This increase is not large, and in many situations may not be justified given the added expense of heating water.
5. Methanol was investigated as a cosolvent for the removal of PCE from the subsurface. The PCE/methanol/water system was studied to evaluate the effect of methanol concentration on interfacial tension, equilibrium phase composition, and phase density. When volumetric methanol concentrations in the aqueous phase increased from 0% to 60%, interfacial tension between the nonaqueous and aqueous phases decreased by 73%, aqueous phase PCE solubility increased from 225 mg/l to 9140 mg/l in an approximately log-linear fashion, and the equilibrium nonaqueous phase density changed by less than one percent.

6. The phase partitioning behavior of the PCE/methanol/water system was predicted using UNIQUAC (Abrams and Prausnitz, 1975). The predictions were in reasonable agreement with experimental data, suggesting that such models may be used in lieu of extensive experimentation to predict the phase partitioning behavior of other NAPL/alcohol/water systems.

7. Methanol predominately partitions into the aqueous phase and does not promote NAPL swelling. Thus, it is not expected to have as dramatic an effect on NAPL mobilization as other alcohols which strongly partition into the nonaqueous phase. In certain situations uncontrolled mobilization of free-phase NAPL is undesirable.

8. A 60% methanol/water mixture was used to remediate a glass bead porous medium contaminated with PCE at residual saturation. The addition of methanol to the system resulted in the mobilization of 12% of the residual PCE from the column. The remaining PCE was dissolved from the column at a significantly faster rate than with water alone: only 30 pore volumes were required for remediation, while a water flood would have required approximately 1000.
9. The mobilization of residual PCE during the 60% methanol/water flood was due to two factors: a reduction in the interfacial forces holding trapped PCE droplets within the porous medium, and an increase in the density difference between PCE and the aqueous phase. PCE at relatively high residual saturation located above fine microlayers in the porous medium was readily mobilized.

10. A unique x-ray system was used to nondestructively measure the changing amount of PCE in the porous medium during the alcohol flood. Using these measurements, mass transfer rate coefficients were determined for PCE dissolution into a 60% methanol/water mixture. Predictions for mass transfer rate coefficients from existing correlations were within a factor of five of data measured in the upper portion of the column.

11. The addition of methanol increased the maximum potential mass flux for PCE dissolution by one order of magnitude as the methanol volumetric fraction increased from 0% to 60%. This dramatic improvement in mass flux is due to the increase in aqueous phase PCE solubility.

12. Alcohol flooding using methanol shows considerable promise for remediating NAPL-contaminated aquifers.
Recommendations

The need to obtain improved technologies for remediating NAPL-contaminated aquifers has led to investigation of many enhanced remediation techniques. This study has illustrated the limitations of hot water flooding over the temperature range from 5°C to 40°C and the benefits of flooding a PCE-contaminated porous medium with a methanol/water mixture. Clearly, of the two techniques studied, alcohol flooding shows more promise for the remediation of sites contaminated with PCE. However, for other NAPLs with lower boiling points and for situations of rate-limited mass transfer, hot water flooding may still be an effective technology.

The next steps are: (1) study the effect of heated water on the dissolution and mobilization of NAPLs with lower boiling points; (2) better quantify the effect of methanol or other alcohols on the mobilization of residual NAPLs; (3) study the interaction of alcohol and hot water flooding with heterogeneity, both of NAPL residual and soil structure, in two-dimensional laboratory experiments and with computer simulation; and (4) compare the utility of alcohol and hot water flooding with surfactant or steam flooding. This additional work, especially the investigation of heterogeneity using two-dimensional laboratory experiments and computer simulation, will enable a better assessment of the utility of these methods for field applications.
1 Thermally Enhanced NAPL Dissolution

1.1 Background

1.1.1 Introduction

Conventional technologies for remediating contaminated aquifers are often ineffective and excessively expensive. From a technological and economical point of view, it is clear that there is a need for more efficient remediation methods. Therefore, development and implementation of innovative treatment technologies for hazardous waste site remediation is an important problem.

Recently, different technologies have been suggested for enhancing the remediation of contaminated aquifers, many of which have been used for years for enhanced recovery of oil in petroleum engineering. To a certain extent, the knowledge, techniques and field experiences gained in the oil industry are applicable to the problem of subsurface remediation. In this report, results are summarized from an investigation of two techniques for remediating sites contaminated with nonaqueous phase liquids (NAPLs) at residual saturation below the water table: thermally enhanced remediation (or hot water flooding), and alcohol flooding. Both techniques have been suggested for enhanced recovery of oil in petroleum engineering. We begin by reviewing relevant investigations utilizing thermal techniques in the petroleum literature and subsurface hydrology. Results are then presented from a study of heated water on enhanced remediation. In the second part of this report the investigation of alcohol flooding for enhanced remediation is discussed.
1.1.2 Thermal Techniques for Enhanced Oil Recovery

The removal of oil from subsurface strata using hot water and steam has been studied within the petroleum industry for a number of years. Beginning with an early field test reported by Stoval [1934], the use of steam and hot water for enhanced oil recovery has progressed and become increasingly popular. Several recent reviews of investigations and implementations of thermal methods in petroleum engineering have been reported (Buerger et al., 1985; Boberg, 1988; Baibakov and Garushev, 1989).

Willman et al. [1961] found that oil recovery by steam injection was always greater than recovery by cold or hot water injection, and that using steam or hot water is of greatest advantage with heavier oils, since there are significant viscosity reductions as the temperature is increased. He demonstrated in laboratory experiments that steam injection achieved greater oil recoveries than water floods and required less injected liquid for these recoveries. Volek and Pryor [1972] conducted steam injection experiments on a vertical column containing residual oil. The rates of oil recovery were between 66% and 84% immediately following steam breakthrough.

Edmondson [1965] conducted experiments with oils of viscosities 20 cp and 70 cp at 38°C. At 149°C, the oils had viscosities of 1.5 cp and 2.5 cp, respectively. He noted that in flooding experiments at 149°C, piston-like displacement occurred with very little oil produced after water breakthrough. Edmondson [1965] attributed the differences in waterflood behavior of the two oils to differences in interfacial tension. In both the investigation of Willman et al. [1961] and Edmondson [1965], temperature had a significant effect on the relative permeability ratio.
Several researchers have tried to investigate the changes in the relative permeabilities of oil and water with temperature (McCaffery, 1972; Lo and Mungan, 1973; Sufi et al., 1982; Quettier and Corre, 1988). However, results obtained from these investigations have been contradictory.

1.1.3 Thermal Techniques for Remediation of Contaminated Aquifers

To a certain extent, the knowledge and techniques for thermal recovery of oil developed in petroleum engineering are applicable to the problem of steam and hot water treatment for subsurface remediation. There are, however, significant differences. Enhanced oil recovery and aquifer remediation have two different goals: in enhanced oil recovery the objective is to remove all large oil banks, while for aquifer remediation the objective is to remove essentially all separate phase contaminant, even small amounts trapped at residual saturation which result in aqueous phase concentrations below the maximum contaminant level permitted. Because of these differing objectives, studies of enhanced oil recovery neglect many processes which are important in contaminant remediation. These include, for example, dissolution and transport of the organic contaminants in the aqueous phase, and partitioning of the contaminant between the solid phase, aqueous phase, and nonaqueous or oil phase (Hunt et al. 1988a and 1988b; Miller et al., 1990; Falta et al., 1992a and 1992b; Davis and Lien, 1993). These partitioning processes between phases may be rate limited.

The research efforts of Davis and Lien (1993) were focused on the use of moderately hot water for enhancing the displacement of light oily wastes from sands. The oils filled water-wet sand columns before displacement with heated water. Displacement experiments were conducted over the range of 10°C to 50°C, with increases in oil recovery of
approximately 17% to 22% over this range. The main mechanism for the improvement in oil recovery was the reduction of the oil viscosity.

A series of experiments conducted with trichloroethylene (TCE), a bicomponent mixture of benzene and toluene, and a multicomponent gasoline demonstrated the feasibility of steam injection for effective recovery of separate phase liquid contaminants (Hunt et al., 1988b). While the NAPL could not be displaced from the column at water velocities up to 15 m/day, steam was shown to displace the NAPL as a slug just ahead of the steam condensation front, at injection velocities equivalent to 1.5 m/day. The temperature and pressure data indicated multiphase flow behavior within the steam zone. Water flooding following steam flooding demonstrated that contaminant removal was nearly complete. The experimental results showed that only approximately one pore volume of steam was required to achieve cleanup. Theoretical analysis of energy requirements showed that steam displacement is economically attractive.

A series of one- and two-dimensional experiments were completed including the steam displacement of TCE, a benzene-toluene mixture, and gasoline (Steward and Udell, 1989; Basel and Udell, 1989; Basel and Udell, 1991). Steward and Udell [1989] showed that unlike isothermal processes where flow fingering and channeling phenomena limit the mass transfer rates, the movement of the steam zone is controlled by temperature gradients and medium heat capacities. Thus preferential channeling of steam is expected to be of lesser importance. The stability of the condensation front was enhanced due to heat losses from incipient fingers. Rather than small-scale fingering phenomena found during the injection of a gas into a saturated porous media, only large-scale steam tongues on the order of large scale heterogeneities are found during steam injection (Basel and Udell, 1989). For hydrocarbon compounds with lower vapor pressures than decane, the distillation front would move with a velocity less than that of the steam condensation
front (Yuan and Udell, 1993). This condition would be typical for the removal of a compound such as diesel fuel, which is relatively nonvolatile. More volatile compounds such as gasoline have been observed to form a liquid bank ahead of the steam condensation front (Hunt et al., 1988b).

The details of a numerical simulator developed for the purpose of modeling the steam remediation process and validation of one-dimensional steam injection experiments (Hunt et al., 1988b) were given by Falta et al. (1992a and 1992b). A simple criterion was derived for the optimal removal of NAPLs by steam displacement as a function of fluids and porous medium characteristics. It was shown that the efficiency of the steam displacement process depends on the NAPL vapor pressure at the steam temperature and on the NAPL residual saturation. The results of this study indicate that NAPLs having boiling points less than about 175°C may be efficiently removed as a separate phase by steam injection. The displacement of NAPLs with boiling points above about 175°C may not be as efficient as displacement of NAPLs with lower boiling points, although the rate of removal is still much larger than with water and air injection methods.

Field studies were performed to verify the controllability of the movement of the steam zone and to examine the effectiveness of steam injection to recover contaminants from a spill site (Udell, 1992). In this field experiment, steam was injected below the water-table at a site in Livermore, California, contaminated with gasoline. After 24 days of continuous steam injection, the data of cross-hole electrical three-dimensional tomography indicated great success. Results from this study suggest that control over the movement of the steam condensation front can be maintained if the large-scale permeability field is known.
Western Research Institute developed the Contained Recovery of Oily Wastes (CROW) process by adapting technology used for secondary petroleum recovery and for primary production of heavy oil and tar sand bitumen (*United States EPA*, 1992). Steam and hot-water displacement were used to move accumulated oily wastes and water to production wells for aboveground treatment. Steam was injected below the deepest penetration of organic liquids, while hot water was injected above the impermeable soil regions to heat and mobilize the oil waste accumulations. This technology was tested both in the laboratory and at pilot-scale at a wood-treatment site in Minnesota. Removal of NAPLs in the pilot test were the same as that predicted by laboratory studies.

1.1.4 Summary of Thermal Techniques

The laboratory experiments and field scale results presented above indicate that thermal methods can be technologically effective for removal of NAPLs from the subsurface. These investigations have also shown that steam and hot water flooding involve several complex processes. An important process which was not investigated in a systematic manner is the effect of heated water on the rate of mass transfer from NAPLs at residual saturation. Hot water flushes of contaminated aquifer materials will not remove all NAPLs by displacement; instead, trapped droplets will remain at residual saturation, although the heated water will enhance the dissolution process. In addition, although steam flooding will likely displace most NAPLs present, on the edges of the injection zone water heated to temperatures much lower than the boiling point will exist and may be in contact with NAPLs at residual saturation. In this region heated water will have an important effect on NAPL dissolution. The focus of this investigation was to quantify the effect of heated water on the rate of mass transfer for NAPLs at residual saturation,
as well as to determine any impact of heated water on mobilization of trapped NAPL droplets.

1.2 Experimental Methods

1.2.1 Materials

The NAPL used in experiments was tetrachloroethylene (PCE), a denser-than-water chlorinated solvent (HPLC grade, Sigma Chemical Co., Milwaukee, WI; and spectro grade, Eastman Kodak Co., Rochester, NY). Methanol (HPLC grade, Mallinckrodt Specialty Chemicals Co., Paris, KY) was used as a solvent for aqueous PCE samples, and methylene chloride (spectranalyzed grade, Fisher Scientific, Pittsburgh, PA) was used for PCE extractions. Properties of these three chemicals are listed in Table 1. The water used in all experiments was distilled and deionized to 50,000 ohm resistance (Mega-Pure System, models D2 and MP11A, Corning Medical and Scientific, Corning, NY). For column experiments, the water was also deaerated by boiling, then stored under vacuum.

The two types of media used in experiments were glass beads and a natural coastal sand referred to as the Camp Lejeune sand. The sand was gathered from well borings at the Camp Lejeune Marine Corps Base in eastern North Carolina. The glass beads (size 50-80 mesh, U.S. sieve, McMaster-Carr Supply Company, Atlanta, GA) are slightly coarser than the Camp Lejeune sand, but have a similar particle size distribution. Properties of each medium are listed in Table 2. Both the beads and the sand are characterized by very low total organic carbon (TOC) content, thereby minimizing sorption effects.
Table 1. Properties of chemicals used in experiments.

<table>
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<tr>
<th>Property</th>
<th>PCE</th>
<th>Methanol</th>
<th>Methylene Chloride</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Specific gravity(^a)</td>
<td>1.623</td>
<td>0.791</td>
<td>1.327</td>
<td>Lide [1990]</td>
</tr>
<tr>
<td>Dynamic viscosity(^a) (mPa s)</td>
<td>0.93(^b)</td>
<td>0.45</td>
<td>0.55(^b)</td>
<td>Lide [1990]</td>
</tr>
<tr>
<td>Aqueous solubility(^a) (mg/l)</td>
<td>220(^c)</td>
<td>miscible(^d)</td>
<td>13,455(^e)</td>
<td>see notes</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>121</td>
<td>65</td>
<td>40</td>
<td>Lide [1990]</td>
</tr>
</tbody>
</table>

\(^a\) at 20°C unless otherwise indicated
\(^b\) at 15°C
\(^c\) measured this study
\(^d\) Lide [1990]
\(^e\) Horvath [1982]

Table 2. Media properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Glass Beads</th>
<th>Camp Lejeune Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{10}^a)</td>
<td>(\mu m)</td>
<td>237</td>
<td>167</td>
</tr>
<tr>
<td>(d_{50}^a)</td>
<td>(\mu m)</td>
<td>277</td>
<td>225</td>
</tr>
<tr>
<td>(d_{90}^a)</td>
<td>(\mu m)</td>
<td>506</td>
<td>338</td>
</tr>
<tr>
<td>Uniformity coefficient, (U_i^b)</td>
<td></td>
<td>1.20</td>
<td>1.44</td>
</tr>
<tr>
<td>Particle density, (\rho_s)</td>
<td>(g/cm(^3))</td>
<td>2.48</td>
<td>2.66</td>
</tr>
<tr>
<td>Bulk density (column), (\rho_b)</td>
<td>(g/cm(^3))</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td>porosity (column), (\phi)</td>
<td></td>
<td>0.39</td>
<td>0.42</td>
</tr>
</tbody>
</table>

\(^a\) \(d_{50}\) is the median particle diameter.
\(^b\) Uniformity coefficient = \(d_{50}/d_{10}\)

1.2.2 Temperature Control

Most of the experiments were conducted at multiple temperatures. Mass transfer and solubility experiments were conducted with jacketed glassware and a water bath (series
9500, PolyScience Co., Niles, IL, adjustable to 0.1°C) that allowed for temperature control under a fume hood. Other experiments were performed at 10°C, 20°C and 40°C in a constant temperature room (model ESI 4-5 WR, Environmental Specialties, Inc., Raleigh, NC), with an accuracy rating of ±0.5°C.

1.2.3 Interfacial Tension

A ring-type tensiometer (model 70545, Central Scientific Company, Inc., Fairfax, VA) was used to measure the interfacial tension (IFT) between PCE and water. Measurements were made under both instantaneous and equilibrium conditions. Instantaneous measurements were taken immediately after introduction of the two pure phases, while equilibrium measurements were taken after the mixture had aged for at least 48 hours on a mechanical shaker, allowing both phases to reach their mutual solubility limits. A correction factor (ASTM, 1991) was applied to instrument readings.

Previous experience had shown a time-dependency in the equilibrium results. When multiple readings were taken on a single sample, tension values increased with time and number of readings, eventually leveling off. The time required to reach the plateau was reduced by conditioning the tensiometer ring, or immersing it in water for an hour or more before use. The ring-conditioning step preceded surface tension and instantaneous, as well as equilibrium, IFT samples.

The surface tension of water, a known quantity, was also measured to estimate the accuracy of the method. However, the error in surface tension cannot be directly applied to IFT results, because of a difference in measurement methods. The tensiometer ring was pushed down through the PCE-water interface and pulled up through the air-water
surface. Measured surface tensions were all low, with differences between measured and literature values ranging from 0.5% at 40°C to 5.7% at 10°C.

1.2.4 Dissolution

1.2.4.1 Column Design  The column used in dissolution experiments was a 2.5-cm internal diameter jacketed column with Teflon plunger tips, attached to 2-mm internal diameter Teflon tubing (model 5819, Ace Glass, Inc., Vineland, NJ). The plunger tips were inset with glass frits. The porous medium was packed in the column to a depth of about 1 cm for mass transfer, or 5 cm for solubility experiments. Teflon valves and fittings (Omnifit USA, New York, NY) were used with the column. A variable-speed syringe pump (Model 22, Harvard Apparatus, South Natick, MA) was used to pump fluids through the packed column.

Before the column was constructed, a nylon filter with 0.2-μm pores (Nylaflo filter #66602, Gelman Sciences, Inc., Ann Arbor, MI) was glued to the face of one plunger tip with a solvent-resistant, silicone-based sealant (RTV sealant, #730, Dow Corning Corp., Midland, MI). The filter and seal were then wetted and tested for air-entry at a specified pressure. For each type of media, the required pressure, in cm of water, was determined from air-water pressure-saturation curves. The lowest pressure required to bring the system to minimum water content was about 60-cm water for glass beads, and 100-cm water for the Camp Lejeune sand. Following the method of Wilson et al. [1989] and applying a safety factor of two, water pressures used for the air-entry test were 120-cm water for glass bead experiments and 200-cm water for Camp Lejeune sand experiments.

The initial arrangement of the column is shown in Figure 1. Between the nylon filter and the packed bed, a glass fiber disc (grade G6, Fisher Scientific, Pittsburgh, PA) was
used to protect the nylon filter and to maintain a hydraulic connection between layers. On the opposite end of the packed bed were two woven stainless steel screens: first a fine-mesh screen to prevent loss of the fine fraction of the medium, then a coarse-mesh screen for support (mesh sizes 30 and 150, Small Parts, Inc., Miami, FL). The glass frit was removed from the second plunger tip.

Figure 1. Construction of mass transfer column.

The first step in creating a residual NAPL saturation ($S_n$) was to displace most of the water in the initially water-saturated bed with PCE (Figure 2). With the nylon filter above the packed bed, PCE was pumped at a rate of 0.05 ml/min upward through the column. The water-wet filter allowed the passage of water but not PCE out of the packed bed. System pressure, monitored with a manometer, was allowed to rise as high as the
filter test pressure corrected to cm PCE. Generally, water flow from the column ceased before the target pressure was reached. The PCE pumping was stopped at this point.

Following the infiltration step, water was pumped through the column in the opposite direction (downward) to flush out the excess PCE. Generally, a maximum flow rate of 18 ml/min was used, and five to ten pore volumes (PV) of water were flushed through. (For MT9, rates of up to 50 ml/min were used, for a total of 36 PV.) The column was then inverted, and the plunger tip and tubing that had been in contact with separate phase PCE were replaced with an unmodified plunger tip and clean tubing.

Solubility experiments and some of the mass transfer experiments (MT4 and MT6) were conducted at $S_n \approx 0.25$, which resulted from the preceding steps. For experiments MT9
through MT12, however, a lower residual saturation was produced by dissolving a portion of the PCE before sampling. To dissolve the NAPL, water was pumped through the column in alternating directions, at flow rates of 2 to 10 ml/min. Total water volumes ranged from 2 to 4 liters.

1.2.4.2 Sampling Column experiments were designed to allow the measurement of effluent PCE concentration, temperature, flow rate, packed bed dimensions, and final $S_n$. Flow volumes, and thus dissolution, were minimized in mass transfer experiments in order to assume constant $S_n$ over the duration of the experiment.

The main elements of the sampling apparatus are shown in Figure 3. Temperature was controlled with the jacketed column, a jacketed beaker (#5340, 600 ml, Ace Glass, Inc., Vineland, NJ), and the constant temperature bath. Fluid temperatures were monitored with thermocouples at column inlet and outlet points.

Flow rates were controlled with the syringe pump. A rate of 1.0 ml/min was used for solubility experiments, corresponding to an interstitial velocity of about 6.5 m/d. For mass transfer, all experiments were run at a rate of 5 ml/min (42 to 51 m/d for glass beads, 37 to 40 m/d for Camp Lejeune sand).

Effluent samples were drawn directly from the effluent tubing with a syringe (250-μl Gastight, Hamilton Co., Reno, NV). Initially, a standard syringe needle 5-cm long was directed into the tubing outside of the column, with the result that the effluent had, in some cases, changed temperature by the time it reached the needle. In order to eliminate the temperature change as a source of error in concentration measurements, the method was modified for later experiments. For MT11, MT12 and solubility experiments, an extra-long syringe needle (about 14 cm) inserted through a Teflon septum was
used to collect samples from within 1 cm of the packed bed, where the intended temperature was sustained. Samples were not filtered, since the temperature change en route to the filter could cause dissolved NAPL to condense and be erroneously removed from the sample. Six to ten effluent samples were collected at each temperature, with the exception of one series of only three samples. Samples of 0.25 ml were injected into 3 ml of methanol in 4-ml glass vials, and sealed with Teflon septa. PCE concentrations were analyzed with a UV spectrophotometer within 24 hours after sample preparation. Equipment blanks were drawn from the influent water, using a procedure similar to that for effluent samples.

Problems with flow rate were encountered in two of the experiments. In MT11, at 20°C and 40°C, the flow rate was visibly slow while the first two to three samples were drawn, then increased to the correct rate. Similarly during MT9 sampling at 5°C, water leaked
from the packed bed around the plunger tips, effectively decreasing the flow rate. A slow flow rate would result in increased PCE concentrations in the effluent.

At the end of each mass transfer experiment, the PCE remaining in the column was extracted with methylene chloride to determine the final $S_n$. Six to eight samples of diluted extract were analyzed for PCE concentration with a UV spectrophotometer. $S_n$ was calculated from the concentration of PCE per volume of solvent, the volume of solvent added to the column, and packed bed porosity. A test of the method, using a column spiked with a known volume of PCE, produced an estimate of $S_n$ correct to within two percent of the actual value.

Finally, to determine the loss of NAPL over the course of the experiment, the mass of PCE which was eluted from the column was added to the final extracted volume to compute the initial $S_n$. As a percentage of the volume of PCE initially present in the packed bed, losses ranged from 1.4% (MT4) to 5.2% (MT11). Thus, the average $S_n$ values for the experiments were relatively constant.

1.2.4.3 UV Spectrophotometry

PCE concentrations in fluid samples were analyzed with a UV spectrophotometer (models U-2000 and U-3300, Hitachi Instruments, Inc., Danbury, CT). Methanol-based samples were analyzed at a wavelength of 225 nanometers (nm) with reference to a baseline of water. Methylene chloride-based samples were analyzed against a methylene chloride reference at a wavelength of 240 nm.

Standard solutions of the same fluids were analyzed along with the samples to calibrate UV absorbance values to PCE concentration. Fresh standards were prepared for each round of analysis. The linear correlation between absorbance and PCE concentration
was determined by regression of the standard absorbances. The coefficients of multiple determination for calibration curves were consistently above 0.99, and were usually above 0.999.

1.3 Results

1.3.1 Solubility

Measured values of solubility ($C_s$) are shown in Figure 4. Each experimental concentration shown is an average of six to nine samples. Three of the points are from a mass transfer experiment that produced concentrations at the solubility limit. That experiment, MT8, was run with the Camp Lejeune sand at a PCE residual saturation of about 0.25 and a flow rate of 5 ml/min.

Other researchers' results are presented for comparison. The commonly cited figures of about 150 mg/l at 20°C are represented by Horvath [1982], who fitted a polynomial equation to a group of previously published experimental data. More recently, organic solubilities in water were measured by Stephenson [1992]. Stephenson's [1992] results are in better agreement with the magnitude of this study's results. A value of 225 mg/l was measured as part of the alcohol flooding portion of this study (reported in Table 9), which is supportive of the value reported here.

Instead of continuously increasing with temperature, PCE solubility has a minimum around 20°C (about 225 mg/l). Solubility at 5°C (240 mg/l) is slightly higher than at 40°C (235 mg/l). These values were used in calculations of mass transfer rate coefficients.
1.3.2 Phase Density

The variation of water density with temperature is well-known. For this study, densities were taken from *Weast* [1985] and are shown in Figure 5.

PCE density was estimated from a regression equation developed by the American Institute of Chemical Engineers (*AIChe*, 1985). The density correlation, fitted to four
experimental data sources, is accurate to within three percent between the temperatures of 250.80°K and 620.00°K (-22.35°C and 346.85°C). This correlation is

\[
\rho_n = \frac{A}{B^{1+(1-\frac{T}{C})D}}
\]

where \(\rho_n\) is the PCE phase density (kmol/m^3), \(T\) is temperature (°K), \(A = 1.3170\), \(B = 0.32758\), \(C = 620.00\), and \(D = 0.35630\). This correlation is also plotted in Figure 5.

1.3.3 Interfacial Tension

Average values of equilibrium and instantaneous IFT are shown in Figure 4. Instantaneous sample averages were based on five tension readings; equilibrium sample averages were taken from the last six to fourteen readings in a series of measurements.

In addition to the measurements, IFT was estimated by three empirical methods: Antonov [1907], Donahue and Bartell [1952], and Girifalco and Good [1957]. The method of Donahue and Bartell [1952] is restricted to temperatures near 25°C. Lyman, et al. [1982] cite the superior theoretical basis of the Girifalco and Good [1957] approach, but recommend Antonov [1907] for utility and accuracy. Using Antonov’s [1907] rule, Lyman, et al. [1982] found a low average error for hydrocarbons, especially those with low solubilities. In Figure 6, mutually saturated fluids were assumed when using the empirical methods of Antonov [1907] and Donahue and Bartell [1952].
Experimental results by other researchers are also shown in Figure 6. Demond’s [1988] measurement was made by a pendant drop method, several hours after the two fluids were introduced. The measurement methods used by Girfalco and Good [1957] and USCG [1978] were not reported by the authors.

An inverse relationship between IFT and temperature was predicted by empirical correlations, but was not confirmed by the experimental results. The variability among the
Figure 6. Effect of temperature on PCE/water interfacial tension.

Experimental averages is less than one percent. Thus, the thermal variation in PCE/water IFT is small, and the role of IFT in thermal flushing is insignificant in this range of temperatures.
1.3.4 Viscosity

The variation of aqueous phase viscosity with temperature is well-known and was taken from *Weast* [1985]. These data are plotted in Figure 7.

PCE viscosity was estimated from a regression equation developed by the American Institute of Chemical Engineers (*AIChE*, 1985). The viscosity correlation, fitted to six
experimental data sources, is accurate to within ten percent, between the temperatures of 250.80°K and 567.79°K (-22.35°C and 294.64°C). Although the error associated with viscosity seems high, the results agree to within 1.3% with experimental viscosity data by McGovern [1943] for the temperature range of interest. The AIChE [1985] correlation is

$$\mu = \exp(A + \frac{B}{T} + C\ln T)$$

where $\mu$ is viscosity (Pa sec), $T$ is temperature (°K), $A = -1.9780$, $B = 555.00$, and $C = -1.2216$. This correlation is also shown on Figure 7.

1.3.5 Molecular Diffusion Coefficient

The greatest temperature variability among the fluid properties occurs for the diffusivity of PCE in water. Figure 8 shows $D_m$, estimated from the empirical correlation of Tyn and Calus [1975], reported in Reid et al. [1987]. Reid et al. [1987] reported errors less than ten percent with the Tyn and Calus [1975] method.

1.3.6 Dissolution

1.3.6.1 Mass Transfer Rate Coefficient Six mass transfer experiments (MT4, MT6, MT10, MT12, MT9, and MT11) each yielded data at three temperatures for a total of eighteen data sets. MT4, MT6, MT10, and MT12 were conducted in the glass bead
medium, with $S_n = 0.25$ for MT4 and MT6 and $S_n = 0.11$ for MT10 and MT12. MT9 and MT11 were conducted in the Camp Lejeune sand with $S_n = 0.10$ for MT9 and $S_n = 0.14$ for MT11. Effluent concentrations of PCE in the water phase were measured for each experiment, with at least two and at most nine measurements of the effluent concentration made at each temperature. Individual measurements were used in subsequent analysis for $K^*_f$, the mass transfer rate coefficient. Here $K^*_f = a_{na} k_l$, where $a_{na}$
is the specific interfacial area defined as $a_{na} = A_{na}/V$, $A_{na}$ is the interfacial area between the nonaqueous and aqueous phases, $V$ is the aqueous-phase volume of the porous medium, and $k_I$ is the mass transfer coefficient. The mass transfer rate coefficient can also be defined in terms of the bulk volume of the porous medium, $K_I = \phi(1 - S_n)K_I^*$. To determine $K_I^*$ from the data, an analytical expression taken from Miller et al. [1990] was used, which is applicable for steady-state dissolution and transport

$$K_I^* = \frac{[v_a - \frac{2D_I}{L} \ln(1 - \frac{C(L)}{C_s})]^2 - v_a^2}{4D_I} \tag{3}$$

where $v_a$ is the mean pore velocity of the aqueous phase, $D_I(=\tau D_m + \alpha_I v_a)$ is the longitudinal dispersion coefficient, $\tau$ is the tortuosity, $D_m$ is the molecular diffusion coefficient of the solute in the aqueous phase, $L$ is the length of porous medium, and $\alpha_I$ is the longitudinal dispersivity. The aqueous-phase velocity was computed based on the average column porosity and PCE saturation

$$v_a = \frac{Q}{A\phi(1 - S_n)} \tag{4}$$

where $Q$ is the volumetric flow rate through the column, $A$ is the cross-sectional area of the packed bed, and $\phi$ is the porosity. For any one set of experiments comprising data at three temperatures $v_a$ was constant.
\( \tau \) was calculated from an adapted form of the Millington-Quirk model (Millington and Quirk [1961])

\[
\tau = \frac{[\phi(1 - S_n)]^{10/3}}{\phi^2}
\]

while \( \alpha_1 \) was specified as \( 1.5d_{50} \), where \( d_{50} \) is the median particle diameter. This was based upon the findings of other investigators who measured values of \( \alpha_1 \) between \( (1 - 2)d_p \) (see Figure 7-4 of Bear, 1979), where \( d_p \) is a representative particle diameter.

Effluent PCE concentrations \([C(L)]\) and fitted \( K^*_t \) are summarized in Table 3 for all eighteen experiments. In general, the poorest precision occurred where the fewest samples were collected, e.g., the data for MT4 at 20°C and MT9 at 40°C which were based on two and four samples, respectively. The large confidence intervals on the reported \( K^*_t \) for MT11 at 40°C illustrates the sensitivity of \( K^*_t \) to large \( C(L)/C_s \) values, even with precise measurement of \( C(L) \). The largest value of \( C(L)/C_s \) was 0.94.

Results for the glass bead experiments are plotted in Figures 9 and 10. Over the temperature range from 5°C to 40°C, \( K^*_t \) increased by a factor of 2.16 (MT4), 2.11 (MT6), 1.30 (MT10), and 2.56 (MT12). In agreement with other investigators, including Miller et al. [1990], Powers et al. [1992], and Imhoff et al. [1994a], \( K^*_t \) increased with \( Re = v_a\rho_a d_p/\mu_a \), the Reynolds number. However, the variation in \( Re \) has a slightly different implication for this work. The researchers listed varied \( Re \) by changing the aqueous phase flow rate. In this study, the flow rate was constant, so differences in \( Re \) were due primarily to changes in viscosity with temperature. \( K^*_t \) also increased with \( S_n \), which was also observed by other investigators.
Table 3. Measured $C(L)$ and computed $K_i^*$ with 95% confidence intervals.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>5°C</th>
<th>20°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glass Beads:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT4</td>
<td>107.9 ± 3.7</td>
<td>117.2 ± 24.8</td>
<td>168 ± 1.0</td>
</tr>
<tr>
<td>MT6</td>
<td>116.6 ± 6.6</td>
<td>129.1 ± 11.4</td>
<td>175.2 ± 5.5</td>
</tr>
<tr>
<td>MT10</td>
<td>3340 ± 280</td>
<td>4490 ± 640</td>
<td>7060 ± 490</td>
</tr>
<tr>
<td>MT12</td>
<td>67.2 ± 8.7</td>
<td>67.5 ± 14.3</td>
<td>81.9 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>1440 ± 220</td>
<td>1620 ± 430</td>
<td>1880 ± 48</td>
</tr>
<tr>
<td></td>
<td>50.5 ± 6.5</td>
<td>86.9 ± 5.2</td>
<td>105.8 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>1000 ± 150</td>
<td>2150 ± 170</td>
<td>2560 ± 78</td>
</tr>
<tr>
<td><strong>Camp Lejeune Sand</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT9</td>
<td>109.0 ± 21.5</td>
<td>58.4 ± 11.6</td>
<td>140.3 ± 25.3</td>
</tr>
<tr>
<td>MT11</td>
<td>2170 ± 570</td>
<td>1090 ± 260</td>
<td>3300 ± 1070</td>
</tr>
<tr>
<td></td>
<td>59.9 ± 6.7</td>
<td>99.5 ± 12.9</td>
<td>212.3 ± 6.6</td>
</tr>
<tr>
<td></td>
<td>1100 ± 150</td>
<td>2370 ± 430</td>
<td>9840 ± 1150</td>
</tr>
</tbody>
</table>

Data from the Camp Lejeune sand are shown in Figures 11 and 12. Trends in these data are less clear than those associated with data from the glass bead experiments. This may be due to errors in measured flow rates, which could have caused elevated $C(L)$ and $K_i^*$ values at three of the six points, i.e., MT9 at 5°C, and MT11 at 20°C and 40°C. Despite these possible errors and the scatter in the data, $K_i^*$ increases with temperature, $S_n$, and $Re$, just as in the data from the glass bead experiments.
1.3.6.2 Modeling  A number of empirical models, listed in Table 4, have recently been formulated to describe steady-state mass transfer in saturated porous media (Miller et al., 1990; Powers et al., 1992; Imhoff et al., 1994a). Following the approach of Powers et al. [1992] and Imhoff et al. [1994a], experimental data were compared to the existing models by plotting $Sh = K_i d_p / D_m$ versus $Re$ for each, shown in Figure 13.
Figure 10. Mass transfer rate coefficient versus $Re$ for glass bead experiments.

The models have been modified for purposes of comparison, where necessary. Powers et al. [1992] computed $Re$ using the superficial rather than the interstitial velocity. The form listed in the table was modified for consistency with other models. Parker et al. [1991] did not specify a model but found that their mass transfer results were underestimated by the correlation of Miller et al. [1990] by an average factor of 2.9 (Powers et al., 1992). The model listed in Table 4 is an estimated representation of the data from Parker et al. [1991]. Imhoff et al. [1994a] and Powers et al. [1992] defined the
mass transfer rate coefficient in terms of the bulk volume of the porous medium rather than the aqueous-phase volume. The correlation of Miller et al. [1990] and Parker et al. [1991] and the data reported here were modified to be in agreement with this definition. Finally, the model attributed to Geller [1990] was put in the dimensionless form presented by Imhoff et al. [1994a].
$Sh$ was predicted from each correlation using a selected set of conditions applicable to each investigation. The conditions chosen were those which most closely resembled experiments MT10 and MT12 ($S_n = 0.11$, $\theta_n = 0.04$, $d_p = 0.0277$ cm) from this study. Ranges of valid $Re$ are given in Table 4; other parameters used in individual models are listed in Table 5.
Table 4. Mass transfer correlations.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Correlation</th>
<th>Valid Conditions</th>
</tr>
</thead>
</table>
| Geller [1990], estimated by Imhoff et al. [1994a] | $Sh = 70.5Re^{0.33} \theta_n^{0.44} S_{ni}^{0.56} (d_p/d_{ni})^{1.67} \phi^{-0.67}$ | $0 < \theta_n < 0.037$
|                                        |                                                                             | $0.006 < Re < 0.013$                                                             |
| Miller et al. [1990]                   | $Sh = 12(\phi - \theta_n)Re^{0.75} \theta_n^{0.60} Sc^{0.50}$              | $0.016 < \theta_n < 0.07$
|                                        |                                                                             | $0.0015 < Re < 0.1$                                                              |
| Parker et al. [1991], taken from Powers et al. [1992] | $Sh = 34.8(\phi - \theta_n)Re^{0.75} \theta_n^{0.60} Sc^{0.50}$              | $0.02 < \theta_n < 0.03$
|                                        |                                                                             | $0.1 < Re < 0.2$                                                                 |
| Powers et al. [1994]                   | $Sh = 4.13Re^{0.598} \delta^{0.673} U_i^{0.369} (\theta_n/\theta_{no})^\beta$ | $0 < \theta_n < 0.065$
|                                        | $\beta_4 = 0.518 + 0.114\delta + 0.1U_i$                                    | $0.012 < (\phi - \theta_n)Re < 0.2$                                             |
|                                        | $\delta = d_{50}/0.05\text{ cm}$                                            |                                                                                  |
| Imhoff et al. [1994a]                  | $Sh = 340Re^{0.71} \theta_n^{0.87}(x_f/d_p)^{-0.31}$                         | $0 < \theta_n < 0.04$
|                                        |                                                                             | $0.0012 < Re < 0.021$                                                           |
|                                        |                                                                             | $1.4 < x_f/d_p < 180$                                                            |

*a where $x_f$ is the distance into the region of residual NAPL*
Figure 13 shows the experimental data occupying the same region as other researchers' correlations. The variation in $Sh$ between models has been attributed by Imhoff et al. [1994a] to differences in techniques used to establish residual NAPL saturations. That argument is supported by the fact that the displacement method used in this study was similar to methods used by Powers et al. [1992] and Imhoff et al. [1994a], whose correlations in the figure are closest to the experimental data. The displacement techniques
<table>
<thead>
<tr>
<th>$D_{m}$ (cm/sec)</th>
<th>$u_{p}$ (cm)</th>
<th>$S_{w}$ (cm)</th>
<th>$f$ x</th>
<th>$\Omega$</th>
<th>$\phi$</th>
<th>$d_{so}$ (cm)</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3E-06</td>
<td>8.8E-06</td>
<td>8.0E-06</td>
<td>8.0E-06</td>
<td>8.0E-06</td>
<td>8.0E-06</td>
<td>8.0E-06</td>
<td>8.0E-06</td>
</tr>
<tr>
<td>0.25</td>
<td>1.45</td>
<td>0.392</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.376</td>
<td>0.38</td>
</tr>
<tr>
<td>0.036</td>
<td>0.045</td>
<td>0.043</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.038</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Table 6. Parameter values used in mass transfer correlations.
were intended to imitate the NAPL-emplacement processes occurring in real groundwater systems. In contrast, Parker et al. [1991] and Miller et al. [1990] stirred NAPL with their porous media to create NAPL residual, possibly creating smaller, more spherical NAPL blobs (Powers et al., 1992). The technique used by Geller [1990] resembled the displacement methods except that residual NAPL occupied only a part of the porous medium in her experiments. Consequently, her work required a complex, multidimensional method of analysis to account for lower dissolution rates (Imhoff et al., 1994a).

Also apparent in Figure 13 is a discrepancy in the trend of data from this study and that from other investigations. $Sh$ decreases with increasing $Re$ in this study, but increases with increasing $Re$ in other studies. The reason for the opposing trends is found in $Sh$. None of the existing models was based on temperature-variant data, so variations in $Sh$ are due primarily to $K_l$. For data from this investigation, $Sh$ is controlled not only by $K_l$, which increases by about 100%, but also by $D_m$, which increases by 162% over the temperature range used in the experiments. In the isothermal models represented in the figure, $D_m$ is constant, or varies only slightly with different compounds.

The diffusivity is a key factor in theoretical models of interfacial mass transfer. Mass transfer by diffusion alone is represented by the stagnant film model, in which the mass transfer coefficient is directly proportional to diffusivity, whereas models incorporating advective as well as diffusive processes predict that $K_l$ is proportional to $D_m$ to a power less than one, frequently 0.5. In dimensionless form, these translate to $Sh \propto Sc^{0.0}$ for purely diffusional mass transfer, and $Sh \propto Sc^{0.5}$ for combined diffusion and advective processes.
Miller et al. [1990] included $Sc^{0.5}$ in their model, advocating the combined effects of advective and diffusive transport, but their use of relatively $D_m$-invariant data precluded its validation. As was seen in Figure 8, the variation in $D_m$ with temperature can be substantial: between 5°C and 40°C, $D_m$ decreases by 83%.

Given the sensitivity of the data from this study to $D_m$, a more appropriate comparison to existing correlations would include $Sc$. In Figure 14, the model predictions are modified by $Sc^{0.5}$, based on the estimated $D_m$ values given in Table 5. The trends of the experimental data are brought into closer agreement with previous works, suggesting that $Sh$ is a function of $Sc$. The contrasting trends of Figures 13 and 14 indicate that the exponent of $Sc$ is probably close to 0.5.

In order to determine the relationship between $Sh$ and $Sc$, a dimensionless model was fit to the experimental data. Because of the small number of data, the number of fitted parameters was kept to a minimum, and only the simplest power-law form was considered. The model employed was of the form used by Miller et al. [1990]:

$$Sh^* = \beta_0 Re^{\beta_1} \phi^{\beta_2} Sc^{\beta_3}$$

where $\beta$'s are parameters to be estimated or fitted, and $Sh^* = K_i^* d_p / D_m$. Since the two media types were similar in size and because of the uncertain quality of the sand results, additional measures of media geometry, such as those used by Geller [1990] and Powers et al. [1992], were not of primary relevance to this study. Similarly, since transient dissolution and dissolution fronts were not pertinent to this study, initial NAPL conditions...
Fixed values for exponents $\beta_1$ and $\beta_2$ were chosen, based on their counterparts in the existing models, so that only the remaining two parameters were fitted. The software
package SYSTAT [1988] was used to fit $\beta_0$ and $\beta_3$, using both linear and nonlinear regression. Linear regression was used by first linearizing (6) with a logarithmic transformation. Because of uncertainty in the quality of data using the Camp Lejeune sand, only the twelve measured $K_i^T$ from the glass bead experiments were used. In both regression analyses the squared residual for each data point was weighted with its estimated standard deviation in the least squares regression.

Results of the model analyses are summarized in Tables 6 and 7. Most values for $\beta_3$ lie between 0.4 and 0.8. Using $R^2$ as a measure of the quality of the fit, the data are best approximated with the highest exponents on $Re$ (0.75) and $\theta_n$ (1.0). However, any combination of specified parameters produces an acceptable fit. Recognizing the limits of the data set (a small number of data and limited replicates), it makes sense to choose a model on the basis of preferred values for $\beta_1$ and $\beta_2$, rather than on statistical superiority alone.

An exponent of $\beta_1 = 0.75$ was selected for $Re$, both because of the good regression results and for its agreement with other researchers. Both Miller et al. [1990] and Imhoff et al. [1994a] proposed this or a similar value. Powers et al. [1992] found a best-fit exponent of 0.736 for $Re$ when $Sh$ was posed as a function of only $Re$ and $\theta_n$ (not their preferred model).

For $\beta_2$, a value of 0.9 was chosen. Again, this value brought good results in regression analysis and has some support in the literature. A similar value of 0.87 appears in the model by Imhoff et al. [1994a]; Powers et al. [1994], in a transient dissolution model, found optimal values for the $\theta_n$ exponent ranging from 0.750 to 0.960, depending on porous media characteristics. Although the experimental data of this study were from steady-state experiments, the lower NAPL saturation levels represented in half of the
Table 6. Results of nonlinear regression.

<table>
<thead>
<tr>
<th>Specified Parameters</th>
<th>Fitted Parameters with 95% Confidence Intervals</th>
<th>Adjusted R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β₁</td>
<td>β₃</td>
</tr>
<tr>
<td>0.33</td>
<td>0.44</td>
<td>0.26 ± 0.87</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>4.61 ± 5.76</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>10.05 ± 7.17</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>12.93 ± 8.35</td>
</tr>
<tr>
<td>0.50</td>
<td>0.44</td>
<td>2.33 ± 3.68</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>3.59 ± 4.24</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>7.80 ± 5.38</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>10.03 ± 6.47</td>
</tr>
<tr>
<td>0.60</td>
<td>0.44</td>
<td>2.02 ± 3.09</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>3.10 ± 3.54</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>6.72 ± 4.57</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>8.63 ± 5.60</td>
</tr>
<tr>
<td>0.75</td>
<td>0.44</td>
<td>1.62 ± 2.37</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>2.48 ± 2.70</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>5.37 ± 3.59</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>6.89 ± 4.53</td>
</tr>
</tbody>
</table>

data set were established by dissolution of a higher initial saturation. Consequently, the NAPL saturation element of the transient dissolution correlation is relevant to this work.

With the chosen values of β₁ and β₂, the regression results for the nonlinear fit (with 95% confidence intervals) are

\[
β₀ = 5.369 ± 3.594
\]
\[
β₂ = 0.479 ± 0.091
\]

(7)
Table 7. Results of linear regression.

<table>
<thead>
<tr>
<th>Specified Parameters</th>
<th>Fitted Parameters with 95% Confidence Intervals</th>
<th>Adjusted R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta_1$</td>
<td>$\beta_3$</td>
</tr>
<tr>
<td>0.33</td>
<td>0.44</td>
<td>0.79 ± 2.11</td>
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<tr>
<td></td>
<td>0.60</td>
<td>1.23 ± 1.69</td>
</tr>
<tr>
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<td>0.90</td>
<td>2.06 ± 1.08</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>2.34 ± 0.97</td>
</tr>
<tr>
<td>0.50</td>
<td>0.44</td>
<td>0.54 ± 2.03</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.99 ± 1.62</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>1.82 ± 1.04</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>2.09 ± 0.96</td>
</tr>
<tr>
<td>0.60</td>
<td>0.44</td>
<td>0.40 ± 1.98</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.84 ± 1.58</td>
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<tr>
<td></td>
<td>0.90</td>
<td>1.67 ± 1.02</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.95 ± 0.95</td>
</tr>
<tr>
<td>0.75</td>
<td>0.44</td>
<td>0.18 ± 1.91</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.62 ± 1.51</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>1.45 ± 0.99</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.73 ± 0.95</td>
</tr>
</tbody>
</table>

Using linear regression on the transformed model

$$\beta_0 = 1.455 \pm 0.995$$

$$\beta_2 = 0.506 \pm 0.137$$  \(8\)

Of the two models, the nonlinear form is slightly more robust: although the $R^2$ value is slightly lower, confidence intervals are narrower for the nonlinear than for linear re-
gression. The normal probability plots of the standardized residuals are reasonably linear for both cases, so neither approach can be invalidated on that basis. In either case, model analysis predicts an exponent for $Sc$ of approximately 0.5 for the glass bead experiments.

1.4 Discussion

1.4.1 Physical and Chemical Properties

The effect of temperature variation between $5^\circ C$ and $40^\circ C$ on physical and chemical properties of PCE was determined by laboratory investigation and from an examination of the scientific literature. These results are summarized in Table 8.

Table 8. Effect of temperature variation between $5^\circ C$ and $40^\circ C$ on properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Change</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (water)</td>
<td>-1%</td>
<td>AIChE [1985]</td>
</tr>
<tr>
<td>Density (PCE)</td>
<td>-3%</td>
<td>AIChE [1985]</td>
</tr>
<tr>
<td>Viscosity (water)</td>
<td>-57%</td>
<td>AIChE [1985]</td>
</tr>
<tr>
<td>Viscosity (PCE)</td>
<td>-31%</td>
<td>AIChE [1985]</td>
</tr>
<tr>
<td>Diffusivity (PCE in water)</td>
<td>+162%</td>
<td>Tyn and Calus [1975]</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>±1%</td>
<td>measured</td>
</tr>
<tr>
<td>Solubility (PCE in water)</td>
<td>-2%</td>
<td>measured</td>
</tr>
</tbody>
</table>

Over the range of temperatures studied, the viscosity and diffusivity were the only properties which were significantly affected. The viscosity of both water and PCE decreased by 57% and 31% respectively, while the molecular diffusivity of PCE in water increased...
by 162%. These properties affected the rate of mass transfer as was demonstrated in
the effect of temperature on the mass transfer rate coefficient. However, because tem-
perature over this range did not significantly alter the PCE/water interfacial tension,
mobilization of residual PCE droplets due to increases in water temperature was not ex-
pected.

1.4.2 Mobilization

The mobility of trapped PCE droplets is dependent upon interfacial, viscous and grav-
itational or buoyancy forces. Interfacial forces act to trap droplets within the porous
structure, while viscous and gravitational forces act to mobilize droplets in the direc-
tion of the groundwater velocity (viscous) or gravity (buoyancy for heavier-than-water
droplets). To assess the importance of these forces on mobilization, investigators com-
monly examine two dimensionless groupings: the Capillary number, $Ca = \frac{v_a \mu_a}{\sigma_{na}}$, the
ratio of viscous to interfacial forces; and the Bond number, $Bo = (\rho_n - \rho_a)gd_p^2/4\sigma_{na}$, the
ratio of gravity to interfacial forces. Here, $v_a$ is the pore-water velocity of the aqueous
phase, $\sigma_{na}$ is the IFT between the nonaqueous and aqueous phases, $\rho_n$ and $\rho_a$ are the
nonaqueous and aqueous-phase densities, $g$ is the gravitational acceleration, and $d_p$ is
a representative grain diameter for the porous medium. Mobilization of residual NAPL
may occur if $Ca$ and/or $Bo$ are increased above critical values.

Based upon the changes in physical properties associated with temperature changes be-
tween 5°C and 40°C, neither of these dimensionless numbers will be changed signifi-
cantly. For this reason, pumping heated water within a PCE-contaminated aquifer is
not expected to mobilize PCE residual. This conclusion is consistent with observations
in the mass transfer experiments, where no PCE droplets were observed to mobilize from
the column.
1.4.3 Dissolution

Over the temperature range from 5°C to 40°C, the heated water had a very small effect on the solubility limit of PCE in the aqueous phase, but a significant effect on the rate of PCE dissolution. The measured mass transfer rate coefficients were within the range of values predicted from existing correlations. However, to correctly account for the trend of $Sh^*$ with $Re$, it was necessary to include $Sc$ in the mass transfer model: the diffusivity of PCE in water is significantly affected by temperature, and with the exception of the correlation of Miller et al. [1990] other models assumed a linear dependence of $K_i^*$ on $D_m$. From this study it was determined that for dissolution of residual PCE $Sh^*$ is proportional to $Sc^{0.5}$, which is equivalent to $K_i^* \propto D_m^{0.5}$.

The maximum potential enhancement of PCE dissolution due to heated water is illustrated by examining the maximum potential mass flux, $K_i^*C$, as a function of temperature. (Actual mass flux per unit aqueous-phase volume of the porous medium is $K_i^*(C_s - C)$. The maximum potential mass flux is an upper bound.) The maximum potential mass flux is plotted versus temperature in Figure 15, where $K_i^*$ was estimated from equations (6) and (7), and $C_s$ taken from measured solubilities. The mass flux increases by a factor of two as the temperature increases from 5°C to 60°C. This improvement in the mass flux is due primarily to the increase in $K_i^*$. This increase is not large, and in many situations may not be justified given the added expense of heating water. However, for other NAPLs where $C_s$ is more significantly affected by temperature hot water flooding may still be an effective technology.
Figure 15. Maximum potential mass flux of PCE for representative conditions using equations (6) and (7).
2 Alcohol Flushing

2.1 Background

2.1.1 Introduction

Recently, it has been suggested that surfactants, alcohols, and mixtures of these chemicals may be effective for in situ treatment of aquifers contaminated with hazardous organic compounds. These technologies were originally developed in the petroleum industry, and several reviews have been written on this work (Reed and Healy, 1977; Lake, 1983). To set the background for this investigation, the literature on alcohol flooding in the petroleum industry is reviewed below. This is followed by a review of the work to date using alcohol flooding for remediation of contaminated aquifers.

2.1.2 Alcohol Flooding for Enhanced Oil Recovery

The interest in miscible alcohol flooding in the oil industry increased after the appearance of papers by Pausell [1953] and Gatlin and Slobod [1960]. These authors found in a series of laboratory experiments that recovery of oil displaced by concentrated alcohol solutions was close to 100%. Gatlin and Slobod [1960], Tuber et al. [1961] and Holm and Csaszar [1962] obtained oil recovery rates close to 100% for naphtha, Soltrol, and Kendx in sand columns, using iso-propanol alone or a combination of methanol with either iso-propanol or n-butanol.
Taber et al. [1961] reported that the commercial application of alcohol-slug processes was probably impractical because of the high cost of alcohols and the relatively large amount of alcohol necessary for significant improvement in oil recovery. In this research, Taber et al. [1961] defined the essential characteristics of a system of slugs behaving in a nearly piston-like fashion. This investigation used iso-propanol (IPA) and tertiary butyl alcohol (TBA). The authors studied equilibrium phase behavior for two ternary systems: IPA/Brine/Soltrol and TBA/Brine/Soltrol. It was shown that an essential first step in any investigation of alcohol flooding is the determination of the phase diagram, complete with tie lines and plait point. As a result of the study of phase behavior for these two systems, Taber et al. [1961] predicted and then experimentally demonstrated that two kinds of alcohol displacement exist. In the first type (TBA/Brine/Soltrol), the nonaqueous (or oil) phase dominates as miscibility is approached and, therefore, remains continuous throughout the flood. In the second type, the aqueous phase dominates as miscibility is approached; therefore, the nonaqueous phase passes through a residual saturation state before miscibility is achieved. The behavior of these kinds of systems is characterized by a plait point location on the binodal curve. The following relationships were also studied: recovery versus alcohol slug size, recovery versus initial oil saturation, phase viscosity versus alcohol concentration, and relative permeabilities of stabilized banks.

Several researchers have attempted to simulate alcohol flooding (Wachman, 1963; Donohue, 1963). The experimentally determined phase behavior effects were incorporated into numerical models developed by these authors. The following conclusions were drawn on the basis of these studies: (1) It is possible to simulate the basic features of alcohol displacement in porous media by means of suitably designed numerical models; (2) A theoretically sound method of selecting the immovable oil and water fractions is to base
these upon the relative permeability data; (3) Numerical models can more closely reproduce experimental data when they incorporate nonequilibrium effects.

In the field of physical chemistry, research has shown that alcohols can dissolve significant quantities of oil in water (De Visser et al., 1977; Knickerboker et al., 1979). However, this process is not efficient in dissolving heavier oils (Bellocq et al., 1981). Alcohols with longer chains, such as butanol, pentanol, or hexanol, are more effective, but less soluble in water. To solubilize these heavier oils, a surfactant must be added (Rouz-Desgranges et al., 1981).

Larson et al. (1982) formulated the primary mechanisms of residual oil recovery by alcohol flooding. These mechanisms include solubilization, interfacial tension (IFT) reduction, and swelling of the nonaqueous phase. As the rate of solubilization or dissolution of oil into the aqueous phase increases, oil can be produced in the aqueous phase. The most effective mode for oil recovery is the achievement of complete miscibility. In practice, this condition is difficult to achieve using a finite volume alcohol slug, since the dispersive mixing at the alcohol front may dilute alcohol to a lower concentration, and the alcohol slug may disappear with travel distance. In the two-phase flow region, increasing alcohol concentration leads to a decrease of IFT between the aqueous and nonaqueous phases. This reduction in IFT causes an improvement of the displacement process or oil mobilization. Taber (1969) stated that swelling of oil interacting with alcohol is one of the main mechanisms contributing to enhanced oil recovery. Swelling occurs when the alcohol preferentially partitions into the oil phase rather than into water. In general, higher molecular weight alcohols tend to partition preferentially into the oil phase (Taber et al., 1961; Holm and Csaszar, 1962, Lam et al., 1983). As the oil phase swells it becomes easier to displace and may mobilize.
Lam et al. [1983] studied mobilization of residual oil by an alcohol slug under equilibrium and nonequilibrium conditions. An oil globule is displaced when the IFT is reduced to an extent that the pressure gradient created by motion of the continuous phase is sufficient to overcome the capillary forces holding the globule in place (Taber, 1969; Melrose and Brandner, 1974; Abrams, 1975). Two different classes of experiments were performed by Lam et al. [1983] to determine the sensitivity of swollen residual oil displacement to the capillary number. The oil globules had been swollen by mass transfer from a continuous phase flowing too slowly to displace the drop. A set of experiments was performed on an oil drop that initially contained 15 wt% of n-propanol and some water, with the oil phase composition on the binodal curve. Surprisingly, slightly swollen globules required a larger capillary number for mobilization than the original droplet. Thus, the capillary number required for mobilization can go through maximum as the volume of the oil droplet increases, due to the complexity of pore and globule geometry. A small increase in the volume of a residual oil globule disconnected from other adjacent drops is likely to make the drop more difficult to mobilize; however, large increases in swollen globule volume (greater than 15%) will tend to increase the mobility of the globule, making it much easier to displace. The last statement is very important for practical applications, since it indicates a threshold value for the amount of alcohol required for efficient oil recovery.

2.1.3 Remediation of Contaminated Aquifers by Alcohol Flooding

Removal of residual NAPLs from contaminated ground waters is in many ways analogous to oil recovery from subsurface reservoirs. The effects of solubilization, IFT reduction, and NAPL swelling can be examined using similar techniques.
It is well recognized that the nature of the solvent has an impact on the solubility of organic contaminants (Yalkowsky, 1986; Gupte and Danner, 1987; Pinal et al., 1990). These authors have investigated the theoretical and experimental aspects of alcohol cosolvency on hydrophobic organic chemical solubility. It has been shown that increasing the alcohol volume fraction in water/alcohol systems increases hydrophobic organic chemical solubility in an essentially log-linear manner. Several theoretical approaches have become available over the past decade for dealing with oily contaminant solubility in solvent mixtures. Among these are the following: the UNIQUAC/UNIFAC models (Fredenslund et al., 1975; Prausnitz et al., 1980), the log-linear model (Yalkowsky 1986), and the three-suffix equation method (Williams and Amidon, 1984). Application of the solubility parameter theory to mixed solvents was discussed in a review by Barton [1975]. The results of these investigations showed the possible approaches for choosing the most effective combination of alcohols for different mixtures of contaminants (Pinal et al., 1990).

Zenon [1986] studied the feasibility of in situ alcohol treatment for hydrocarbon contaminated soils. Zenon [1986] used short-chain alcohols (methanol, ethanol, iso-propanol) to increase the dissolution of 1,2,3-trichlorobenzene (TCB) in water. Concentrations as high as 30% to 50% alcohol were required to increase TCB solubility by a factor of ten or more. Iso-propanol was found to be more efficient than ethanol or methanol.

The authors of recent experimental investigations (Boyd, 1991; Brandes, 1992; Patwardhan, 1992; Brandes and Farley, 1993) concluded that alcohol flooding was a promising technology for removing residual NAPLs from ground water. These researchers conducted a set of laboratory experiments at 23°C with isopropyl (IPA), and tert-butanol (TBA) alcohols, and with the NAPLs trichloroethylene (TCE) and tetrachloroethylene
Ternary phase diagrams were determined experimentally for the following systems: (1) IPA/TCE/water, (2) TBA/TCE/water, and (3) TBA/PCE/water. A ternary diagram for the system IPA/PCE/water was estimated by the UNIFAC method. The IFT of these systems were estimated using the method developed by Fu et al. [1986]. The water and alcohol flooding experiments were conducted to evaluate the effectiveness of using different alcohols at different concentrations. Based on their experimental results, Brandes and Farley [1993] concluded the following: (1) 100% recovery of residual TCE can be achieved by using one pore volume of a solution of 70% (by volume) TBA or IPA and 30% water. (2) Use of IPA for displacement of residual PCE is ineffective. Relatively effective removal of PCE (90% recovery) can be accomplished using one pore volume of a solution of 70% (by volume) TBA and 30% water. (3) The cause of the more effective displacement of residual NAPL by TBA is the preferential partitioning of this alcohol into the nonaqueous phase. The swelling of the NAPL phase leads to the formation of a high saturation NAPL bank. (4) The experimental data demonstrated significant reduction in NAPL phase density for long chain alcohols such as TBA. (5) All experimental results are consistent with predictions based on analysis of the corresponding ternary diagrams.

2.1.4 Summary

The review of experimental data presented above demonstrates that alcohol flooding is a complex process which includes mass transfer and alteration of physico-chemical properties of nonaqueous and aqueous phases. Although many features of this process are now known, significant questions remain. These include: Where NAPL and aqueous phases remain immiscible during an alcohol flood, what effect does the alcohol have on the
rate of NAPL dissolution? Is mobilization of NAPL residual during an alcohol flood predictable in real porous media, where the soil structure may be complex and the distribution of NAPL residual nonuniform? Given the importance of ternary phase diagrams for representing the behavior of NAPL/water/alcohol systems and the effort required in measuring them experimentally, how accurate are predictive methods? The intent of this investigation was to address each of these questions.

2.2 Experimental Methods

2.2.1 Overview

To investigate alcohol flooding on enhanced aquifer remediation, the PCE/methanol/water system was selected for study. The importance of PCE as a groundwater contaminant was discussed earlier. Methanol was chosen as a representative alcohol because (1) it is relatively inexpensive, (2) once diluted to small concentrations in groundwater it is readily biodegradable, and (3) it is representative of a class of alcohols which do not significantly partition into NAPLs and thus will not enhance NAPL migration due to swelling of NAPL droplets. Because of the potential difficulty in controlling NAPL movement in the subsurface (e.g., denser than water NAPLs may sink to lower regions of the aquifer) alcohols which do not enhance NAPL mobility are preferred in some situations.

The experimental study began with an examination of the effect of a select range of methanol/water volumetric fractions (0%, 20%, 40%, and 60% methanol by volume) on the system behavior: phase equilibria, phase density, and interfacial tension. A ternary
phase diagram was generated from the experimental data, and then compared with theoretical predictions. With the physical and chemical properties from these experiments coupled with existing data for viscosity and molecular diffusivity from the literature, the system was well-characterized. Finally, a column experiment was performed to measure the effect of a methanol/water mixture on the dissolution and mobilization of residual PCE in a porous medium. Analysis of data from this experiment made use of the physical and chemical properties measured earlier.

2.2.2 Materials

All chemicals were HPLC grade and were used without further purification. Alcohols were purchased from Fisher Scientific, and PCE from Aldrich Chemical Company. Water was deionized and distilled in our laboratory as described earlier. Hydranal-Coulomat/CG cathode solution and Hydranal-Coulomat/AG anode solution for Karl Fischer titrations were purchased from Reidel-deHaen through Fisher Scientific.

All glassware was washed with Alconox laboratory detergent and tap water, rinsed with tap water, soaked overnight in 1.0 N HCl solution, rinsed thoroughly (at least three times) with tap, followed by deionized, distilled water, and oven-dried at 102-105°C. Glassware used in experimental measurements of interfacial tension was submerged overnight in a warm solution of dichromate in sulfuric acid, rinsed thoroughly with tap, followed by deionized, distilled water, and drip-dried on clean filter paper in a reasonably dust-free environment, as per ASTM Designation D 971-91 (ASTM, 1991).

All liquid measurements were made using volumetric pipets, volumetric flasks, or Hamilton Gas-tight syringes, depending on the volume desired.
2.2.3 Equilibrium Phase Partitioning: Generator Columns

In order to describe the equilibrium conditions of a PCE/methanol/water system, it is necessary to measure the equilibrium concentrations of PCE, water and methanol in both the nonaqueous and aqueous phases. Two different experimental techniques were used to create nonaqueous-aqueous phase solutions which were in equilibrium: batch-contacting experiments and experiments using generator columns.

Liquid-liquid equilibria have traditionally been achieved by batch-contacting. Fixed volumes of solute and solvent are combined in a flask or mixing vessel and shaken (shake-flask batch) or magnetically stirred (stir-flask batch) at a controlled temperature. The equilibration period is typically followed by a stabilization period during which solute particulates or colloidal dispersions are separated out of the bulk solvent phase, which is then sampled and analyzed by an appropriate technique. Mutual solubilities may be determined by sampling both equilibrated phases of a binary mixture.

Discrepancies in published solubility data illustrate problems with batch-contacting techniques, particularly when the goal is to saturate water with a hydrophobic organic compound. Because many organic compounds are only sparingly soluble in water, their concentrations may be drastically affected by colloidal or particulate suspensions, by losses due to solute volatilization, and by adherence to the surfaces of transfer vessels. Microemulsion formation may be promoted by turbulent mixing practices typically employed in shake-flask batch methods to enhance mass transfer. More gentle contacting by slow stirring may reduce (but not necessarily eliminate) emulsification, but only at the expense of expediency: Equilibration periods as long as several weeks are not uncommon (Barrie Webster et al., 1989). Extended mixing periods may increase the potential for volatilization losses. In addition, several replicates over time are necessary
to confirm equilibrium. Batch results obtained even by the same researchers confirm
the dependence of solubility data on experimental conditions including the methods of
equilibration (vigorous shaking or gentle stirring) and solvent-excess solute separation
(gravity-settling, filtration, or centrifugation) (Bharath et al., 1984). Solubility data are
also sensitive to variations within a given method (equilibration time, settling time, filter
pore size, centrifugation speed, etc.).

Continuous flow-through methods resolve many of the problems associated with batch
techniques. A solid support with a large surface area such as glass beads, diatomaceous
silica, or a chromatographic media, is coated with the analyte and packed into a column.
The solvent flows through the column, is dispersed through the packed bed, and contacts
the solute at a rate sufficiently slow to prohibit emulsion formation and ensure liquid-
liquid equilibrium. The large solute-solvent interfacial area within the porous bed pro-
motes rapid equilibration even at moderate flow rates.

The generator column technique is a continuous flow-through process introduced in the
1970s (Veith and Comstock, 1975). Recently, it has become the preferred method for
the aqueous dissolution of hydrophobic chemicals (May et al., 1978; DeVoe et al., 1981;
Wasik et al., 1983; Billington et al., 1987) and has also been applied to measurements
of vapor pressure and octanol/water partition coefficients (DeVoe et al., 1981; Wasik et
al., 1983).

The advantages of generator columns over batch methods for preparing aqueous solu-
tions saturated with hydrophobic organic compounds are presented in detail in the lit-
erature (May et al., 1978; DeVoe et al., 1981; Wasik et al., 1983; Billington et al.,
1987). These include

1. equilibration is rapid;
2. colloidal or particulate suspensions are absent;

3. exposure to the atmosphere is minimized;

4. column surfaces become equilibrated with the saturated solution, minimizing adsorption;

5. large volumes of saturated solutions can be generated continuously;

6. analytic requirements and waste generation are minimal;

7. the necessary equipment is inexpensive and readily available;

8. columns are reusable; the support can even be cleaned and coated with a different analytic;

9. columns may be placed in series, either to confirm equilibrium using a single solute, or to equilibrate a particular solvent with a number of analytes; and

10. once the apparatus is assembled, varying external parameters such as temperature, flow rate, or the composition of the feed solution is a simple task.

PCE aqueous solubility was measured by the continuous flow-through generator columns at 20°C. The techniques employed for the generator columns were in accordance with those published by the National Bureau of Standards (DeVoe et al., 1981) with a few minor modifications. 5-ml borosilicate volumetric pipets served as the generator columns. Each pipet consisted of two sections 6.0 mm in outside diameter connected by an enlarged bulb section, with an outside diameter of approximately 9.0 mm. The volumetric pipets were shortened such that the total column length was approximately 25 cm. The
section with a 6.0-mm outside diameter located below the bulb section was packed with 120/140 mesh glass beads manufactured by Cataphote, Inc. The beads, held in place by glass wool plugs, provided an inert support for the stationary NAPL phase, 12–15 cm in length.

The pipets, glass beads, and glass wool plugs were silanized to deactivate all internal column surfaces by pre-treating with Glass-Treat, a silanizing agent manufactured by Alltech Associates containing dimethyl-dichloro-silane. The surfaces were then rinsed with anhydrous methyl alcohol purchased from Fisher Scientific, and air-dried under a chemical fume hood. The ends of the columns were wrapped with Teflon tape and fitted with Teflon ferrules and stainless steel Swagelock fittings. The upper (outlet) end of one column was connected to the lower (inlet) end of the second column with a Z-shaped section of stainless steel tubing, approximately 35 cm in length. The tubing was seated with stainless steel ferrules into the Swagelock fittings at the column ends. Stainless steel tubing connected the outlet of the second column to a stoppered 500-ml vacuum flask, vented to a carbon trap to collect fluid waste and harmful vapors. The combined pore volume of two generator columns in series was estimated to be in the range of 2.5 ml. Figure 16 is a schematic of the generator column setup.

Because PCE solubility is expected to increase markedly in more concentrated cosolvent mixtures, two larger packed columns were added in front of the generator columns to provide adequate PCE for dissolution for cosolvent mixtures with large methanol/water fractions. The columns, manufactured by Ace Glass Co., Inc., were each 50 ml in volume, threaded at both ends, and supplied with screw-in end caps and Teflon frits with glass plate inserts. The large columns were packed wet under PCE by pumping in PCE upflow from a Harvard Apparatus Infusion-22 syringe pump equipped with a Hamilton 100-ml Gastight syringe, while pouring 120/140 mesh glass beads through a funnel at
the top of the column. After packing and loading with PCE, the columns were flushed by pumping water down-flow through the column, pushing out a front of dense, free phase PCE, and leaving the packed bed residually saturated with PCE. Teflon tubing was used to connect the columns in series and to flow solvent, supplied by a Hamilton Gastight 100-ml glass syringe through the system.

The solvent used in the generator column experiments consisted of aqueous mixtures of methanol, including 0%, 20%, 40%, and 60% methanol by volume. The flow rate was maintained between 0.5 and 1.0 ml per minute. Preliminary experiments confirmed that flow rate had no significant effect on the results within the range of flow rates employed. The effluent reservoir was maintained at an elevation such that pressures within the columns were always above atmospheric. Samples were extracted from the effluent of
the generator columns. Two of the nuts in the Swagelock crosses at the top of each generator column were fitted with Teflon-lined silicone septa and used as sampling ports. Hamilton 1-ml Gastight syringes were used to collect several 1-ml samples, alternating between the two generator columns in series. The samples were filtered with a 0.2-μm nylon syringe filter housed in a stainless steel Fisher Scientific syringe holder. The samples were immediately diluted into 9 ml of isopropanol, dispensed earlier into preweighed 11.1-ml borosilicate screw-top vials. The diluted samples were then dispensed into Hewlett Packard 2-ml autosampler vials and crimp-sealed until analysis by gas chromatography. Samples were analyzed using the same equipment and procedures as were employed when analyzing batch-equilibrated samples.

Nonfiltered samples were also collected and analyzed during preliminary experiments. PCE concentrations from samples collected using the two techniques did not differ in a statistically significant manner, indicating that there were a minimal number of colloidal particles larger than 0.2 μm in solution. Data reported below are only from filtered samples.

2.2.4 Equilibrium Phase Partitioning: Batch Experiments

Because it was impossible to sample the nonaqueous phase in generator column experiments, batch experiments were also performed to measure equilibrium concentrations of PCE, water and methanol in both nonaqueous and aqueous phases. Equal volumes (approximately 30 ml each) of PCE and aqueous solutions of methanol, including 0%, 20%, 40%, 60% percent methanol by volume, were batch-equilibrated by the shake-flask method in 50-ml Erlenmeyer flasks at 20°C. Two batch flasks were prepared at each
methanol/water fraction. The flasks were continuously shaken on a Junior Orbital Autoshaker at 100 revolutions per minute (rpm), with periodic inversion and vigorous shaking by hand for a minimum of 12 hours before sampling. To minimize leakage and volatile losses, the flasks were completely filled and sealed with threaded screw-caps wrapped with Teflon tape.

In order to maintain the aqueous phase at a known methanol concentration, the aqueous phases were periodically replaced with fresh methanol/water solutions. Equilibrium was confirmed by at least two consecutive measurements of PCE in the aqueous phase over time that agreed within experimental error.

2.2.4.1 Sample Collection and Dilution

Before sampling, the flasks were removed from the shaker, inverted, and the phases allowed to separate until no turbidity was observed in either phase. The flasks were then vented by puncturing the Teflon-lined silicone septa with U-shaped sections of stainless steel tubing, approximately 1.6 mm internal diameter and 300 mm in length, to equalize pressure during sampling. Ten 1-ml samples of the nonaqueous phase were first withdrawn from each flask using 1-ml Hamilton Gas-tight syringes and diluted into 9-ml of isopropanol (IPA) in 11.1-ml borosilicate vials with open-top screw caps and Teflon-lined silicone septa. These samples were used to determine the methanol concentration in the nonaqueous phase.

5-ml Hamilton Gas-tight syringes were then used to collect 5-ml samples of each aqueous phase, which were filtered with a 0.2-μm nylon syringe filter housed in a stainless steel Fisher Scientific syringe holder. Samples were filtered to remove colloidal or particulate suspensions, which may have resulted during batch contacting. The filtered samples were diluted into 5-ml of IPA in 11.1-ml borosilicate vials. The aqueous phase samples were used to determine the PCE and methanol concentration within the aqueous phase.
The flasks were refilled by topping off with fresh methanol/water solutions, the septa were replaced, and the flasks resealed and returned to the shaker for future sampling.

Pasteur pipets were used to quickly dispense the diluted samples of each phase into 2-ml Hewlett Packard GC autosampler vials, which were crimp-sealed with minimal head space to minimize volatility losses before analysis.

A second set of samples was collected from the nonaqueous phase of each flask for determination of the water content. At least five 1-ml samples of the nonaqueous phase were extracted from each flask using 1-ml Hamilton Gas-tight syringes. Sample masses were determined by weighing the syringe immediately before and after sampling. Nonaqueous phase samples batch-equilibrated with methanol/water mixtures were also transported to a Hoechst Celanese Reidel-deHaen Laboratory for independent analysis of water content.

2.2.4.2 Gas Chromatographic Analysis

A Hewlett Packard Model 5890A gas chromatograph with Hewlett Packard 7673A Automatic Sampler Tower and HPChem Station were used to determine PCE and methanol concentrations within the aqueous and nonaqueous phase samples. The gas chromatograph was equipped with a Flame Ionization Detector (FID) and a Supelco Carbopack 3% SP 1500 packed column, 80/120 mesh, 3.2-mm internal diameter and 304.8 cm in length. The flame was maintained by a flow of 20 PSI hydrogen gas and 36 PSI compressed air. The carrier gas was Helium at approximately 20 ml/min with Nitrogen as the make-up gas at approximately 10 ml/min to maintain a total column head pressure of 30-40 PSIG. 1.0-μl samples of the diluted aqueous or nonaqueous phase samples were automatically injected by the autosampler with two sample washes, two sample pumps and eight solvent washes of IPA between samples to eliminate carry-over peaks from previous samples.
The temperature program used for sample analysis began with an initial temperature of 100°C for three minutes to separate the early-eluting alcohols, followed by a ten degree/minute temperature ramp to 190°C. The ramp was then retarded to 1.5 degrees per minute to a final temperature of 202°C. The final temperature ramp was necessary to flatten the baseline while the PCE peak emerged.

The HPChem Station permitted post-run manipulation of the data including re-integration and threshold alterations.

**2.2.4.3 Calibration Standards** Standards of known concentrations of PCE in methanol/water mixtures and methanol in PCE were used to develop calibration curves from which sample concentrations were determined. The gas chromatograph peak area was a linear function of concentration for both PCE and methanol over the entire range of concentrations studied. All regressions had R² values greater than 0.995, with typical values of greater than 0.999.

The standards were prepared by successive volumetric dilutions of concentrated stock solutions. The standards were diluted in an identical manner as the samples, and standards were analyzed periodically during sample analyses. To account for instrument drift, data from standards bordering each subset of data were combined to evaluate that subset. Dilution blanks were also used throughout sampling analysis to monitor potential carry-over due to high concentrations and column overload.
2.2.4.4 Karl Fischer Coulometric Titrations

A Fischer Coulomatic Titrimeter Model 447 was used to measure the water content of samples collected from the nonaqueous phase. In the presence of sulfur dioxide, an organic nitrogen base, and an alcohol, water was consumed by a stoichiometric reaction with iodine. The instrument automatically titrated the sample to dryness by generating iodine coulometrically from Karl Fischer Hydranal reagents. At the endpoint, a trace excess of highly conductive free iodine caused a sharp decrease in cell resistance, detected amperometrically by a dual platinum electrode. Sample water content was automatically calculated based on the electrical charge required to produce the iodine needed to complete the titration.

Karl Fischer Titrations were conducted in accordance with ASTM Designation E 203-92 (ASTM, 1992) and the manufacturer's User's Manual for the Fisher Coulamatic Titrationator Model 447. The cathode and anode compartment vents were fitted with Drier-Rite tubes to prevent the intrusion of atmospheric moisture into the otherwise closed titration vessel.

2.2.5 Equilibrium Phase Partitioning: Titrations

The solubility curve in ternary phase diagrams corresponds to the entire set of combinations of the three components which bounds regions where two phases exist. The use of ternary phase diagrams for illustrating phase partitioning in three component systems is described in detail below. The titration method is used to help define points on the solubility curve.

In the titration method one of the components of a ternary system is added in small increments to a binary mixture containing the remaining two components in separate pha-
ses. The titration continues to miscibility defining a ternary composition that represents a point on the solubility curve (Sayer, 1991).

A clean, pre-weighed 50-ml Erlenmeyer flask with a threaded, open-top screw cap and Teflon-lined silicone septum was used as the titration vessel. To minimize volatility losses and the release of noxious vapors, the vessel remained sealed during the titrations except for a small hole punched through the septum through which the tips of the burette and the volumetric pipets could be inserted. 1.0-ml deionized, distilled water and 0.1-ml PCE were pipetted into the titration vessel, forming two separate phases. A 10-ml glass burette accurate to 0.05 ml was inserted into the vessel through the hole in the septum. The binary mixture was then slowly titrated with methanol until a single miscible phase formed with no turbidity. The volume of methanol titrated and the final mass of the vessel were recorded. PCE and water were added in 0.1- and 1.0-ml increments, respectively, to form various binary mixtures which were then titrated with gentle swirling to miscibility with the cosolvent methanol. Masses were recorded following each addition of PCE or water and at the titration endpoint. For each titration, the volume of methanol titrated was recorded.

2.2.6 Phase Density

Mass per volume measurements were used to determine equilibrated phase densities. Following batch equilibration as previously described, ten ml of NAPL were pipetted into each of seven pre-weighed 10-ml volumetric flasks and their masses recorded. Sample masses were calculated by difference. This procedure was repeated for each batch-equilibrated system studied for a total of thirty-five nonaqueous phase samples. A similar technique was applied to the aqueous phase: Depending on the total volume of PCE-equilibrated methanol/water remaining after batch equilibration, three to six pre-weighed
50-ml volumetric flasks were carefully filled and weighed. Sample masses were determined by difference. The procedure was repeated for each PCE/methanol/water batch system studied.

2.2.7 Interfacial Tension

Interfacial tension between the nonaqueous and aqueous phases was measured instantaneously and following batch equilibration by the Downward Thrust Ring Method using a Du Nouy Interfacial Tensiometer CSC No. 70545, in accordance with the manufacturer's User's Manual and ASTM Designation D 971-91 (ASTM, 1991). At least five instantaneous and twenty equilibrated measurements were made for each methanol/water fraction studied. The instrument was calibrated against a known weight and its accuracy confirmed by comparing experimental measurements of the surface tension of water to values cited in the ASTM Standard Method. The values obtained experimentally fell well within the acceptable range. The platinum-iridium ring was conditioned by soaking it in the aqueous-methanol mixture to be tested before introducing it to the sample itself. The ring was cleaned between samples by methanol-flaming in the oxidizing portion of a Bunsen Burner flame.

2.2.8 Mobilization and Dissolution

A series of column experiments were conducted to study the flow and transport processes associated with the removal of trapped PCE ganglia by flushing with a methanol/water mixture. The procedures followed were similar to those developed by Imhoff et al.
[1994a] for a water/trichloroethylene system. These experiments provided data for assessing the effect of the methanol/water mixture on both mobilization and dissolution of PCE ganglia.

Glass beads identical to those used in the heated water experiments were used as the porous medium. The column was made of glass and was 27-cm long with a 2.5-cm internal diameter. A Teflon plunger covered with a fine nylon screen was used at the top of the column. At the bottom of the column, a similar Teflon plunger was covered with a coarse stainless steel screen overlaid by a fine Teflon screen, and served as the supporting and sealing mechanism. Glass beads were packed under water by slowly pouring the beads through a plexiglass tube fitted with a wire mesh screen on one end. The momentum of the falling beads was reduced by the screen before falling through a two to three centimeter layer of water. Glass beads were added in lifts of approximately five centimeters and each lift rodded throughout before additional beads were added.

Once packed with glass beads, the column was mounted and vertically aligned between an x-ray source and detector used for the nondestructive measurement of porosity and PCE saturation (McBride and Miller, 1994). Figure 17 presents a schematic of the experimental setup used in this study. The x-ray source-detector system provided radiation attenuation data used to calculate $\phi$ and $S_n$ as a function of vertical location; the collimated radiation beam was 5 mm by 5 mm in cross section and provided an average measurement covering 25% of the horizontal column cross-section at each vertical sampling location. The random errors associated with these measurements were as follows: estimated standard error was 0.0018 for $\phi$ and 0.0037 for $S_n$. Measurements of this precision at a vertical resolution of 5 mm have not been reported to our knowledge for any cosolvent-enhanced remediation experiments.
To permit a visual confirmation of liquid flow through the transparent column walls and tubing, spectrophotometric grade PCE was mixed with a small amount of dye, oil-red O, both purchased from Sigma Chemical Company. The dye permitted visual observations of PCE mobilization as well as the development of a dissolution front, the region over which active dissolution was occurring. (Samples of the dyed and pure PCE were prepared and analyzed with gas chromatography and indicated that the dye had negligible influence on PCE solubility.)

0.9 pore volumes (PV) of PCE, denser than water, was then pumped upwards to achieve a gravitationally-stable displacement of water from the column. The displacement was stopped before the invading PCE reached the top of the column. After the injection of PCE, the flow was reversed and water was pumped downward from the top of the column. PCE was displaced by 4.1 PV of water at a flow rate of 1.76 m/day followed by
an additional 4.9 PV of water at a flow rate of 3 m/day. The disappearance of red PCE drops from the outflow indicated that displacement of PCE by water was complete and residual PCE saturation was achieved. After PCE displacement, an x-ray scan of the column was made to determine the residual PCE saturation along the column.

The methanol/water mixture (60% methanol 40% water by volume) was introduced through the top of the column with a peristaltic pump. The reappearance of red PCE drops in the column outflow indicated that a significant amount of PCE was mobilized and then displaced by the methanol/water solution. The pumping of the methanol/water solution (approximately 2.1 PV) was continued at a flow rate of 1.76 m/day until red PCE drops disappeared from the outflow.

After displacement of the additional amount of separate-phase PCE by the methanol/water solution, PCE dissolution into the methanol/water mixture became the dominant process during alcohol-enhanced remediation. Because the outflow Teflon tubing contained sorbed PCE, the tubing was replaced for the solubilization stage of the experiment (Figure 17). To capture the arrival and passage of the PCE dissolution front, a programmed series of x-ray scans were performed within a subregion of the column. The number of repeat scans and the length of the subregion were chosen based upon the analysis of the initial PCE saturation profile and estimates of the dissolution front velocity assuming equilibrium mass transfer. Effluent liquid samples were collected from the sampling port (Figure 17) equipped with a three-way valve. Three 0.8-ml samples were obtained at each sampling time by using a Hamilton gas-tight syringe. Each 0.8-ml was diluted in 1-mL iso-propanol alcohol and immediately sealed in 2-ml vials.

The samples of the effluent liquid were combined with calibration standards of known PCE concentration (samples with known concentrations of PCE, methanol, iso-propanol
and analyzed by gas chromatography. The same equipment and procedures used for analysis of aqueous phase samples in the equilibrium phase partitioning experiments were employed here.

2.3 Results

2.3.1 Phase Partitioning

2.3.1.1 PCE Solubility in Methanol/Water Mixtures: Data

Data from the generator columns are described first. Effluent concentrations from both generator columns were measured through time for the four different methanol/water fractions. As the aqueous phase flows through the generator columns contacting PCE, phase equilibrium will be reached: the PCE concentration within the aqueous phase stabilizes and remains constant through time and space (distance traveled through serial columns). For this study, equilibrium was considered established when measured PCE concentrations in the effluent from both columns agreed within experimental error and remained consistent over time through several data pairs.

Figure 18 shows raw data from a generator column solubility experiment where the mobile phase was 40% methanol and 60% water. The data in this figure illustrate a typical trend: sample concentrations rise to a plateau where the concentration stabilizes before tapering off as the PCE in the column becomes depleted.

The initial concentration increase in Figure 18 represents the column conditioning stage of the process. Early concentrations are low due to adsorption to internal column surfaces. As the mobile aqueous phase equilibrates with the column and the stationary
Figure 18. Data from a generator column experiment showing concentration measurements from two columns in series over time.

As discussed previously, shake-flask batch and generator column techniques were employed to measure PCE solubility in methanol/water mixtures. Data obtained by both techniques are presented in Table 9.
Table 9. Measured PCE solubility in methanol/water mixtures at 20°C.

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Generator Columns</th>
<th>Shake-Flask</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean PCE Concentration (mg/l)</td>
<td>Sample Std. Dev. (mg/l)</td>
</tr>
<tr>
<td>0</td>
<td>225.44</td>
<td>1.25</td>
</tr>
<tr>
<td>0.2</td>
<td>453.20</td>
<td>3.31</td>
</tr>
<tr>
<td>0.4</td>
<td>1465.67</td>
<td>9.84</td>
</tr>
<tr>
<td>0.6</td>
<td>8986.44</td>
<td>35.64</td>
</tr>
</tbody>
</table>
The first result presented in Table 9 is the solubility of PCE in the aqueous phase with no methanol present. Table 10 is a partial listing of results from an extensive literature survey of PCE solubility in the aqueous phase: reported PCE solubilities range from 150–997 mg/l at 20–25°C. Of these, only three references describe the methods employed, all of which were batch techniques. The value appearing most frequently for PCE solubility in water in the temperature range of 20–25°C is 150 mg/l. The primary references for this value date back to the 1930s (*Wright and Schaffer*, 1932) and 40s (*McGovern*, 1943). Although a discussion of the original methods is not available, it is reasonable to assume that these studies relied on batch techniques because generator columns were not commonly employed for solubility studies before the 1970s.

Table 10. Literature values of PCE aqueous solubility.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. °C</th>
<th>Conc. (mg/l)</th>
<th>Methods Cited</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Wright and Schaffer</em> [1932]</td>
<td>25</td>
<td>189</td>
<td>not specified</td>
</tr>
<tr>
<td><em>McGovern</em> [1943]</td>
<td>&quot;</td>
<td>150</td>
<td>&quot;</td>
</tr>
<tr>
<td><em>Ethyl Corp.</em> [1958]</td>
<td>&quot;</td>
<td>997</td>
<td>cited from <em>Horvath</em> [1982]</td>
</tr>
<tr>
<td><em>Gladis</em> [1960]</td>
<td>&quot;</td>
<td>150</td>
<td>cited from <em>Horvath</em> [1982]</td>
</tr>
<tr>
<td><em>Sconce</em> [1962]</td>
<td>&quot;</td>
<td>150</td>
<td>not specified</td>
</tr>
<tr>
<td><em>DuPont</em> [1966]</td>
<td>&quot;</td>
<td>199</td>
<td>&quot;</td>
</tr>
<tr>
<td><em>Moiseeva et al.</em> [1977]</td>
<td>20</td>
<td>206.5</td>
<td>shake flask, GC analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>scintillation counting</td>
</tr>
<tr>
<td><em>Coca and Diaz</em> [1980]</td>
<td>&quot;</td>
<td>199</td>
<td>shake flask, density</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and refractive index</td>
</tr>
<tr>
<td><em>Schwille</em> [1988]</td>
<td>20</td>
<td>200</td>
<td>not specified</td>
</tr>
<tr>
<td><em>Montgomery</em> [1991]</td>
<td>20</td>
<td>150</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
The discrepancies between PCE solubility values found in the literature, the inherent problems associated with batch contacting, the scarcity of empirical data, and the lack of explicit methodology to support the validity of such data make the reliability of published solubilities for PCE in water questionable. To date, this study is the only one known to apply the preferred generator column technique to the measurement of PCE aqueous solubility. The mean aqueous phase PCE solubilities determined in this study by batch contacting and generator columns are statistically different: the hypothesis that the means are the same is rejected at a significance level of 0.001. Because greater confidence is placed in the generator column technique, the best estimate from this study of PCE solubility in an aqueous phase with no methanol is that reported above for the generator column.

Saturation concentrations of PCE in 20% and 40% methanol/water solutions measured by batch and by column studies agree within one sample standard deviation, indicating that batch and generator column results did not differ significantly for these methanol/water fractions. Better agreement is expected between the two techniques for the intermediate methanol/water fractions, where volatile losses will be less important in the batch experiments, and where problems of depletion of the solute in the generator columns is not yet critical. For the 60% methanol/water solution, the hypothesis that the mean PCE concentrations determined from the two techniques are the same is rejected at a significance level of 0.001.

PCE concentrations in 60% methanol/water obtained by batch-contacting were considerably higher than those measured from generator columns. As discussed earlier, a common problem associated with batch techniques that would cause a positive error is the presence of colloidal solute suspensions. That such suspensions are the cause of the discrepancy in these data is unlikely for several reasons. First, the formation of stable
emulsion decreases with solute hydrophobicity as the cosolvent fraction in the aqueous phase is increased. Second, sampling precautions were employed to eliminate this potential error. These include phase separation by gravity and sample filtration through a 0.2-µm Nylaflo filter. Finally, if the aqueous phase samples contained PCE emulsions, large deviations would occur between sample concentrations depending on the amount of free-phase solute, if any, collected in each sample. This tell-tale deviation was not observed between batch samples. In fact, the sample standard deviation for the 60% methanol run was considerably lower for batch samples than for generator column samples.

The larger deviation obtained by the generator column technique, coupled with a significantly lower mean value and smaller sample size, makes the 60% generator column data suspect. Longer column conditioning times were necessary to equilibrate the column and the stationary phase with the mobile phase. PCE dissolution during conditioning coupled with dramatic increase in PCE solubility in the 60% methanol/water fraction made it difficult to supply an adequate mass of solute to establish and maintain equilibrium concentrations. Of all the sample concentrations measured, only a few were stable enough to potentially represent equilibrium. After a brief stabilization period, sample concentrations began to plummet as the PCE supply became depleted. Whether or not equilibrium was ever truly attained is questionable. The challenges encountered here suggest that the continuous flow-through generator column technique may be inappropriate for solubility determinations in which the solute is moderately soluble in the solvent under study. The method is deemed superior to batch techniques, however, for saturating water with slightly soluble compounds, as demonstrated by a comparative evaluation of the data for PCE aqueous solubility.
The solubilities of hydrophobic organic chemicals in aqueous cosolvent mixtures have been approximated by a log-linear solubility equation

\[ \log C_m = \log C_s + fa \]  

where \( C_m \) and \( C_s \) represent the solubilities of the organic in the cosolvent mixture and water, respectively; \( f \) is the volume fraction of cosolvent; and \( a \) is the slope of a plot of \( \log(C_m/C_s) \) versus cosolvent volume fraction (Rubino et al., 1984, Rubino and Yalkowsky, 1985).

The measured solubilities, obtained by batch (60% methanol/water) and by column techniques (0%, 20%, 40%), are plotted in Figure 19 with the line predicted by the proposed solubility equation. These data were chosen for regression because they were the most reliable from the two experimental techniques used. The log-linear solubility equation gives an acceptable fit to the measured values, but predicts considerably higher values than those measured for PCE solubility in 20% and 40% methanol/water. A simple exponential regression of the experimental data, presented in Figure 19, yields \( R^2 = 0.959 \). As only one ternary system was studied in this investigation, an evaluation of the merit of any predictive equation or its applicability to other systems is speculative and would be inappropriate based on such limited data.
2.8.1.8 Methanol Solubility in Nonaqueous Phase

Batch studies were necessary to define the equilibrium compositions of the nonaqueous phase for the methanol/water fractions greater than zero. It was physically impossible to remove sufficient nonaqueous phase from the generator columns for sample analysis. Nonaqueous phase samples,
Table 11. Methanol concentrations in batch-equilibrated nonaqueous phase samples.

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Mean Methanol Concentration (mg/l)</th>
<th>Sample Std. Dev. (mg/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1540.48</td>
<td>2.83</td>
<td>24</td>
</tr>
<tr>
<td>0.4</td>
<td>1616.02</td>
<td>4.33</td>
<td>18</td>
</tr>
<tr>
<td>0.6</td>
<td>3159.17</td>
<td>14.46</td>
<td>15</td>
</tr>
</tbody>
</table>

batch-equilibrated with 20%, 40%, 60% methanol/water mixtures were analyzed to determine equilibrium concentrations of methanol. The results are summarized in Table 11.

Nonaqueous phase methanol increases only slightly when the methanol/water fraction in the aqueous phase is doubled from 20% to 40%, but the 50% increase from 40% to 60% methanol/water nearly doubles nonaqueous phase methanol.

2.3.1.4 Water Content in Nonaqueous Phase Karl Fischer coulometric titrations were used to determine nonaqueous phase water content. The results are presented in Table 12. Nonaqueous phase water content increases with increasing methanol/water fraction, which is consistent with increasing methanol concentration within the nonaqueous phase. The largest increases for both water and methanol are observed for the 60% methanol/water solution. As methanol nonaqueous phase partitioning increases, the cosolvent carries more water with it into the nonaqueous phase.

The measured nonaqueous phase water content for the system containing no methanol (i.e., PCE equilibrated with pure water) was confirmed by independent researchers at a
Table 12. Nonaqueous phase water content.

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Mean Water Content (ppm by mass)</th>
<th>Sample Std. Dev. (mg/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.70</td>
<td>0.28</td>
<td>17</td>
</tr>
<tr>
<td>0.2</td>
<td>57.09</td>
<td>0.56</td>
<td>10</td>
</tr>
<tr>
<td>0.4</td>
<td>58.80</td>
<td>0.64</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>68.10</td>
<td>0.44</td>
<td>10</td>
</tr>
</tbody>
</table>

division of Hoechst Celanese, specializing in water content determinations by Karl Fischer Titration. These experts reported a value of 55.7 +/− 1 ppm water in PCE. This independent measurement served as a check on the experimental techniques followed here.

2.3.1.5 Ternary Phase Diagram: Data

Ternary diagrams are used to graphically describe equilibrium in ternary systems. They are particularly useful when the components form immiscible mixtures because phase equilibria and overall compositions can be defined simultaneously. They are typically used in chemical and petroleum engineering in the development of extraction or recovery processes. For example, in enhanced oil recovery by surfactant- or alcohol-flooding, ternary phase diagrams represent two-phase systems of oil, water, and surfactant or alcohol. It is logical to extend the use of ternary phase diagrams to the proposed recovery of groundwater contaminants by cosolvent flooding.

In a ternary diagram, each apex of an equilateral triangle represents a pure component. Conventionally, the water apex appears at the left, the nonaqueous or water immiscible component on the right, and the apex at the top is reserved for a cosolvent or a component that is mutually soluble in both of the other two components. The sides of the
triangle represent binary mixtures of the components they connect (i.e., the component at the opposite apex is absent); the interior points represent all possible ternary compositions.

A solubility curve forms the boundary between miscibility and immiscibility. All ternary compositions designated by points that fall below the curve represent equilibrium between and within two immiscible phases. All points located above the curve represent stable compositions of a single miscible phase. Within the immiscible region, a ternary mixture is defined by two equilibrium phase compositions, represented by the endpoints of the tie lines passing through the overall composition point. Tie lines connect the composition points of immiscible phases at equilibrium.

To generate the ternary phase diagram for the PCE/methanol/water system, concentration data from the Karl Fischer titrations, cosolvent titrations, and from batch and generator column solubility studies were converted to mole fractions, normalized to one hundred, and compiled into the ternary diagram shown in Figure 20. Nonaqueous phase concentrations were taken from the batch contacting experiments, while aqueous phase concentrations came from both the batch contacting experiments (60% methanol/water fraction only) and the generator column experiments (0%, 20%, and 40% methanol/water fraction). Data near the methanol apex came from the cosolvent titrations.

From the diagram, the partitioning behavior of the cosolvent methanol is obvious. Two immiscible phases persist throughout nearly all of the compositions possible in the PCE/methanol/water ternary system. The crest of the solubility curve approaches the methanol apex, indicating that high methanol concentrations (greater than 80% methanol by volume) are required to achieve miscibility. The tie lines slope downward toward the PCE apex, indicating preferential partitioning of methanol into the aqueous phase. In
the enhanced oil recovery literature, this type of phase diagram is referred to as plait point-right or shrinking oil phase. If we follow a path of incremental additions of methanol to an immiscible mixture of PCE and water, the NAPL phase shrinks, relative to the overall composition, until it is consumed by the expanding aqueous phase as the system reaches miscibility.
2.3.1.6 Ternary Phase Diagram: Model Predictions

A macroscopic phase equilibrium is generally determined by two factors: (1) a mass balance (conservation) requirement, and (2) a thermodynamic chemical equilibrium requirement. Mass conservation simply means that nothing leaves the flask. The thermodynamic chemical equilibria requires the chemical potentials of the components to be the same across the phases.

The chemical potential of a chemical species \( i \) in phase \( \alpha \) is expressed as

\[
\mu_i^{\alpha} = \mu_i^0 + RT\ln X_i^{\alpha} \gamma_i^{\alpha}
\]  

(10)

where \( \mu_i^0 \) is the standard chemical potential, \( X_i^{\alpha} \) is the mole fraction, and \( \gamma_i^{\alpha} \) is the activity coefficient. Raoult’s convention of the standard state, i.e. a chemical at the pure liquid state and at the temperature of interest, is adopted here. The system is in equilibrium with respect to the chemical species \( i \) when the chemical potential in phase \( \alpha \), \( \mu_i^{\alpha} \), is identical to the chemical potential in phase \( \beta \), \( \mu_i^{\beta} \). This requirement yields

\[
X_i^{\alpha} \gamma_i^{\alpha} = X_i^{\beta} \gamma_i^{\beta}
\]  

(11)

which suggests that the concentration (mole fraction) of the chemical species \( i \) in the phase \( \beta \), \( X_i^{\beta} \), can be calculated as long as \( X_i^{\alpha} \), \( \gamma_i^{\alpha} \) and \( \gamma_i^{\beta} \) are known. This idea can be extended to multi-component, multi-phase systems.
The activity coefficient is determined by how a molecule interacts with the surrounding molecular environment. Therefore, the activity coefficient can be expressed as a function of composition, $X_i$, nature of the chemicals, temperature, and pressure. There are many mathematical models predicting activity coefficients. These include Margules, van Laar, Scatchard-Hildebrand, Wilson, T-K-Wilson, ASOG, NRTL, UNIQUAC and UNIFAC (Walace, 1985). The UNIQUAC (Universal Quasi-Chemical) model (Abrams and Prausnitz, 1975) was used in this study. From these models it is evident that $\gamma_i$ is a nonlinear function of several variables including the mole fraction, $X_i$, the nature of the chemicals, and temperature.

Once the activity coefficients are expressed (approximated) in mathematical form, it is possible to select the mole fractions, $X_i$, for all phases and species so that the constraints for thermodynamic equilibria and mass conservation are satisfied. From a chemist's point of view, this selection is the search for the lowest free energy state. This optimization is not as simple as it first appears, since the activity coefficients are strongly dependent on the mole fractions in a nonlinear fashion.

The PCE/methanol/water system exists as either two phases or one phase, depending on the amount of methanol, PCE, and water in the system. In the case of a two-phase system, a partition coefficient, $K_i$, can be defined as

$$K_i = \frac{X_i^\beta}{X_i^\alpha} = \frac{\gamma_i^\alpha}{\gamma_i^\beta}$$  \hspace{1cm} (12)

Defining $z_i$ as the mole fraction of species $i$ in the entire two-phase system and $\omega$ as the fraction of the total material (mole basis) that is present in the first phase, the material
balance becomes

\[ z_i = \omega X_i^\alpha + (1 - \omega)X_i^\beta \]  \tag{13}

Inserting the partition coefficient into (13),

\[ z_i = [\omega + K_i(1 - \omega)]X_i^\alpha \]  \tag{14}

For specified \( z_i \) equations (14) represent mass conservation requirements for each species. In addition to these three equations, a fourth equation representing mass conservation for the entire mixture was considered

\[ \sum_i \frac{(K_i - 1)z_i}{\omega + K_i(1 - \omega)} = 0 \]  \tag{15}

Equation (15) was recommended by Prausnitz et al. [1980] and is based on the requirement
and $K_i$ defined by (12). For specified $z_i$, the system of four equations (three equations (14) plus (15)) and four unknowns ($X_{PCE}^\alpha, X_{\text{water}}^\alpha, X_{\text{methanol}}^\alpha$, and $\omega$) was solved numerically using the Newton-Raphson technique. In this solution strategy $K_i$ was computed from (12) using activity coefficients estimated from UNIQUAC (based on the mole fractions of the three species in each phase), thus enforcing thermodynamic chemical equilibrium. Equations (14) and (15) enforced mass conservation. This optimization was carried out for the PCE/methanol/water system. The predictions are compared with the experimental results in Figure 21 and are in reasonable agreement. However, the predicted methanol concentration in the PCE phase was higher than measured. The reason for this discrepancy is not clear.

### 2.3.2 Phases Density

Composition changes brought about by alcohol partitioning are inevitably accompanied by changes in the physical properties of the phases. The consequences of these changes could critically impact the use of cosolvents in enhanced groundwater remediation. For
example, a nonaqueous phase which becomes less dense because of alcohol flushing may more easily be mobilized upward through the groundwater.

Pure and batch-equilibrated nonaqueous phase densities for various methanol/water fractions are given in Table 13. These data are presented graphically in Figure 22. Similar data for aqueous phase densities are given in Table 14 and Figure 23.
Table 13. Pure and batch-equilibrated NAPL densities at 20°C.

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Batch-Equilibrated NAPL Density (g/ml)</th>
<th>Sample Std. Dev. (g/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.6137</td>
<td>0.0036</td>
<td>7</td>
</tr>
<tr>
<td>0.2</td>
<td>1.6128</td>
<td>0.0042</td>
<td>7</td>
</tr>
<tr>
<td>0.4</td>
<td>1.6116</td>
<td>0.0030</td>
<td>7</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6094</td>
<td>0.0043</td>
<td>7</td>
</tr>
<tr>
<td>0.8</td>
<td>1.6052</td>
<td>0.0046</td>
<td>7</td>
</tr>
</tbody>
</table>

Nonaqueous phase density decreases slightly with increasing methanol/water fraction in the aqueous phase due to the increasing proportions of methanol and water dissolved in the NAPL. Because methanol does not partition favorably into the nonaqueous phase, NAPL density changes are minimal. Cosolvents that preferentially partition into the NAPL phase demonstrate larger density reductions (Brandes, 1992). NAPL swelling due to cosolvent partitioning could potentially cause free-phase mobilization of NAPL trapped in porous media and has been successfully employed in enhanced oil recovery. Although the objectives of the oil industry and the remediation specialist are similar, they deviate in some critical aspects. Uncontrolled mobilization of a groundwater contaminant could prove disastrous. In the case of a DNAPL, swelling and mobilization could expedite downward migration, making it harder and more expensive to recover. Theoretically, DNAPL density reductions could curb downward migration, but no evidence has been offered to date that the resultant migration could be accurately predicted and controlled, or that mobilized DNAPL could be effectively recovered in the field. Although statistically significant, it is unlikely that the density changes observed in this study between pure and batch-equilibrated PCE would have a significant impact on PCE subsurface migration.
Aqueous phase densities change more significantly with the addition of methanol to the system: the aqueous phase density decreases by almost 12% as the methanol/water volumetric content increases from 0% to 80%. Density changes of this magnitude will affect the transport of the alcohol mixture in the subsurface, as the lighter methanol/water mixture will tend to rise above denser, native groundwater. This effect must be accounted for in any remediation effort.
Table 14. Aqueous phase densities at 22°C. Error bars are so small as not be be visible.

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Batch-Equilibrated Aqueous Phase Density (g/ml)</th>
<th>Sample Std. Dev. (g/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9982</td>
<td>0.0007</td>
<td>3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.9704</td>
<td>0.0007</td>
<td>3</td>
</tr>
<tr>
<td>0.4</td>
<td>0.9420</td>
<td>0.0003</td>
<td>5</td>
</tr>
<tr>
<td>0.6</td>
<td>0.9083</td>
<td>0.0007</td>
<td>5</td>
</tr>
<tr>
<td>0.8</td>
<td>0.8837</td>
<td>0.0008</td>
<td>5</td>
</tr>
</tbody>
</table>

2.3.3 Interfacial Tension

A second physical property which may change in alcohol flooding is the interfacial tension (IFT) between the nonaqueous and aqueous phases. Potential IFT reductions affected by the addition of cosolvents are appealing to remediation strategists, since reductions in IFT enhance the mobility of NAPLs. IFT reductions, in addition to enhanced solubilities, are probably the most promising aspects of the use of cosolvents in groundwater remediation.

Interfacial tension (IFT) measurements for the PCE/methanol/water system, given in Table 15, show a significant decrease with increasing methanol/water fraction. Figure 24 shows that a power-law model provides an acceptable fit to the data, yielding $R^2 = 0.9997$.

The large IFT reduction realized by the addition of just 20% methanol suggests that the cosolvent methanol may lead to mobilization of PCE residual even at low to moderate concentrations. With reduced IFT, smaller viscous and buoyancy forces are required to
mobilize NAPL droplets. Other alcohols exhibiting greater partitioning into the non-aqueous phase, but similar reduction in IFT, would lead to much more significant mobilization.
Table 15. Batch-equilibrated interfacial tensions.

<table>
<thead>
<tr>
<th>Methanol (volume fraction)</th>
<th>Batch-Equilibrated IFT (dynes/cm)</th>
<th>Sample Std. Dev. (dynes/cm)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44.5</td>
<td>0.08</td>
<td>25</td>
</tr>
<tr>
<td>0.2</td>
<td>27.0</td>
<td>0.10</td>
<td>20</td>
</tr>
<tr>
<td>0.4</td>
<td>18.6</td>
<td>0.16</td>
<td>21</td>
</tr>
<tr>
<td>0.6</td>
<td>11.9</td>
<td>0.09</td>
<td>20</td>
</tr>
<tr>
<td>0.8</td>
<td>5.9</td>
<td>0.05</td>
<td>20</td>
</tr>
</tbody>
</table>

2.3.4 Viscosity

Aqueous phase viscosity may change during alcohol flooding. Because reliable data exist for the viscosity of methanol/water mixtures, this parameter was not measured. Instead, viscosities are listed in Table 16 for methanol/water mixtures as reported by Flick [1991], and are shown graphically in Figure 25.

2.3.5 Molecular Diffusion Coefficient

The molecular diffusion coefficient of a NAPL in the aqueous phase will be altered by a cosolvent. An increase in the molecular diffusion coefficient will result in a faster rate of mass transfer from the NAPL into the aqueous phase. Thus, in order to accurately predict the rate of PCE dissolution during a methanol/water cosolvent flush, it is important to quantify the effect of methanol on the PCE molecular diffusion coefficient within the aqueous phase.
Figure 24. Interfacial tension between aqueous and nonaqueous phases as a function of methanol volume fraction. Error bars are so small as not to be visible.

Diffusion in mixed solvent systems has been studied by Holmes et al. [1962], Cullinan and Cusick [1967], Kett and Anderson [1969], and Leffler and Cullinan [1970]. Because of the existence of reliable relations to predict the diffusion coefficient (Reid et al., 1987), two were selected to estimate the effect of methanol on the molecular diffusion coefficient of PCE in the aqueous phase: the Wilke-Chang (Wilke and Chang, 1955) and Leffler-Cullinan equations (Leffler and Cullinan, 1970).
Table 16. Viscosity of methanol/water mixtures from Flick [1991].

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Aqueous Phase Viscosity (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.89</td>
</tr>
<tr>
<td>0.1235</td>
<td>1.18</td>
</tr>
<tr>
<td>0.2433</td>
<td>1.41</td>
</tr>
<tr>
<td>0.3595</td>
<td>1.55</td>
</tr>
<tr>
<td>0.4711</td>
<td>1.58</td>
</tr>
<tr>
<td>0.5771</td>
<td>1.57</td>
</tr>
<tr>
<td>0.6769</td>
<td>1.40</td>
</tr>
<tr>
<td>0.7698</td>
<td>1.22</td>
</tr>
<tr>
<td>0.8550</td>
<td>1.01</td>
</tr>
<tr>
<td>0.9319</td>
<td>0.79</td>
</tr>
<tr>
<td>1.0000</td>
<td>0.55</td>
</tr>
</tbody>
</table>

\[
D_{Am}^o = \frac{7.4 \times 10^{-8} (\kappa_m M_m)^{0.5} T}{\mu_m \nu_A^{0.6}} \quad \text{Wilke-Chang equation} \quad (18)
\]

\[
D_{Am}^o = \frac{(D_{AB}^o \mu_B)^{x_B} (D_{AC}^o \mu_C)^{x_C}}{\mu_m} \quad \text{Leffler-Cullinan equation} \quad (19)
\]
Figure 25. Viscosity of methanol/water mixtures from Flick [1991].
where $D_{AB}^{\infty}$ = infinite dilution diffusion coefficient of $A$ in $B$ (cm$^2$/sec) \\

$\kappa_m$ = association factor for $m$ \\

$M_m$ = molecular weight of $m$ (g/mole) with $\kappa_m M_m = \sum_{j=i}^{n} X_i \kappa_i M_i$ \\

$V_A$ = molar volume of $A$ at the normal boiling point (cm$^3$/mol) \\

$T$ = temperature ($^\circ$K) \\

$\mu$ = viscosity (centipoise) \\

subscripts $A$, $B$, and $m$, represent species $A$, species $B$, and mixture.

In using these relations, viscosity data were taken from Noda et al. [1982], infinite dilution diffusion coefficients estimated from Wilke-Chang or taken from Hayduk and Laudie [1974], and the molar volume of PCE at the normal boiling point computed from the critical volume using the Tyn and Calus method (Reid et al., 1987). The association factor was taken as 2.6 for water and 1.9 for methanol Reid et al., [1987]. Predicted diffusion coefficients for PCE in the aqueous phase are shown in Table 17 and Figure 26.

The molecular diffusion coefficient decreases with increasing methanol/water fraction up to a methanol/water fraction of 40% and then increases with increasing methanol/water fraction. This behavior is a result of the variation of viscosity with methanol/water fraction. The diffusion coefficient is strongly dependent on the viscosity. Over the entire range of methanol/water fractions, the diffusion coefficient changes by at most a factor of two.
Table 17. Predicted diffusion coefficients of PCE from Wilke and Chang [1955].

<table>
<thead>
<tr>
<th>Aqueous Phase Methanol (volume fraction)</th>
<th>Molecular Diffusion Coefficient (10(^{-5}) cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.018</td>
</tr>
<tr>
<td>0.107</td>
<td>0.825</td>
</tr>
<tr>
<td>0.212</td>
<td>0.688</td>
</tr>
<tr>
<td>0.269</td>
<td>0.651</td>
</tr>
<tr>
<td>0.398</td>
<td>0.601</td>
</tr>
<tr>
<td>0.482</td>
<td>0.607</td>
</tr>
<tr>
<td>0.619</td>
<td>0.672</td>
</tr>
<tr>
<td>0.679</td>
<td>0.729</td>
</tr>
<tr>
<td>0.736</td>
<td>0.806</td>
</tr>
<tr>
<td>0.848</td>
<td>1.038</td>
</tr>
<tr>
<td>0.902</td>
<td>1.240</td>
</tr>
<tr>
<td>0.919</td>
<td>1.305</td>
</tr>
<tr>
<td>0.960</td>
<td>1.550</td>
</tr>
<tr>
<td>1.0</td>
<td>1.907</td>
</tr>
</tbody>
</table>

2.3.6 Mobilization

The experiment using a 60% methanol/water mixture to remediate a glass bead porous medium contaminated with PCE provided valuable data on the effect of a methanol/water mixture on NAPL mobilization and dissolution. In the presentation of this data, the initial conditions within the column before initiation of the methanol/water flush are discussed first.

Figure 27 shows the distribution of porosity and the PCE volumetric fraction before and after water displacement. The PCE volumetric fraction is the fraction of the total column volume occupied by PCE. The trend of decreasing initial PCE volumetric content with vertical column location was a result of the PCE emplacement procedure. PCE
Figure 26. Predicted diffusion coefficients of PCE in methanol/water mixtures.

was pumped upward from the bottom; because PCE is denser than water the difference in pressure between the PCE and water was greatest at the bottom of the column and smallest at the leading edge of the invading PCE. After flushing the column with water from the top boundary, the distribution of residual PCE no longer showed any trend with vertical position.
Figure 27. Distribution of PCE volumetric fraction and porosity in column. PCE volumetric fraction is shown before and after displacement by water.

Although the final PCE residual showed no systematic trend, it was not very uniform. PCE volumetric content varied between approximately 0.125 and 0.05 in the lower 24 cm of the column. Careful visual observations indicated that the saw-tooth shape of the PCE residual occurred in the vicinity of fine sand microlayers: larger PCE residuals occurred above the fine layers and smaller PCE residuals occurred below them. The location of the fine layers were indicated by slightly smaller porosities. From Figure 27, large
PCE residuals were observed to occur immediately above locations where small porosities were measured.

After flushing the column with 10.0 PV of water, the column was flushed with 2.1 PV of a 60% methanol/water mixture. During this flush residual PCE droplets were mobilized from the column and observed in the column effluent. No additional PCE droplets were observed to leave the column after this flush.

A subsequent x-ray scan revealed that the injection of the methanol/water solution resulted in the mobilization of 12 ± 1% of the initial PCE residual. The methanol increased the aqueous-phase viscosity from 0.89 cp to approximately 1.50 cp, decreased the nonaqueous-aqueous phase interfacial tension from 44.9 dynes/cm to 11.9 dynes/cm, and increased the density difference between the nonaqueous and aqueous phases from 0.615 g/ml to 0.701 g/ml. PCE mobility is enhanced in this situation as interfacial forces trapping PCE droplets are reduced and viscous and gravity forces enhanced. The distribution of PCE before and after mobilization is shown in Figure 28. Much of the PCE which was mobilized came from column locations where PCE residuals were elevated due to underlying fine layers.

2.3.7 Dissolution

After no additional PCE mobilization was observed, effluent PCE concentrations were measured as the 60% methanol/water mixture was pumped downward through the column. These data are shown in Figure 29. Effluent PCE concentrations were at the solubility limit until approximately 20 PV, after which they decreased rapidly. Nonequilibrium dissolution is indicated by the tailing of the data after 20 PV. This condition persisted for approximately 10 PV. The tailing of the PCE concentration front at the end of
the experiment confirmed that dissolution of the residual PCE into the methanol/water solution was occurring under nonequilibrium conditions.

The effect of the methanol/water mixture on remediation can be seen by comparing the number of pore volumes required for PCE removal in this experiment with that required for a water flush. Assuming local equilibrium between residual PCE and water, over
1000 PV would be required to remove PCE by dissolution in a water flush, while approximately 30 PV were required using the 60% methanol/water solution. This is in addition to the enhanced removal through PCE mobilization. Although this comparison is not entirely realistic because of the importance of mass transfer limitations, it does indicate the significance of increasing the PCE solubility from 225 mg/l to 9135 mg/l when going from a 0% to 60% methanol/water solution.
2.3.8 Mass Transfer Rate Coefficient

To quantify the rate of mass transfer associated with the dissolution of PCE in the methanol/water mixture, the importance of additional mass transfer mechanisms must be assessed. As a methanol/water mixture moves into a region with residual PCE, the methanol and water may partition into the PCE ganglia. According to the data obtained in batch experiments for the methanol/water/PCE system, the equilibrium concentration of methanol in PCE was less than 0.2% by volume for a 60% methanol/water mixture. In addition, the partitioning of water into PCE was negligible. Thus, these additional mass transfer processes can be neglected in the analysis of column experiments.

Following the procedure of Imhoff et al. [1994a], the PCE saturation and effluent PCE concentrations can be used to compute the mass transfer rate coefficient for PCE dissolution, $K_l$, at various locations along the column:

$$K_l(x, t) = \frac{\rho_n \phi(x) \frac{\partial S_n}{\partial t}(x, t)}{C(0, t) - \frac{\rho_n}{U} \int_0^x \phi(x') \frac{\partial S_n}{\partial t}(x', t) \, dx' - C_s} \quad (20)$$

$$K_l(x, t) = \frac{\rho_n \phi(x) \frac{\partial S_n}{\partial t}(x, t)}{C(L, t) + \frac{\rho_n}{U} \int_x^L \phi(x') \frac{\partial S_n}{\partial t}(x', t) \, dx' - C_s} \quad (21)$$

where $K_l$ is the mass transfer rate coefficient; $x$ is the distance from inlet; $t$ is the time; $S_n$ is the PCE saturation; $C_s$ is the equilibrium PCE concentration in the aqueous phase;
$C(0,t)$ and $C(L,t)$ are PCE concentrations at the inlet and outlet of the porous medium, respectively; $\rho_n$ is the NAPL phase density; $\phi$ is the porosity; and $U$ is the Darcy flux of the aqueous phase.

Equations (20) and (21) were obtained by simplification of the advection-dispersion-dissolution equation (Imhoff et al., 1994a). As stated in equations (20) and (21), $K_l$ is a function of parameters measured experimentally: $\phi(x)$, $C(0,t)$ or $C(l,t)$, and $\partial S_n/\partial t(x,t)$. The profile of PCE saturation versus time obtained by using x-ray attenuation measurements for $x = 7.25$ cm is shown in Figure 30 for illustration. PCE saturation began to decrease at approximately three hours after beginning the 60% methanol/water flush and then decreased in an almost linear fashion until at 16 hours PCE saturation was below the detection limit. Polynomials varying in degree from three to seven were fit to the saturation versus time data at each column location, and the derivative of these polynomials was used to estimate $\partial S_n/\partial t(x,t)$. In Figure 30 the fitted polynomial was of the seventh degree.

The mass transfer coefficient, $K_l$, can be calculated by using the PCE concentration at either the column inlet (20) or outlet (21). Comparison of $K_l$ calculated by the two equations permits an examination of the effect of any mass balance error on computed $K_l$: the sum of the first two terms in the denominator of equations (20) and (21) are calculated values of $C(x,t)$, and differences in these calculated values represent mass balance errors (or errors in estimated $C(x,t)$) associated with x-ray measurement of PCE saturations within the column.

Errors in computing $K_l$ arise from several sources: $\phi(x)$, $\partial S_n/\partial t(x,t)$, and $C(x,t)$. Imhoff et al. [1994a] performed an error analysis which indicated that for the majority of the
Figure 30. PCE saturation versus time for $x = 7.25$ cm.

data the largest source of error in $K_l$ arises from errors in computed $C(x,t)$. For this reason, an estimate for the error in $K_l$ can be made from

\[
\text{estimated percent error in } K_l = \frac{| K_l \text{ equation (20)} - K_l \text{ equation (21)} |}{K_l \text{ equation (20)}}
\]  

(22)
If the estimated percent error in $K_I$ is large, then the determination of $C(x,t)$ is in error and has a significant effect on $K_I$. Only those values of $K_I$ computed from (20) were used for which the estimated percent error is less than 20%.

The programmed series of x-ray measurements during PCE dissolution were performed only for the upper 12.5 cm of the column. Using equations (20) and (21), $K_I$ could be computed only for these column locations. In this case, $C(0,t)$ is the inlet PCE concentration which was taken as zero, and $C(L,t)$ corresponds to the PCE concentration 12.5 cm below the column inlet. Although this concentration was not measured, it could be inferred from the x-ray measurements: when x-ray measurements indicated that PCE saturation was not changing at $x = 12.5$ cm, $C(12.5,t) \approx C_s$. Mass transfer was not occurring because of dissolution, which would happen only if the aqueous-phase PCE concentration was at the solubility limit. Once PCE saturations began to decrease at $x = 12.5$ cm, $C(12.5,t)$ was unknown and equation (21) could not be used to estimate $K_I$.

$K_I$ was computed using equations (20) and (21) for the locations $x = 1.75$ cm through $x = 3.25$ cm and are shown as a function of changing $S_n$ in Figure 31. Data are shown for which the estimated error in $K_I$ is less than 20%; sensitivity analyses indicated that fitted models for $K_I$ were insensitive to the value of the error norm at or below this value. $K_I$ were computed for other column locations, but equation (22) could not be used to estimate the error for these data since $C(12.5,t)$ was unknown for the times when active mass transfer was occurring in these regions. Thus, the greatest confidence could be placed in data at locations $x = 1.75$ cm through $x = 3.25$ cm, and only these data were used in regression analyses.
Figure 31. Mass transfer rate coefficient versus changing PCE volumetric fraction for sampling locations $x = 1.75, 2.25, 2.75, \text{ and } 3.25 \text{ cm}$.

The data were put in dimensionless form and power-law models including $Sh$, $Re$, $Sc$, and $\theta_n$ were fit to the data. The model used here was

$$Sh = \beta_0 Re^{\beta_1} \theta_n^{\beta_2} Sc^{\beta_3}$$

(23)
This is the same model used earlier for flushing with heated water. In this experiment the Darcy flux was kept constant and only $\theta_n$ was varied: thus, $Re$ changed minimally during the experiment. Therefore, for the regression analyses, values of $\beta_1$ and $\beta_3$ were chosen based on the work of other investigators: a value of 0.75 was chosen for $\beta_1$ and 0.5 for $\beta_3$. 0.75 was chosen because of similar values successfully fitted in earlier investigations (see discussion earlier for flushing with heated water). 0.5 was selected because this was the recommended value from the experiments with heated water.

Nonlinear regression was used to fit the data to equation (23) with the selected values for $\beta_1$ and $\beta_3$ using SYSTAT [1988]. The best-fit parameters with 95% confidence intervals are

$$\beta_0 = 0.41 \pm 0.27$$
$$\beta_2 = 0.57 \pm 0.16$$

(24)

The value of $\beta_2$ is smaller than values fitted by other investigators for transient dissolution: 0.87 was reported by Imhoff et al. [1994a], while Powers et al. [1994] reported values ranging from 0.75 to 0.96, depending on porous media characteristics. $\beta_2$ is closest to the value of 0.60 reported by Miller et al. [1990], but those data were for steady-state dissolution and not the transient dissolution of NAPL ganglia. The low value of $\beta_2$ is due to the influence of the two data points at the largest $\theta_n$ shown in Figure 31; more data for $\theta_n \geq 0.03$ may yield a different exponent.

To evaluate $\beta_0$, $Sh$ is plotted versus $\theta_n$ in Figure 32 for the model fitted here and for those from other investigations using conditions in this work. The correlations of Imhoff
et al. [1994a] and Powers et al. [1994] were modified to include $Sc^{0.5}$, since $Sc^{0.5}$ differed by a factor of two between their experiments and this study. The model shown from Imhoff et al. [1994a] is for conditions near the inlets to their columns before flow bypassing associated with dissolution fingers occurred (Imhoff et al. 1994b).

Figure 32. Comparison of predicted $Sh$ from several correlations for NAPL dissolution with the best-fit model from the 60% methanol/water dissolution experiment.
The data from the 60% methanol/water experiment are approximately twice as small as that predicted from the correlation of Powers et al. [1994], five times smaller than the prediction from Imhoff et al. [1994a], and nine times smaller than the prediction from Miller et al. [1990]. The procedures for creating the NAPL residual in this study are most similar to those employed by Powers et al. [1994] and Imhoff et al. [1994a], and these correlations were expected to be in closest agreement with results from this work.

One explanation for the differences in mass transfer between the experiment reported here and the experiments of Powers et al. [1994] and Imhoff et al. [1994a] may be differences in the initial residual PCE. After PCE invasion the average PCE volumetric content between $x = 1.75$ cm and $x = 3.25$ cm was 0.11. However, NAPL volumetric contents before displacement were always greater than 0.25 in the experiments of Powers et al. [1994] and Imhoff et al. [1994]. The smaller invasion NAPL saturations in this study suggest that NAPL invaded fewer, smaller pores at the very top of the column than in the other studies (Powers et al., 1994; Imhoff et al., 1994). After NAPL displacement with a water flood, a larger fraction of the trapped NAPL ganglia occupied large pores than in other investigations. Thus for the same NAPL volumetric content, NAPL dissolution in this study may have occurred from a smaller number of ganglia that were larger in size than in other investigations. Fewer, larger ganglia would have a smaller total area for mass transfer and result in smaller dissolution rates for the same NAPL volumetric content.

This explanation for the differences in observed mass transfer rates is plausible. The effect of methanol on IFT is not accounted for in the models for $K_t$ and also may have influenced the dissolution rate. Further research is required to quantify the effect of NAPL emplacement procedure and changes in IFT on NAPL dissolution. Even noting these
differences the data reported here are within a factor of five of predictions from correlations developed by experimenters for similar porous media and somewhat similar NAPL emplacement procedures and in one case within a factor of two.

2.4 Discussion

2.4.1 Physical and Chemical Properties

All of the important physical and chemical properties of the PCE/methanol/water system were measured or taken from reliable literature sources. The effects of methanol on physical and chemical properties of the PCE/methanol/water system are summarized in Table 18.

Table 18. Effects of methanol increase from 0% to 60% methanol fraction on properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Change</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE solubility in aqueous phase</td>
<td>+3960%</td>
<td>measured</td>
</tr>
<tr>
<td>MeOH solubility in nonaqueous phase</td>
<td>3159 mg/l</td>
<td>measured</td>
</tr>
<tr>
<td>Water content in nonaqueous phase</td>
<td>+22%</td>
<td>measured</td>
</tr>
<tr>
<td>Density (nonaqueous phase)</td>
<td>-0.3%</td>
<td>measured</td>
</tr>
<tr>
<td>Density (aqueous phase)</td>
<td>-9%</td>
<td>measured</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>-73%</td>
<td>measured</td>
</tr>
<tr>
<td>Viscosity (aqueous phase)</td>
<td>+72%</td>
<td>Flick [1991]</td>
</tr>
<tr>
<td>Diffusivity (PCE in aqueous phase)</td>
<td>-41%</td>
<td>predicted from Wilke and Chang [1955]</td>
</tr>
</tbody>
</table>
Methanol was found not to partition significantly into the PCE unless methanol concentrations were large enough that the PCE became completely miscible with the aqueous phase (methanol volumetric fractions ≥ 80%). Thus, an alcohol flush using methanol in a PCE-contaminated aquifer is not expected to swell the PCE. However, methanol did significantly affect the viscosity of the aqueous phase, the interfacial tension between the aqueous phase and PCE, the diffusivity of PCE, and the PCE solubility. There was a small effect on the density difference between the nonaqueous and aqueous phases. These latter effects will increase potential mobilization of trapped PCE droplets, alter the mass transfer rate coefficient for dissolution, and reduce the number of pore volumes required for remediation because of the increased PCE solubility. These effects were observed in the enhanced remediation experiment described in the preceding section.

The UNIQUAC model was examined for predicting the phase partitioning behavior of the PCE/methanol/water system. The relatively good predictions of this model suggest that it may be useful for evaluating the partitioning behavior of other NAPL/water/alcohol systems.

2.4.2 Mobilization

The addition of the 60% methanol/water mixture to the column resulted in the mobilization of 28% of the PCE residual. The methanol increased the aqueous phase viscosity from 0.89 cp to approximately 1.50 cp, decreased the nonaqueous-aqueous phase interfacial tension from 44.9 dynes/cm to 11.9 dynes/cm, and increased the density difference between the nonaqueous and aqueous phases from 0.615 g/ml to 0.701 g/ml. PCE mobility is enhanced in this situation as interfacial forces trapping PCE droplets are reduced, and viscous and gravity forces enhanced.
As discussed earlier, investigators commonly examine two dimensionless groupings to assess the relative importance of these forces: the Capillary number, \( Ca = \frac{v_a \mu_a}{\sigma_{na}} \), the ratio of viscous to interfacial forces; and the Bond number, \( Bo = \frac{(\rho_n - \rho_a)gd_p^2}{4\sigma_{na}} \), the ratio of gravity to interfacial forces. In this experiment, the addition of the 60% methanol/water mixture increased \( Ca \) from \( 1.7 \times 10^{-6} \) to \( 6.3 \times 10^{-6} \) and \( Bo \) from 0.0026 to 0.0097 (based on \( d_{p1} = d_{50} = 0.0277 \) cm). The increase in \( Ca \) is not the likely cause of PCE mobilization, since experiments in glass bead media by \textit{Morrow et al.} [1988] indicate that viscous forces mobilize residual oil only for \( Ca \geq 1.0 \times 10^{-4} \). However, PCE mobilization due to small increases in \( Bo \) was observed by \textit{Morrow et al.} [1988]. For similar increases in \( Bo \) they observed decreases in oil saturation that, within experimental error, were in agreement with the results from the 60% methanol/slash water experiment.

The significant PCE mobilization observed in the methanol/water experiment is likely due to the effect of microlayering on the creation of high PCE residuals. As water imbibed it may have bypassed PCE in the coarser media immediately above fine layers, trapping PCE islands consisting of many pores. Large pores and clusters of large pores surrounded by smaller pores have been observed to retain all of their nonwetting phase in imbibition experiments (\textit{Chatsis et al.}, 1984). This mechanism would result in higher levels of PCE residual immediately above fine layers, which is consistent with the x-ray measurements. Higher levels of PCE residual suggest larger PCE ganglia, which may be more easily mobilized (\textit{Ng et al.}, 1978).

Further work is required to better quantify the effect of changes in \( Bo \) on buoyancy-driven mobilization of NAPL ganglia. However, it is clear from this experiment that flushing with a methanol/water mixture may enhance downward migration of NAPL
2.4.3 Dissolution

The methanol/water mixture affected both the rate of PCE dissolution and the solubility limit of PCE in the aqueous phase. The measured mass transfer rate coefficients were within a factor of two of predictions from an existing correlation, suggesting that the dimensionless groupings used in these models adequately account for the effect of the methanol/water mixture on the physical and chemical properties affecting mass transfer. Assuming that this is true, $K_I$ can be predicted with equations (23) and (24) for representative conditions and methanol/water fractions not used in this experiment. Predicted $K_I$ are shown in Figure 33. For methanol volumetric fractions from 0% to 80% $K_I$ does not change by more than 25%.

The maximum potential enhancement of PCE dissolution due to a methanol/water mixture is illustrated by plotting the maximum potential mass flux, $K_I C_s$, versus methanol/water fraction. This is shown in Figure 34, where $K_I$ was estimated from equations (23) and (24), and $C_s$ taken from measured solubilities. The maximum potential mass flux increases by one order of magnitude as the methanol/water fraction increases from 0% to 60%. This dramatic improvement in the mass flux is due to the increase in aqueous phase PCE solubility. This effect was demonstrated in the enhanced remediation experiment, where the number of pore volumes required for cleanup was decreased from over 1000 to approximately 30 by the use of the 60% methanol/water mixture.
Predicted $K_f$ for PCE for representative conditions using equations (23) and (24).

$U = 1.76 \text{ m/day}$

$\theta_n = 0.02$

$\phi = 0.37$
Figure 34. Maximum potential mass flux of PCE for representative conditions using equations (23) and (24).
References


Taber, J. J. 1969. Dynamic and Static Forces Required to Remove a Discontinuous Oil Phase from Porous Media Containing Both Oil and Water. SPE Journal. 2:3-12.


