Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media

M. Schnarr a, C. Truax b, G. Farquhar c,*, E. Hood c, T. Gonullu c, B. Stickney c

a Geotrans, Boulder, Co, USA
b Jacques Whitford, Vancouver, BC, Canada
c Department of Civil Engineering, University of Waterloo, Waterloo, Ont., N2L 3G1, Canada

Received 30 December 1994; revised 18 December 1996; accepted 18 December 1996

Abstract

Few proven technologies exist that may be used to treat dense non-aqueous phase liquid (DNAPL) contaminants. In-situ chemical flushing is a proposed technology which consists of flushing DNAPL source zones with a reactive solution to degrade the contaminant mass below ground.

A laboratory and controlled field experimental program was conducted to assess the potential of potassium permanganate (KMnO₄) as a reagent for in-situ DNAPL remediation. The results of laboratory experiments indicated that two common DNAPL contaminants, perchloroethylene (PCE) and trichloroethylene (TCE), were rapidly degraded to chloride and carbon dioxide. Column experiments, using residual PCE flushed with oxidant concentrations as high as 10 g L⁻¹, indicated that chloride could be used as a reaction tracer. From the chloride data, it appeared that the rate of PCE removal from the columns was a complex process dependent upon the kinetics of both dissolution and oxidation.

Two experimental applications of in-situ oxidation were conducted in the Borden aquifer isolated within a 7.5 m³ double sheet-pile cell. The cell was fitted with injection and recovery wells through which aqueous solutions of KMnO₄ were flushed to oxidize solvent source zones in situ. In the initial experiment, flushing of a 1 L PCE residual source with 10 g L⁻¹ KMnO₄ at total flow rates of up to 100 L per day, completely removed the source within 120 days. A second experiment, using an 8 L mixture of PCE and TCE slowly allowed to infiltrate into the cell, was

* Corresponding author.

0169-7722/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PHT 0169-7722(97)00012-0
conducted using a system to recycle the oxidant. The oxidant was added at 10 g L⁻¹ with a flow of approximately 50 L per day. After 290 days of flushing, it was concluded from the monitoring data that 62% of the initial source (as equivalent chloride mass) had been oxidized and it was evident that oxidation was continuing in the upper third of the cell.

These experiments have suggested that the effectiveness of in-situ chemical oxidation will depend primarily upon the distribution of the DNAPL in the subsurface and its effects upon dissolution. In both experiments, spatial variability of chloride measurements appeared to reflect both the DNAPL location and distribution. © 1998 Elsevier Science B.V.

**Keywords:** Potassium permanganate; Porous media; DNAPL contaminants

---

1. Introduction

Trichloroethylene (TCE) and perchloroethylene (PCE) are two chlorinated organic solvents frequently identified as ground water aquifer contaminants (Westrick et al., 1984; Smith, 1990; Plumb, 1991). The US Environmental Protection Agency drinking water standards for each of these compounds is 5 μg L⁻¹ compared with their solubilities of approximately 1,500 mg L⁻¹ and 240 mg L⁻¹, respectively (Pankow and Cherry, 1996). With five to six orders of magnitude difference between solubility and regulated concentration, the presence of dense non-aqueous phase liquids (DNAPLs), especially in the form of pools in the subsurface, will remain as a very long-term source of contamination until either source containment, isolation or removal has occurred (Mackay and Cherry, 1989; Johnson and Pankow, 1992).

Frequently at sites where DNAPLs are present, pump and treat remediation is selected as a remedial alternative; however, pump and treat approaches to aquifer restoration have demonstrated a distinct lack of success even at sites without DNAPLs (National Research Council, 1994). At sites where DNAPL is present, this approach is primarily limited by low contaminant solubility, contaminant mass storage in low permeability zones, and the relatively large masses of the DNAPL present in the aquifer (Doty and Travis, 1991). The lack of success of pump and treat at these sites has added emphasis to remedial efforts designed to isolate, remove or treat DNAPL sources with the potential benefits of reducing the duration of a subsequent pump and treat containment process and reducing downgradient aqueous phase concentrations.

One example of a mass treatment technology is in-situ oxidation, an approach which consists of flushing a zone of DNAPL contamination with a reactive solution. This technology is conceptually appealing since it combines hydraulic containment of a source zone with contaminant treatment below ground. Various reactive compounds have been suggested including hydrogen peroxide, Fenton’s reagent, ozone and potassium permanganate (Cho and Bowers, 1991). To date, documented use of this technology is limited to a single industrial application in which hydrogen peroxide was used to remove an LNAPL release containing 50% formaldehyde with some success (Cowie and Weider, 1986). To our knowledge, the results presented in this paper are the first evaluation of potassium permanganate (KMnO₄) as an in-situ reagent and the first evaluation of in-situ chemical flushing of DNAPL contaminants.
2. Permanganate ion as an oxidant

The use of the permanganate ion (MnO$_4^-$) to indiscriminately scavenge and oxidize organic contaminants has a long history in both drinking water and wastewater treatment (Steel and McGhee, 1979; Eilbeck and Mattock, 1987), including removal of iron and manganese (Benefield et al., 1982), phenols (Vella et al., 1990), trihalomethane precursors (Colthurst and Singer, 1982) and more recently, TCE (Vella and Veronda, 1992). The reactive properties of MnO$_4^-$ with both organic and inorganic compounds have been described in detail by Stewart (1965) and Lee (1980). Permanganate oxidation of organic compounds is used in the commercial production of various compounds with its most serious limitation being its lack of solubility in most hydrocarbons (Lee, 1980) including PCE and TCE. For example, MnO$_4^-$ oxidation of alkenes is used in the synthesis of the corresponding glycols. In addition to its characteristics as an oxidant, potassium permanganate has a high aqueous solubility (64 g L$^{-1}$ at 20°C (Perry et al., 1984)), a property which would allow for a significant loading rate of oxidant into a contaminated zone. As a solid, KMnO$_4$ is easily handled and currently costs approximately CDN$4 per kg.

3. Oxidation mechanism

There are few references dealing directly with the oxidation of specific chlorinated organic compounds by KMnO$_4$. In general, the existing research has focused on synthesis, rather than destruction, of commercially useful oxidation products from alkenes. Lee (1980) has identified two potential reaction mechanisms for alkene oxidation. Both mechanisms begin with the formation of a hypomanganate diester with subsequent steps generally dependent upon pH and the MnO$_4^-$ concentration. Oxidation of alkenes is generally performed in an aqueous solution due to the fact that KMnO$_4$ is insoluble in most hydrocarbons without the use of a phase transfer catalyst (Lee, 1980).

4. Oxidation stoichiometry

Based on laboratory observations and the redox reactions for each compound, overall reactions between KMnO$_4$ and TCE and PCE were determined. Laboratory observations leading to these equations include the formation of a brown precipitate, determined to be MnO$_2$(s), and the evolution of a gas, later confirmed as being CO$_2$.

Recognizing that MnO$_4^-$ was reduced to MnO$_2$(s) and assuming that the carbon in TCE and PCE was completely oxidized to CO$_2$, the following half cell reactions apply:

\[
\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}
\]

\[
\frac{1}{2}\text{C}_2\text{Cl}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + \frac{1}{2}\text{Cl}_2 + \text{Cl}^- + 3\text{e}^-
\]

which produce

\[
\text{C}_2\text{Cl}_4 + 2\text{MnO}_4^- \rightarrow 2\text{CO}_2 + 2\text{MnO}_2(\text{s}) + \text{Cl}_2 + 2\text{Cl}^- \quad (1)
\]
In a similar fashion, the reaction for TCE is:

$$\text{C}_2\text{Cl}_3\text{H} + 2\text{MnO}_4^- \rightarrow 2\text{CO}_2 + 2\text{MnO}_2(s) + 3\text{Cl}^- + \text{H}^+ \quad (2)$$

Stoichiometrically, 0.81 kg of Cl\(^-\) are produced per kg of TCE oxidized (Eq. (2)). A similar situation exists for PCE except that Eq. (1) suggests the formation of Cl\(_2\). Based on thermodynamic considerations, it was assumed that the Cl\(_2\) is an intermediate and that Cl\(^-\) would be the sole chlorine species present. Therefore, oxidation of 1 kg of PCE should produce 0.86 g Cl\(^-\).

5. Column experimentation: quantifying oxidation with chloride ion

5.1. Experimental outline

Eq. (1) and (2) suggest several possibilities for monitoring the progression of in situ oxidation applications. Some preliminary column experiments indicated that CO\(_2\) in the gas and aqueous phases could be used as a reaction tracer during TCE oxidation but that this would be impractical in natural porous media containing carbonate minerals and natural organic matter. During these experiments significant gas production was observed; in one experiment, the extremely vigorous gas production actually disrupted the soil within the column. It was anticipated that measuring the variation in Cl\(^-\) in the effluent during oxidation would provide both a measure of the mass of TCE or PCE oxidized as well an indication of the relative rates of mass removal.

Chloride analyses were performed using an ORION ion selective electrode with a portable meter (ORION Model 720A). Measurements of KMnO\(_4\) concentrations were performed either by titration with thiosulphate or spectrophotometrically (Spectronic 20D). Analysis of TCE and PCE was performed with a Shimadzu GC-9A gas chromato-

![Diagram of column apparatus](image-url)

Fig. 1. Column apparatus; source consists of homogeneous PCE residual (1640 mg).
Table 1

Darcy flux and oxidant concentration for experimental columns

<table>
<thead>
<tr>
<th></th>
<th>COL 1</th>
<th>COL 2</th>
<th>COL 3</th>
<th>COL 4</th>
<th>COL 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darcy flux (cm per day)</td>
<td>42</td>
<td>42</td>
<td>63</td>
<td>68</td>
<td>61</td>
</tr>
<tr>
<td>KMnO₄ (g L⁻¹)</td>
<td>10</td>
<td>7.5</td>
<td>10</td>
<td>7.5</td>
<td>0</td>
</tr>
<tr>
<td>Oxidant loading (g cm⁻² per day)</td>
<td>0.42</td>
<td>0.32</td>
<td>0.63</td>
<td>0.51</td>
<td>0</td>
</tr>
<tr>
<td>Total mass removed @ 650 h (%)</td>
<td>121</td>
<td>103</td>
<td>122</td>
<td>119</td>
<td>92</td>
</tr>
<tr>
<td>% Mass removed as chloride</td>
<td>92</td>
<td>91</td>
<td>96</td>
<td>93</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: The cross-sectional area of each column was 20.3 cm²; porosity 0.41.

To investigate the effects of oxidant concentration and flushing rates upon mass removal, five column experiments were performed using glass columns packed with fine grained sand samples (foc = 0.02%) from the Canadian Forces Base (CFB) Borden aquifer. In each of the column experiments, the sand was initially saturated with water and 1.0 mL of PCE added as a residual source (volumetric saturation ~ 1%) in the sand. Fig. 1 is a schematic diagram of the experimental apparatus. The columns were subsequently flushed with KMnO₄ solutions at the concentrations and average Darcy fluxes specified in Table 1. Actual flow rates into the columns were variable and were assumed to have produced the principal source of error. One column (COL 5) was flushed only with deionized water to evaluate mass removal by dissolution alone. After the oxidant flush, the columns were flushed with deionized water at the same flow rates.

![Graph](image-url)

Fig. 2. Column effluent profiles for Cl⁻, PCE, input KMnO₄ and effluent KMnO₄. Also shown are effluent PCE concentrations for COL 5, which was flushed only with deionized water to compare mass removal by dissolution alone.
Control experiments confirmed that oxidation of the PCE was the only source of Cl\(^-\) from the columns.

Fig. 2 provides combined Cl\(^-\), KMnO\(_4\) and PCE effluent data for the experiment (COL 3) flushed at the highest oxidant loading and is qualitatively similar to results observed in the other columns. This column was flushed with an aqueous solution of 10

![Graph](image)

Fig. 3. (a) Effluent chloride concentrations (COL 1–4) and (b) effluent PCE concentrations (COL 1–5).
g L$^{-1}$ KMnO$_4$ for a period of 214 h and then deionized water for the remainder of the experiment.

In COL 3, PCE in the effluent was initially high (~ 50 mg L$^{-1}$). As the oxidant reached the source zone, Cl$^-$ increased rapidly from non-detectable levels to a peak of 380 mg L$^{-1}$. When oxidant appeared in the effluent, the PCE concentrations dropped below 1 mg L$^{-1}$. The concentration of chloride began to decrease after 70 h of flushing and was less than 1 mg L$^{-1}$ after 180 h of flushing. This decline in Cl$^-$ was accompanied by a gradual increase of KMnO$_4$ in the effluent to above 9 g L$^{-1}$ after 200 h (influent concentration of 10 g L$^{-1}$). The rate of PCE removal had reduced significantly after approximately 170 h.

In COL 5, the PCE concentration in the effluent from the column reached an initial peak of approximately 100 mg L$^{-1}$, and then declined slowly to a concentration of approximately 6 mg L$^{-1}$ after 650 h. The dissolution profile from COL 5 is representative of rate limited dissolution for this particular experimental setting.

Effluent Cl$^-$ and PCE effluent concentrations for each of the columns are shown in Fig. 3(a) and (b). All of the columns flushed with oxidant initially produced no effluent Cl$^-$. Chloride concentrations then rapidly rose to a peak and then slowly declined to non-detectable levels. The two columns flushed at 10 g L$^{-1}$ KMnO$_4$ producing larger chloride peaks. The initial delay in the appearance of Cl$^-$ and KMnO$_4$ in the column effluents was attributed to displacement of the initial pore volume of deionized water and consumption of the KMnO$_4$ through oxidation of organic matter in the sand. In contrast, PCE concentrations in the columns flushed with oxidant were initially high (~ 100 mg L$^{-1}$) and then dropped below 1 mg L$^{-1}$. In each of these columns, the PCE concentrations tended to increase once the deionized water flush began suggesting that

Fig. 4. Accumulated effluent Cl$^-$ mass as a fraction of initial Cl$^-$ mass in column. The accumulated mass remove includes both aqueous PCE and equivalent PCE mass oxidized as calculated from Cl$^-$ data. The initial PCE mass was 1640 mg.
some PCE remained; however relative to the column flushed only with deionized water, effluent PCE concentrations were 1 to 2 orders of magnitude lower.

The accumulated equivalent PCE mass produced from each column is presented in Fig. 4; the mass of the initial PCE source was 1640 mg. The equivalent mass includes both effluent PCE and PCE oxidized calculated from Cl⁻ in the effluent. The mass balance over-estimates the initial mass of PCE from 103%–122%. This error in the mass balance was attributed mainly to variability in the flow rates.

During the deionized water flush following KMnO₄ addition, the PCE concentration in the effluents from COL 1, 2 and 4 increased from about 0.3 mg L⁻¹ to as high as 6 mg L⁻¹ then decreased below the detection limit. COL 3, which had the highest oxidant loading, did not experience this rebound. While most of the PCE had been oxidized in situ, a small amount of PCE remained within each column; however, for COL 3 and COL 4 (both flushed at close to the same flow rate as the dissolution control) the final effluent PCE concentrations were about 1% of those in COL 5.

6. Field experimentation

6.1. Experimental cell details

Two pilot scale experiments were performed at the CFB Borden research site in an unconfined, shallow aquifer consisting of a glaciolacustrine sand (Bolha, 1986). The sand is predominantly medium to fine grained and, while relatively homogeneous, contains numerous horizontal bedding features varying in thickness from millimeters to a few centimeters (Ball et al., 1990; Poulson and Kueper, 1992). The mean hydraulic conductivity of the sand is 7.2 × 10⁻³ cm s⁻¹ (Sudicky, 1986). The experimental cell, consisting of double-walled, sealed joint sheet piling (Starr et al., 1992) extended from the surface down to a clay aquitard at a depth of approximately 2.5 m (Fig. 5). The pore volume of the cell, estimated from the sand porosity of 0.33 (Ball et al., 1990), was approximately 2.48 m³.

Six injection and six extraction wells (2 in ID PVC) were located at opposite ends of the cell as shown; these were screened at upper, intermediate, and lower depths with each pair of well screens extending over one third of the depth. Also shown in Fig. 5 are the multilevel samplers which allowed collection of small volume samples from various points with the cell. The multilevel piezometers consisted of 0.06 in ID Teflon® tubes attached at 1 foot intervals to a central 0.5 in OD PVC pipe. The instrumentation was installed by simultaneously driving and jetting a 3 in ID steel casing to the required depth with a hand-held vibrating hammer, inserting the well casing or multilevel stem, withdrawing the larger steel casing and allowing the formation to collapse around the instrument.

6.2. Sampling methods

Sample collection from the multilevels was performed by connecting individual sample points to a 250 mL Erlenmeyer flask through a stopper. A vacuum was applied to the flask using a 50 mL syringe. Typically, 75–100 mL of sample were collected. Part of this volume was decanted into an 8 mL vial with Teflon® lined septa for TCE
and PCE analysis. A small quantity of granular sodium thiosulphate was added to reduce any KMnO₄ and prevent further solvent oxidation. The remaining volume was stored in a 40 mL EPA vial for Cl⁻ analysis. Sample analyses were conducted using the previously mentioned analytical methods.

7. Experiment I: homogeneous residual source

The DNAPL source for Experiment I consisted of 1 L (1.64 kg) of PCE which was mixed with soil taken from a 0.3 m × 0.3 m × 0.35 m block below the water table. The soil:DNAPL mixture was replaced in the excavated block (Fig. 5). The residual DNAPL saturation was estimated to be 8% (v/v). The cell was subsequently flushed with a 10 g L⁻¹ aqueous solution of KMnO₄ through the injection wells; effluent was withdrawn from the extraction wells. Constant head was maintained in the injection wells by siphoning from a constant head reservoir into each well. Flow rates were controlled by a peristaltic pump at the extraction wells. Initially, both the upper and intermediate extraction wells were pumped at a total flow rate of approximately 100 L per day. After monitoring confirmed that oxidation was occurring only in the upper third of the cell, pumping from the intermediate extraction wells was stopped at 1200 h with the new flow rate of 50 L per day from the upper wells. The cell was flushed with oxidant
Fig. 6. Chloride concentrations observed at MLC-1, directly downgradient of the residual PCE source.

solution for 120 days and then with water for a further 60 days to displace the remaining oxidant and reaction products. Effluent from the cell was continuously treated to remove residual oxidant and aqueous phase PCE.

Fig. 7. Accumulated PCE mass destruction calculated based on observed chloride concentrations.
Chloride monitoring from the multilevel piezometers indicated that Cl\(^-\) was produced only in the upper third of the cell. After approximately 300 h of flushing, a rapid increase in Cl\(^-\) was observed in MLC-1 (Fig. 6). Over the remainder of the experiment, Cl\(^-\) concentrations at this point gradually declined to non-detectable levels. Using the Cl\(^-\) data from the extraction wells, the cumulative mass of effluent Cl\(^-\) was determined to be 1486 g or 91% of the chloride content of the initial source mass (Fig. 7).

Several other quantitative measures were used to evaluate the effectiveness of this experiment. PCE was not detected during the post-oxidation water flush. As well, a core was removed from the source zone after the water flush from which subsamples were taken and analyzed for their PCE content. Solvent concentrations in these subsamples were below the method detection limit (< 0.0003% w/w).

8. Experiment II: heterogenous NAPL source

Experiment II had a mixture of PCE and TCE as a source; source emplacement was designed to simulate a slow leak release. Six 2.5 cm ID stainless steel pipes, 1.0 m long and equipped with drive points, were driven to a depth of 0.25 m in the centre of the cell in the same location as the Experiment I source. Equal masses of TCE and PCE (6.19 kg each, 8.0 L in total) were mixed with Sudan IV and distributed equally into the six source points over a period of 9 days. Volatilization of the TCE/PCE mixture was minimized by adding it below the water table; however, some minor loss from the separatory funnels containing the mixture was likely. The DNAPL mixture was allowed to migrate within the cell for an additional 10 days before beginning in-situ KMnO\(_4\) oxidation.

No effort was made to determine the distribution of the DNAPL within the cell; however, DNAPL was withdrawn from several of the multilevel sampling points throughout the course of the experiment. Initially, pure phase was evident in all the MLW and MLC sampling points but as treatment proceeded, free product persisted at only the lowest point of the centre multilevel (MLC-5).

8.1. Treatment system

The treatment system was designed to supply KMnO\(_4\) at a concentration of 10 g L\(^{-1}\) through all six injection wells at a total flow rate of 48 L per day using the system of peristaltic pumps and a constant head reservoir as in Experiment I.

In Experiment I, the effluent eventually contained unused oxidant at concentrations close to 10 g L\(^{-1}\). An oxidant recycle system was used in Experiment II to reduce the amount of oxidant used and to eliminate the need for continuous effluent treatment. In this system (Fig. 8), effluent was pumped through a coarse cartridge filter and discharged to a equalization and settling tank for removal of suspended MnO\(_4\)\(_{2}\)(s) and other solids. The main effluent line was drained by gravity to the constant head injection reservoir. A sample loop from the main effluent line ran through a spectrophotometer and was used to monitor KMnO\(_4\) concentrations. The spectrophotometer provided an input to a PID controller. In turn, the controller ran a peristaltic pump which diverted a fraction of the main effluent flow to a column packed with crystalline KMnO\(_4\). The
discharge from the column produced an oxidant solution near solubility (64 g L$^{-1}$ at 20°C (Perry et al., 1984)). This stream was mixed back into the main effluent line before the spectrophotometer sample loop.

8.2. Cl$^-$ concentration profiles in multilevels

Fig. 9 presents data from MLC. Low background Cl$^-$ concentrations (generally less than 20 mg L$^{-1}$) were observed prior to KMnO$_4$ addition. After KMnO$_4$ addition, substantial increases in Cl$^-$ concentration were observed. At three levels (MLC-2,
MLC-3 and MLC-5), concentrations exceeded 3000 mg L\(^{-1}\), indicating that significant oxidation was occurring adjacent to these points.

MLC-1 and MLC-4 exhibited little evidence of oxidation. Each experienced a gradual increase in Cl\(^-\) but this was owing principally to Cl\(^-\) in the recycled K\(\text{MnO}_4\) solution. Cl\(^-\) concentrations at each of these two points were generally similar to the profile of injection feed concentrations indicating relatively little DNAPL oxidization at these depths.

8.3. Cl\(^-\) and solvent concentration profiles in extraction wells

PCE concentration data from the extraction wells are presented in Fig. 10; the data points are averages for the pair of wells at each depth. TCE concentrations (not shown) were generally similar but slightly higher. Some trends are evident in spite of high variability in the data. The highest concentrations of both solvents were observed in the upper wells. From 2000 to 2500 h, the concentrations of PCE were in the 10 to 50 mg L\(^{-1}\) range. During this time, the effluent from the extraction wells was nearly colourless indicating that most of the K\(\text{MnO}_4\) had been consumed. Beyond this time, K\(\text{MnO}_4\) concentrations began to increase in the effluent with a corresponding reduction in the PCE concentrations.

The PCE and TCE concentrations declined with time and after approximately 6000 h, remained at concentrations less than 0.01 mg L\(^{-1}\). At this point, the effluent had high K\(\text{MnO}_4\) concentrations approaching the injected concentration.

Chloride concentrations (Fig. 11) in all of the extraction wells increased over time owing to the recycling of the Cl\(^-\) in addition to the oxidant. The changes in concentration relative the concentration of Cl\(^-\) injected in the cell provide some clue to the location of DNAPL mass. The intermediate and lower extraction well profiles are similar to the injection feed profile suggesting that little mass removal is occurring in the

![Fig. 10. Effluent PCE in the three pairs of extraction wells (highest relative concentrations in the upper pair).](image-url)
lower two thirds of the cell; however, up to the end of the oxidant flush, the Cl\(^-\) concentration in the upper extraction well is higher than the injection feed indicating that some solvent mass is still being oxidized.

8.4. Chloride mass balance

Mass balance calculations based on Cl\(^-\) production were used to estimate the extent of DNAPL oxidation. With a single pass system, such as that used in Experiment I, the concentration of Cl\(^-\) in the effluent from the extraction wells was readily converted to an equivalent mass of PCE oxidized. However, the recycle system used in Experiment II complicated the mass balance calculations because of the recycling of Cl\(^-\) back into the cell.

In addition, problems with the reinjection equipment during the initial stages of treatment resulted in periodic effluent losses from the system. It was estimated that 1.1 kg of Cl\(^-\) or 11% of the initial Cl\(^-\) mass was lost in this way.

An approximate method was used to estimate the mass of DNAPL oxidized based on Cl\(^-\) release. The averages of the last five effluent and the feed concentrations shown in Fig. 12 were assumed to represent the average Cl\(^-\) concentration in the entire cell. The total pore volume of the cell plus the liquid volume in the above ground treatment system, was estimated to be 2800 L. Based on this average, it was determined that
Fig. 12. Average effluent and injection feed chloride concentrations used to estimate total chloride mass in system.

approximately 51% of the Cl\(^-\) content of the original solvent source was present in this volume. Including the 11% Cl\(^-\) loss, approximately 62% of the initial mass of chlorine had been released by the oxidant flush.

9. Discussion

While in-situ oxidation removed substantial DNAPL mass in both field experiments, it is likely that the subsurface distribution of DNAPL had a significant effect on the rates of mass removal. In Experiment I, the residual PCE source was rapidly and completely oxidized, a reflection of the homogeneous distribution of the DNAPL as a residual with a relatively large surface area:volume (A:V) ratio which would allow rapid dissolution. As well, the aqueous phase permeability in the source area would be high relative to the permeability of source zones with high NAPL saturations. In more typical DNAPL sources, such as that used in Experiment II, non-wetting phase saturations would be highly variable and could possibly include pooled DNAPL above slight permeability contrasts. For example, in an experimental PCE release at a nearby location, PCE flow was found to be controlled by millimeter scale sand bedding structures with non-wetting phase saturations ranging from 1% to 38.1% (Kueper et al., 1993). Experiment II, containing a variable DNAPL distribution, would likely have some fraction of the solvent source present in both high and low saturations. The low saturations would be readily oxidized (as in Experiment I) but mass removal of high saturation zones would be slow owing both the lower aqueous phase permeability and lower A:V ratios. In the extreme case, where all the DNAPL is present as pools above low permeability zones
and is occupying almost the entire pore space, mass removal would be limited by weak dispersive processes, resulting in lower mass removal from the source zone than achievable by advectively dominated flushing.

Successful prediction of overall rates of mass removal would require rate expressions for both non-equilibrium dissolution and oxidation. In the conceptual model (Fig. 13) proposed in this work to describe mass removal rates, dissolution mass transfer, driven primarily by aqueous phase PCE/TCE concentration gradients, is enhanced by the oxidation reaction which increases these gradients. As the aqueous solvent gradient is increased, the dissolution mass flux is increased. Simultaneously, the concentration gradient of the oxidant would be increased, causing an increase in oxidant mass flux towards the DNAPL:water interface.

The ability of in situ oxidation to remove PCE was clearly demonstrated in Experiment I. Based on the Cl\textsuperscript− mass balance, greater than 90% of the 1.64 kg emplaced mass was oxidized in 120 days; however, it was inferred from source sampling that 100% of the mass had actually been removed. The peak PCE concentration observed in the extraction wells at the beginning of this experiment prior to oxidation was 18 mg L\textsuperscript−1. Assuming that this effluent concentration remained constant, removal of the entire source by water flushing alone would require, at a minimum, 900 days. In agreement with the conceptual model of dissolution and oxidation as parallel kinetic processes, the oxidant flush was able to accelerate dissolution of this source by increasing the concentration gradients of both the dissolved phase solvent and the oxidant. It was evident from the Cl\textsuperscript− profiles that mass removal tailed off after the peak, an indication that mass transfer rates during the oxidant flush were decreasing as DNAPL mass was removed. This would suggest that the mass transfer rate expressions currently in the published literature (e.g. Powers et al., 1994; Geller and Hunt, 1993; Guiguer and Frind, 1994) might be applied to estimate dissolution mass transfer during an oxidant flush.

The release of Cl\textsuperscript− provided a measure of the spatial extent of source. During Experiment I, Cl\textsuperscript− production occurred only in the upper third of the cell zone and the treatment process was adjusted to limit flow to this area alone. In Experiment II, most of the oxidation again appeared to occur in the upper third of the cell based on the
extraction well Cl\textsuperscript{−} profiles. The Cl\textsuperscript{−} concentrations in the multilevel samplers generally supported this; however, the highest Cl\textsuperscript{−} concentrations were observed in MLC-5. This same multilevel contained pure phase during the entire experiment. These data suggest that during the DNAPL release at the beginning of the experiment, a portion of the solvent mixture moved laterally from the injection points, migrated down the multilevel stem and became immobilized at or below MLC-5. This is supported by other observations. During the experiment, Cl\textsuperscript{−} concentrations in the lower extraction wells, covering the vertical position of MLC-5, were only slightly different from the feed concentrations implying that little oxidation was occurring in the bottom third of the cell. This is consistent with the possibility of a small amount of DNAPL located right at the multilevel MLC 5 being oxidized to produce high localized Cl\textsuperscript{−} concentrations but only a small amount of Cl\textsuperscript{−} mass in the extraction wells. Short-circuiting down multilevel stems was also observed by Kueper et al. (1993).

Recycling of the oxidant was an effective method of reducing the amount of oxidant required and the degree of effluent treatment. Experiment I used approximately 80 kg of oxidant while Experiment II, with a substantially larger source mass, used almost 50 kg.

During Experimental I, it was expected that organic material and reduced mineral species in the Borden sand (foc = 0.027% w/w, Ball et al., 1990) would consume oxidant. The oxidant demand of the Borden sand in the cell was estimated, based on effluent KMnO\textsubscript{4} data (not shown) from Experiment I to be at most, 7 kg KMnO\textsubscript{4} m\textsuperscript{−3} Borden sand.

10. Application of in-situ oxidation at industrial sites

Experimentation with KMnO\textsubscript{4} has been limited to oxidation of TCE and PCE. While some other NAPL contaminants may be oxidizable (for example, other chlorinated alkenes), it is probable that many compounds will either be largely resistant to permanganate oxidation or oxidized to secondary organic compounds which may also be hazardous. This factor may make permanganate an unsuitable oxidant at field sites contaminated with solvent mixtures other than PCE and TCE. At field sites with complicated hydrogeology, the DNAPL source is likely to be spatially large with a complex distribution; a comprehensive site characterization program will be required to design of an injection system capable of supplying oxidant to the entire source while minimizing the volume of the treatment zone. At many sites, some DNAPL will be isolated from advective flow causing mass removal to be limited by diffusion of oxidant into that zone. In these zones, it is possible that mass removal by oxidation will be faster than technologies such as cosolvent/surfactant flushing, owing to the increased concentration gradients proposed in the conceptual model. In many cases, it may be that the application of in situ oxidation will rapidly remove the fraction of the DNAPL mass which has the largest driving potential for dissolution (large area to volume ratios in high permeability zones). Removal of this fraction could result in significant lowering of aqueous concentrations with only a modest reduction in DNAPL mass, which would be advantageous from both economic and risk based perspectives.
11. Summary and conclusions

Laboratory and pilot scale field experiments were performed to evaluate the effectiveness of KMnO$_4$ flushing as a means of DNAPL source removal through in-situ oxidation.

Column experimentation indicated that using the reaction product Cl$^-$ was an effective means of following the progress of the oxidation reaction. Calculated mass balances based on Cl$^-$ tended to overpredict mass removal; however, it was inferred from post-oxidation aqueous phase PCE concentrations that nearly complete removal of the PCE source was achieved. As well, mass removal was significantly faster and aqueous phase PCE concentrations were one to two orders of magnitude lower than with aqueous flushing alone.

Two field experiments were completed within a section of the CFB Borden aquifer isolated by double walled sheet piling. In each experiment, monitoring of the process was accomplished by measurements of Cl$^-$ concentrations in multilevel piezometers and extraction wells. In Experiment I with a emplaced residual PCE source, the oxidant flush removed 100% of the DNAPL mass, as determined by aqueous phase concentrations, a chloride mass balance, and source zone core samples. In Experiment II, using a heterogeneous source produced by slowly leaking PCE and TCE into the field cell, about 60% of the DNAPL mass was removed from the source. Several factors appeared to control the effectiveness of in situ oxidation at the field scale. The process of dissolution is the principal determinant of DNAPL mass removal rates. It was clear that the rate of dissolution during an oxidant flush is much more rapid than during a water flush. Linked to the dissolution process is the distribution of the DNAPL and geologic heterogeneity. Complex distributions will require careful site characterization to design an effective oxidant injection system that is capable of delivering oxidant to the entire source zone.

Oxidant recycling was determined to be an effective and practical method of reducing both the total amount of oxidant required as well as the need for effluent treatment.

Chloride monitoring during each experiment was used to estimate the amount of mass destruction and also provided some indication of the location of the DNAPL.

The in situ oxidation technology has potential to be an effective means of removing DNAPL mass at rates much more rapid than conventional pump and treat strategies. It is unlikely that in-situ oxidation could ever remove 100% of the contaminant mass at an actual field site within a realistic time frame; however, it is feasible that rapid removal of the more accessible DNAPL will result in lower plume concentrations subsequent to the chemical flush and reduce the time required for a subsequent pump and treat system. Further work characterizing the dissolution process from various DNAPL distributions during an oxidant flush is presently ongoing to adequately address both these possibilities.

Acknowledgements

The authors are grateful for the support of the University Consortium on Solvents-in-Groundwater Research Program and its sponsors, including the Boeing Company,
Ciba-Geigy Corporation, Dow Chemical Canada/USA, Eastman Kodak Co., General Electric Co., Laidlaw Environmental Systems Ltd., Mitre Corporation, PPG Industries Corporation, and United Technologies Corporation. The efforts and insight of Neil Thomson are gratefully acknowledged. Additional funding was provided by the Ontario Ministry of Environment and Energy and the Natural Sciences and Engineering Research Council of Canada.

References


Doty, C.B. and Travis, C.C., 1991. The effectiveness of groundwater pumping as a restoration technology. ORNL/PM-11866, Oak Ridge National Laboratory, Oak Ridge, TN.


