

# OXIDATION TO REMOVE TCE FROM SOIL

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## ABSTRACT

Laboratory-scale experiments were performed to study the use of oxidants as a means of removing trichloroethylene (TCE) from soil. Known amounts of TCE were spilled into glass columns of water-saturated soil and allowed to redistribute for a period of several hours. A series of experiments were performed in which aqueous solutions of a strong oxidant, and various other chemicals to modify the reactions were flushed through the column. In excess of ninety percent of the free product TCE was destroyed within the soil. Effluent aqueous phase TCE concentrations subsequent to treatment were higher than typical water quality objectives; however, they were lower than those measured for the untreated case and decreased much more rapidly because of the large reduction in free product in the soil. The potential for this oxidation process in field situations appears to be very good.

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### *Editor's Note:*

This paper presents some of the early findings related to the use of permanganate for the *in situ* chemical oxidation (ISCO) of TCE conducted under the direction of Professor G. Farquhar at the University of Waterloo. As a result of the increased interest in ISCO over the last decade, I have prepared this edited version of an unfinished draft manuscript from 1989 which reflects the scientific understanding of ISCO at the time it was written. The experimental findings discussed in this paper have never been published.

Neil R. Thomson,  
University of Waterloo,  
November 2001.

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## 1.0 INTRODUCTION

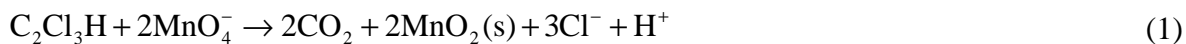
This paper investigates an *in situ* method with the potential for cleaning soil and rock contaminated with trichloroethylene (TCE) and tetrachloroethylene (PCE). These two chemicals are of special interest because: (1) they are among the most extensively used and frequently spilled chlorinated solvents in existence today; (2) they are sparingly soluble in water and yet their solubilities exceed corresponding drinking water standards by five to six orders of magnitude; (3) like many chlorinated solvents, they are more dense but less viscous than water and, in most porous media, form a nonwetting phase; and (4) the two carbon atoms which form the basic molecular structure are double bonded.

Because of these characteristics, spills of TCE and PCE into soil and rock are common and produce serious groundwater problems. They often involve substantial free product residual within the zone of saturation for which there is virtually no proven field scale technology available for satisfactory removal. Direct pumping of free product can be effective as long as water entrainment can be avoided. Eventually however the residual will become discontinuous and can not be pumped. Pumping to control migration of aqueous phase plumes is common practice but is an inefficient means for free product removal. Other methods involving surfactants, heat application, and *in situ* biodegradation are still emerging.

The fact that the carbon atoms are double bonded provides an opportunity for cleaving the bond through oxidation. If the oxidant is strong enough, there is the potential for dechlorination as well.

## 2.0 DOUBLE BOND CLEAVAGE BY POTASSIUM PERMANGANATE

Potassium permanganate ( $\text{KMnO}_4$ ) is a powerful oxidant which has been used for the treatment of several organic contaminants including phenols, formaldehyde, and various pesticides such as Paraquat (DeRenzo, 1978). While most applications of  $\text{KMnO}_4$  are directed toward aqueous phase contaminants, the potential for oxidizing free product also exists. The anticipated reaction for TCE oxidation is given by



Although the reaction will occur over a range of pH, the acidic condition created by the  $\text{H}^+$  production will improve the reaction rate.

There is always concern that a method intended to remove a solvent from soil will in fact create a worse condition either through the production of hazardous by-products or the mobilization of the free product to a more troublesome location. In this case, it is anticipated that an aqueous solution of  $\text{KMnO}_4$  would be pumped into the soil at the location of the solvent residual. The products identified in (1) would be aqueous and could then be pumped to the surface for treatment. The exception is the precipitate  $\text{MnO}_2(\text{s})$  where some will remain in the soil. Dissolved  $\text{Mn}^{+2}$  is regulated in drinking water at concentrations near 0.05 mg/L (Hammer, 1985). Thus the potential for long-term groundwater contamination by  $\text{Mn}^{+2}$  must be

considered. However, manganese is controlled mainly for aesthetic as opposed to health reasons and therefore represents a lesser hazard than TCE.

### 3.0 EXPERIMENTAL PLAN

Experiments were conducted to assess the breakdown of TCE in porous media through the application of  $\text{KMnO}_4$  in an aqueous solution. The following objectives were established:

1. Measure the extent of TCE breakdown and the production of organic intermediates, if any, as well as other products.
2. Perform carbon balances to trace TCE removal.
3. Determine suitable  $\text{KMnO}_4$  feed concentrations and reaction times.
4. Test the effectiveness of cosolvents and other chemicals to enhance the rates of TCE oxidation and by-product recovery.

### 3.1 Equipment and Analyses

The experimental setup used in this work is represented in Figure 1. Porous media was placed in gas absorption bottles with TCE added either as a pool at the bottom of the bottle, or as a residual within the soil above the bottom. In the latter case, the TCE was spread over the sand surface during packing and allowed to redistribute for approximately thirty minutes. Amounts of TCE used ranged from 10 to 25 ml. The porous media used consisted of two sands, mostly comprised of silica and referred in this paper as Sand A and Sand B with the properties listed in Table 1.

Water,  $\text{KMnO}_4$  solutions, and other chemicals were added to the contaminated sand through the glass tube. Effluent water and gas were sampled and subsequently analyzed at the locations shown in Figure 1. Feed solutions were applied to the soil to maintain a specific discharge of  $\sim 5.8 \times 10^{-3}$  cm/s.

Aqueous phase TCE concentrations were determined with a Shimadzu GC-9A gas chromatograph using a dimethyl polysiloxane column and flame ionization detection ( $\text{H}_2$  and air). The system also contained a purge and trap unit operated according to EPA Method 601 (EPA, 1984). Aqueous phase organic and inorganic carbon concentrations were measured with a Beckman Model 915A Organic Carbon Analyzer. Gaseous  $\text{CO}_2$  was determined with a Fisher Model 1200 Gas Partitioner using a Porapak column and a thermal conductivity detector.

Table 1. Soil properties.

Soil Type	Sand A	Sand B
Grain size distribution ( $d_{60}/d_{10}$ )	2.37	1.37
Porosity	0.42	0.38
pH	7.16	7.80
Composition (% w/w)		
$\text{SiO}_2$	99.3	90.2
$\text{Fe}_2\text{O}_3$	0.04	1.64
$\text{Al}_2\text{O}_3$	0.53	0.67
CaMgO	0.04	7.04
Others	0.09	0.45

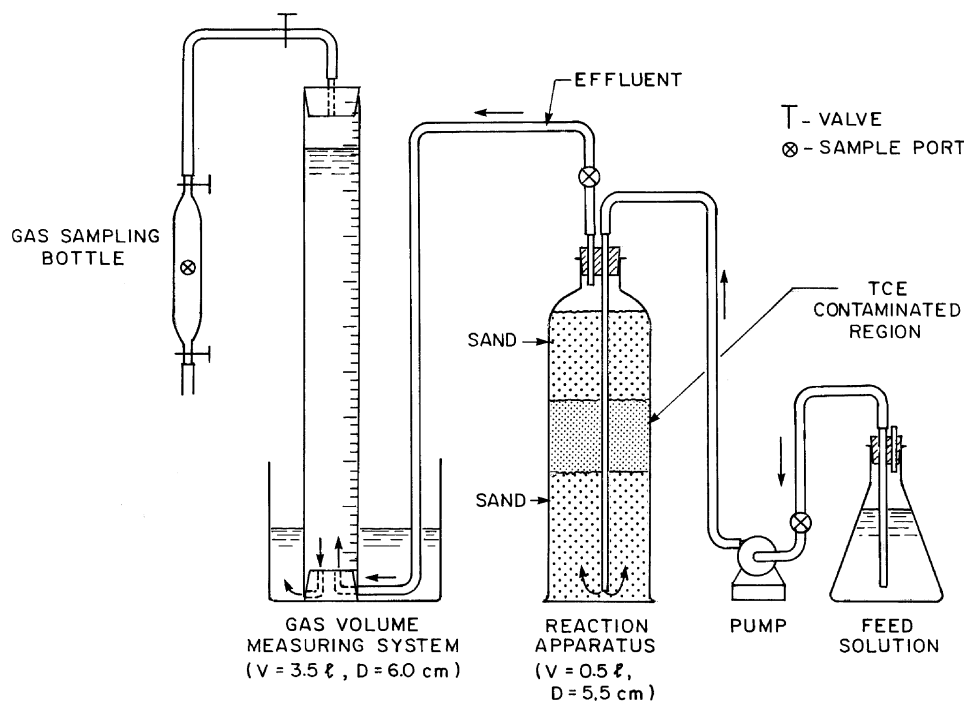


Figure 1. Experimental apparatus.

### 3.2 Experimentation

The results from ten experiments are reported upon here; however, many others were performed as the equipment and procedures were being tested. An overview of the experiments is provided in Table 2.

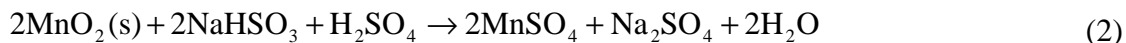
Column 3 of Table 2 indicates the amount of TCE added to the porous medium and whether it was spread on the soil to achieve a dispersed residual, or added as a pool at the bottom of the column. This was done to test the effectiveness of  $\text{KMnO}_4$  for two types of solvent configurations encountered in field situations. After TCE addition, water was flushed through the column for a short time (less than 15 minutes) prior to the application of  $\text{KMnO}_4$  at a specific discharge of  $\sim 5.8 \times 10^{-3}$  cm/s. Experiments 2 to 5 provided an opportunity to compare TCE removal efficiency with respect to the amount of free product in the soil and the residual configuration. Column 4 of Table 2 lists the concentration of  $\text{KMnO}_4$  used and the period over which it was added. Concentrations ranged from 1 to 16 g/L although the results showed that, at 16 g/L of  $\text{KMnO}_4$ , the oxidative reactions were too vigorous for the experimental set-up used. The release of  $\text{CO}_2$  caused the soil to become discontinuous and to be discharged from the column. The total mass of  $\text{KMnO}_4$  added was less than the stoichiometric amount needed to oxidize the TCE

completely as given by (1). This was done to leave some residual for subsequent dissolution enhancement experiments.

Column 5 of Table 2 shows that acetic acid (CH<sub>3</sub>COOH) was added in Experiment 8 during KMnO<sub>4</sub> addition. The purpose was to enhance oxidation of the TCE residual. A 1:4 water dilution was used.

Experiment 9 was performed with the concurrent addition of sodium hexametaphosphate (NaPO<sub>3</sub>)<sub>6</sub> to prevent the precipitation of MnO<sub>2</sub>(s) that forms during the reaction between MnO<sub>4</sub><sup>-</sup> and TCE. The intention was to allow the Mn (IV) species that are produced from this reaction to be swept out of the reaction zone for easier by-product recovery and to minimize MnO<sub>2</sub>(s) blockage of pores that might still contain unoxidized TCE.

Experiments 1, and 6 through 9 were conducted with the addition of sodium bisulphite (NaHSO<sub>3</sub>) in 10% (v/v) sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) subsequent to the KMnO<sub>4</sub> addition to solubilize MnO<sub>2</sub>(s). The intention was to reduce MnO<sub>2</sub>(s) deposits in order to enhance solubilization of residual TCE. The reaction involved was assumed to be:



All experiments were accompanied by the chemical analyses described previously and visual observations to detect MnO<sub>2</sub>(s) (brown colour) formation and movement.

Table 2. List of experiments.

ID Number	Sand	TCE volume and form <sup>1</sup>	KMnO <sub>4</sub>	CH <sub>3</sub> COOH	(NaPO <sub>3</sub> ) <sub>6</sub>	NaHSO <sub>3</sub>	Water Flush
1	A	25 mL / S	1 g/L for 4 hr + 10 g/L for 6 hr			15 g/L for 8 hrs	10 hrs + 16 hrs <sup>3</sup>
2	A	25 mL / S					44 hrs
3	A	10 mL / S					70 hrs
4	B	25 mL / P					39 hrs
5	B	10 mL / P					39 hrs
6	A	10 mL / S	7.5 g/L for 8 hrs			25 g/L for 3 hrs	42 hrs
7	B	10 mL / S	7.5 g/L for 8 hrs			25 g/L for 3 hrs	39 hrs
8	A	10 mL / S	7.5 g/L for 8 hrs	1:4 dilution <sup>2</sup>		25 g/L for 3 hrs	24 hrs
9	A	10 mL / S	7.5 g/L for 8 hrs		5 g/L <sup>2</sup>	25 g/L for 3 hrs	20 hrs
10	A	10 mL / S	16 g/L for 4 hrs				

<sup>1</sup> S: spread residual, P: pooled residual

<sup>2</sup> Added concurrent with KMnO<sub>4</sub> addition.

<sup>3</sup> The first water flush was conducted after the application of KMnO<sub>4</sub> for 10 hrs but before the 8 hr application of NaHSO<sub>3</sub>.

#### 4.0 RESULTS

It was necessary to determine the right combination of TCE mass and KMnO<sub>4</sub> application rates to avoid soil movement due to gas production, and MnO<sub>2</sub>(s) appearance in the effluent because of its interference with the analytical equipment. The values shown in Table 2 generally

achieved these objectives with the combination of higher TCE mass and low  $\text{KMnO}_4$  application rates being best.

#### 4.1 Mass Balance and TCE Conversion Calculations

The results from Experiments 1 and 2 are used to demonstrate the effectiveness of  $\text{KMnO}_4$  addition and to perform a mass balance. Experiment 2 served as a control for Experiment 1 since only water was flushed through the column. The oxidant was applied in Experiment 1 at 1 g/L for 4 hours and then, to increase the rate of oxidation, at 10 g/L for 6 hours. A total of 32 g of  $\text{KMnO}_4$  were added and  $\text{MnO}_2(\text{s})$  did not appear to be washed from the column; however, some brown colour did appear in the effluent. The total volume of  $\text{CO}_2(\text{g})$  collected was 2.29 L. Measured effluent concentrations are shown in Figure 2(a) and the cumulative mass removed is shown in Figure 2(b), while the carbon mass balance data is presented in Table 3.

Initially, the aqueous phase TCE concentrations for Experiment 2 were close to the solubility limit of 1.47 g/L (20°C) and then reduced over the 44 hour experimental time presumably due to source depletion. The effluent aqueous TCE concentration for Experiment 1 is essentially the same as the control during  $\text{KMnO}_4$  addition (the first 10 hours). Although, TCE was being destroyed during this period at the leading edge of the residual, there is still sufficient TCE at the down gradient end of the residual to produce concentrations near the solubility limit.

During the first 10 hours, the total TCE removed due to dissolution in Experiment 2 was 5.4 g (Figure 2b); however, during the same period, a total of 16.8 g of TCE was removed in Experiment 1; 5.4 g due to dissolution and 11.4 g due to oxidation by  $\text{KMnO}_4$ .

The most significant result of Experiment 1 was the amount of TCE destroyed. This is presented by the data expressed on Figure 2(a) as a total inorganic carbon to total organic carbon ratio (i.e., TIC : TOC) for the aqueous phase effluent, and the concentration of gaseous  $\text{CO}_2$  expressed as an equivalent concentration of TCE ( $\text{CO}_2^*$ ) to TCE ratio (i.e.,  $\text{CO}_2^* : \text{TCE}$ ) for the gas phase data. The TIC in the effluent resulted only from  $\text{CO}_2$  in solution from TCE oxidation according to (1), and the TOC was dissolved TCE. Accordingly, TIC:TOC ratios greater than zero signify TCE destruction. The data in Figure 2(a) and Table 3 show ratios near 0.5 during the period of  $\text{KMnO}_4$  addition at 1.0 g/L and ratios greater than 2 when the  $\text{KMnO}_4$  addition rate was increased to 10.0 g/L. Table 3 shows that the total TCE destroyed and detected as dissolved  $\text{CO}_2$  (TIC) was estimated as 9.70 g using (1).

The ratio of  $\text{CO}_2^* : \text{TCE}$  was used to determine TCE removal represented by gaseous  $\text{CO}_2$  discharged from the experimental setup. Figure 2(a) shows no gaseous  $\text{CO}_2$  production when a 1.0 g/L  $\text{KMnO}_4$  solution was applied, but vigorous production when a 10.0 g/L  $\text{KMnO}_4$  solution was used. Table 3 shows that the gaseous  $\text{CO}_2$  produced was equivalent to 3.33 g TCE destroyed, producing a total mass of TCE oxidized of 13.0 g. The initial mass of TCE added was 36.6 g (~25 mL); the total mass of  $\text{KMnO}_4$  added was 32.0 g. This would oxidize a theoretical amount of 13.3 g of TCE (c.f.  $131.4 \div 316 \times 32.0$ ) according to (1). The agreement between the calculated and theoretical TCE destruction is excellent. After 10 hours,  $\text{KMnO}_4$  addition was

stopped and TCE destruction ceased. The TIC:TOC and  $\text{CO}_2^*$ :TCE ratios shown in Figure 2(a) reduced to zero as expected.

The addition of  $\text{KMnO}_4$  produced dark brown deposits of  $\text{MnO}_2(\text{s})$  within the sand. The colouration was clearly visible through the glass reactors. The  $\text{MnO}_2(\text{s})$  deposits did not appear to increase head loss but it was felt that they might shield residual TCE from subsequent dissolution. As a result,  $\text{NaHSO}_3$  at a concentration of 5 g/L was added for a period of 8 hours in Experiment 1 after the 10 hour water flush to reduce the  $\text{MnO}_2(\text{s})$  (see equation (2)). The brownish deposits within the column were seen to disappear slowly during this time.

After 18 hours, and the completion of the  $\text{NaHSO}_3$  addition, the water flush was resumed. During the latter stages of the experiment, the aqueous TCE concentrations dropped well below Experiment 2 values, a response consistent with less free residual TCE residual remaining in the column.

The chromatographic analyses performed throughout the oxidation phase of Experiment 1 showed no evidence of any organic compounds other than TCE.

#### **4.2 Effects of TCE Residual Configuration**

Experiments 2 to 5 were performed to examine the effects of the emplaced TCE configuration (residual or pool) on the rate of TCE dissolution. Experiments 2 and 3 had the TCE spread as a distributed residual throughout the sand, while Experiments 4 and 5 received pools of TCE at the bottom of the cylinder. Experiments 3 and 5 received 10 mL (14.6 g) of TCE, and Experiments 2 and 4 received 25 mL (36.6 g) (see Table 2 for details). No chemical treatment of any sort was applied. Dissolution was the only means of TCE removal with the specific discharge rate held constant at  $\sim 5.8 \times 10^{-3}$  cm/s.

The results of these experiments are shown in Figure 3. The higher aqueous phase TCE concentrations were produced in the columns with the greater mass of TCE added. As well, concentrations were higher from the dispersed residual than from the pooled residual for equivalent initial masses of TCE added. All concentrations reduced with time as would be expected with a depleting source.

#### **4.3 Effects of Co-Solvent, Reductant, and Media on TCE Dissolution**

The previous discussion of the experimental plan (Table 2) identified experiments 6 through 9 as attempts to study the effects of cosolvents, reductant, and the media on TCE removal. In all cases, 10 mL (14.6 g) of TCE were spread as a dispersed residual throughout the soil. Experiments 6 through 9 received a solution of 7.5 g/L  $\text{KMnO}_4$  for 8 hours at the beginning of the experiment followed by 25 g/L of  $\text{NaHSO}_3$  for 3 hours to solubilize the  $\text{MnO}_2(\text{s})$  precipitate. Water was added for the balance of the experimental period. Experiment 3 served as the control experiment since it received no  $\text{KMnO}_4$  or  $\text{NaHSO}_3$ . Other conditions were applied to individual experiments. The results from some of these experiments are shown on Figures 4 and 5.

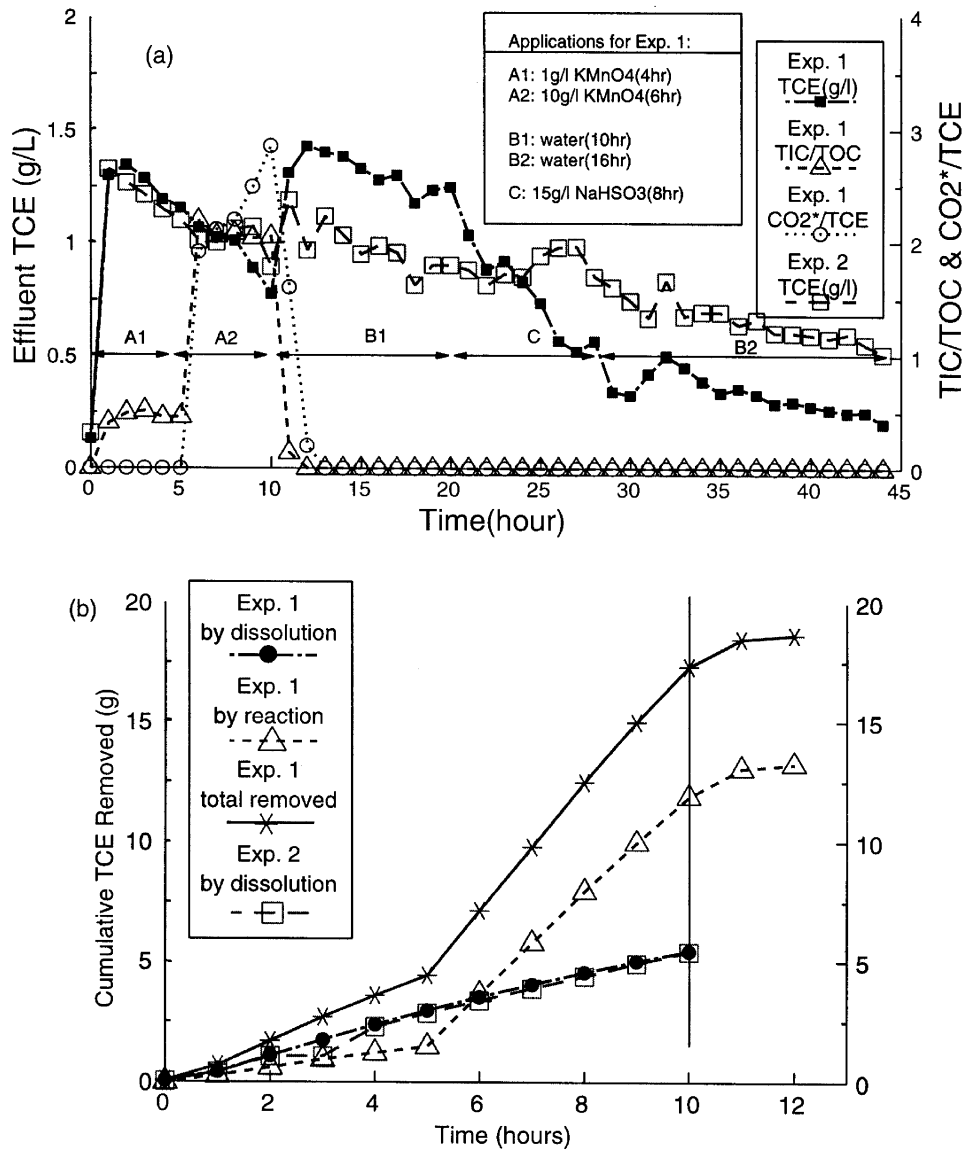


Figure 2. (a) Effluent TCE concentration, TIC to TOC ratio, and CO<sub>2</sub>\* to TCE ratio for Experiment 1, and effluent TCE concentration Experiment 2. (b) Cumulative TCE mass removed for Experiment 1 and 2.

Table 3. Carbon mass balance during Experiment 1

Time [hr]	Effluent TCE		CO <sub>2</sub>		TCE Removed as CO <sub>2</sub> (aq) [g/hr]	TCE Removed as CO <sub>2</sub> (g) [g/hr]	Total TCE Removed [g/hr]
	Concentration [g/L]	TIC/TOC Ratio	Produced [mL]	CO <sub>2</sub> */TCE Ratio			
0	0.13	0.00	0	0.00	0.00	0.00	0.00
1	1.30	0.41	0	0.00	0.20	0.00	0.20
2	1.35	0.49	0	0.00	0.44	0.00	0.44
3	1.29	0.51	0	0.00	0.49	0.00	0.49
4	1.19	0.46	0	0.00	0.45	0.00	0.45
5	1.16	0.46	0	0.00	0.40	0.00	0.40
6	1.07	2.20	350	1.92	1.07	0.25	1.32
7	1.03	2.06	370	2.12	1.66	0.52	2.18
8	1.01	2.08	380	2.21	1.56	0.55	2.11
9	0.89	2.04	380	2.50	1.45	0.55	2.00
10	0.78	2.05	380	2.86	1.26	0.55	1.82
11	1.31	0.14	380	1.61	0.66	0.55	1.21
12	1.43	0.00	50	0.81	0.07	0.31	0.38
13	1.40	0.00	0	0	0.00	0.04	0.04
Totals					9.70 g	3.33 g	13.0 g

Note: CO<sub>2</sub>\* is the concentration of gaseous CO<sub>2</sub> expressed as an equivalent concentration of TCE.

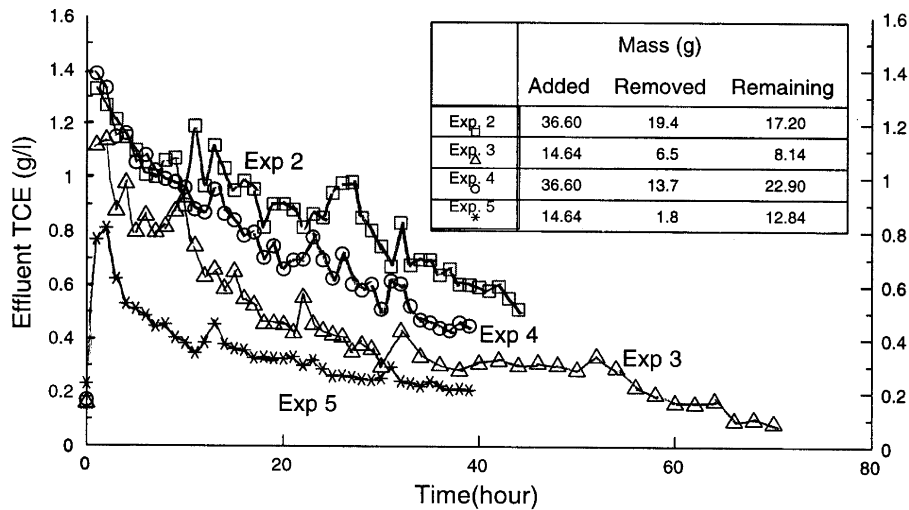


Figure 3. The impact of the initial configuration the pure phase TCE on the effluent concentration profile.

#### 4.3.1 Acetic Acid

Acetic acid diluted 1:4 with water was added to Experiment 8 for 8 hours concurrent with KMnO<sub>4</sub> addition. The intention was to enhance oxidation of the residual TCE. Figure 4 presents data on CO<sub>2</sub> production for Experiment 8 with acetic acid and Experiment 6 without it. The CO<sub>2</sub>

released is proportional to TCE oxidized and it can be seen that more  $\text{CO}_2$  appeared in response to acetic acid addition signifying more TCE destruction.

The effluent aqueous phase TCE concentrations for Experiment 8 showed that during the period of  $\text{KMnO}_4$  addition, TCE was observed to be above the detection limit of  $4 \mu\text{g/L}$ . Concentrations increased during  $\text{NaHSO}_3$  addition (8 hrs to 11 hrs) in which  $\text{MnO}_2(\text{s})$  was solubilized. This was thought to be caused by the exposure of TCE shielded by  $\text{MnO}_2(\text{s})$ . Following this, TCE concentrations were higher in Experiment 6 than in 8. This is consistent with more TCE oxidation in the presence of acetic acid and thus, less TCE residual to contribute to subsequent TCE dissolution.

#### 4.3.2 Polyphosphate

Polyphosphate in the form of  $(\text{NaPO}_3)_6$  at concentration of  $5.0 \text{ g/L}$  was added to Experiment 9 during  $\text{KMnO}_4$  addition to prevent  $\text{MnO}_2(\text{s})$  precipitation and to enhance TCE oxidation. Comparing Experiments 6 and 9 in Figure 4 shows greater  $\text{CO}_2$  production and therefore greater TCE oxidation in the presence of  $(\text{NaPO}_3)_6$  and slightly more than with acetic acid addition. Effluent aqueous phase TCE concentrations in the period after  $\text{NaHSO}_3$  addition were lower in Experiment 9 as compared to Experiment 6 (Figure 5). This is once again consistent with a smaller TCE free produce residual.

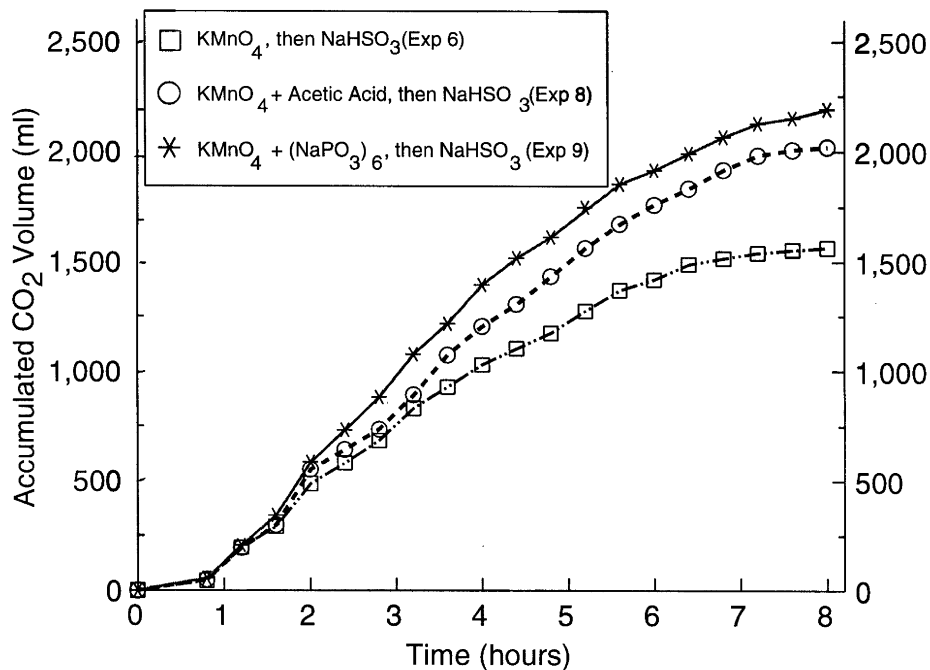


Figure 4. Cumulative volume of  $\text{CO}_2(\text{g})$  collected during Experiments 6, 8, and 9.

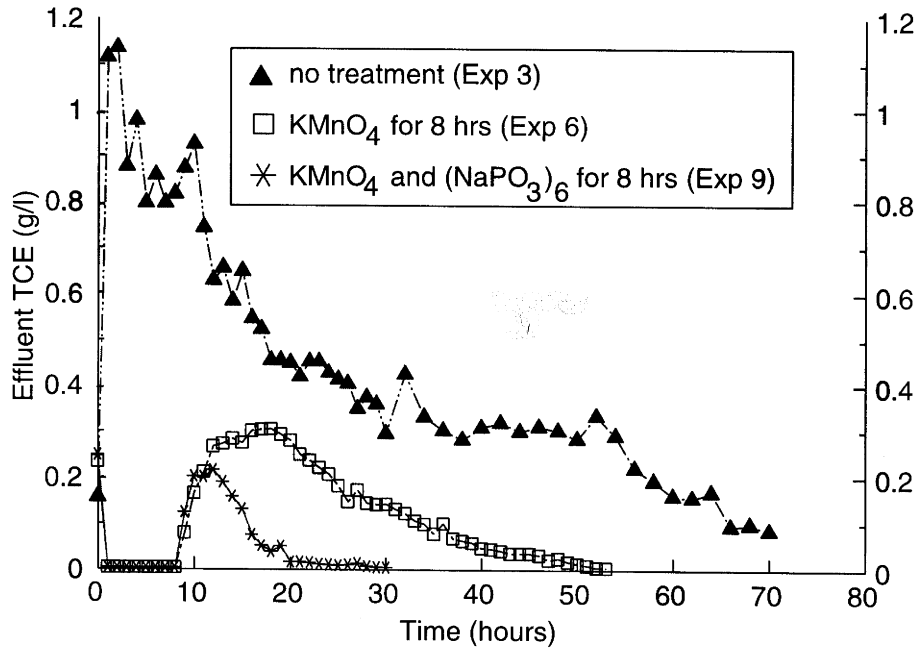


Figure 5. Effluent TCE concentration for Experiments 3, 6, and 9.

#### 4.3.3 Carbonate Soils

Experiment 7 was performed with Sand B which was partially comprised of 7.04% w/w CaMgO. This experiment produced more CO<sub>2</sub> than any other; however, this increased production was not thought to be due solely to TCE oxidation. Equation (1) shows that the oxidation of TCE yields protons which will no doubt cause dissolution of carbonate from the soil and produce CO<sub>2</sub>. Measurements to quantify this production were not made.

The reaction in this experiment was particularly vigorous and some pure phase TCE was lost in the effluent. This produced elevated aqueous phase TCE concentrations during the oxidation phase and reduced the free TCE residual for subsequent dissolution.

#### 4.4 Increased Oxidant Application

Experiment 10 was performed at a KMnO<sub>4</sub> concentration of 16 g/L, over twice as much as Experiments 6 through 9. The results indicated that, as expected, greater oxidant application resulted in more rapid CO<sub>2</sub> evolution and thus faster TCE destruction. Some loss of free product TCE from the reactor resulted from the vigorous CO<sub>2</sub> release. For this reason no subsequent dissolution data were collected.

#### 4.5 Mass Balances

The prior discussion regarding Table 3 showed that for Experiment 1 the actual TCE removal of 13.0 g calculated from dissolved and gaseous CO<sub>2</sub> measurements agreed well with the stoichiometric amount of 13.3 g. This agreement was consistent with calculations made for other experiments. The information presented in Table 4 uses only the stoichiometric amounts because of difficulties with CO<sub>2</sub> measurements in Experiments 7 and 8.

The data in Table 4 show that, of the 14.6 g of TCE added to Experiments 6 through 9, a total of 12.5 g should have been oxidized, leaving 2.16 g as a residual in the soil. The last column in Table 4 shows the amount of TCE dissolved from the columns down to an effluent concentration of 5.0 mg/L after the application of oxidant. These values were calculated from the TCE effluent data after the 8 hours of chemical addition. The 5 mg/L value was used for convenience since the effluent profiles appeared to level off at approximately this value; however, it was acknowledged that further dissolution would occur. The value of 5 mg/L is well above the drinking water standard of 0.005 mg/L.

In the case of Experiment 6, the 3.01 g of dissolved TCE exceeds the estimated 2.16 g value. The oxidation in this case was obviously not as complete as it was with other experiments. The factors which might have caused this were not evident. The amounts dissolved from Experiments 7, 8 and 9 were 0.29, 0.95 and 0.75 g respectively.

Table 4. TCE mass balances for Experiments 6 to 9.

Exp #	Conditions	Initial TCE Mass [g]	Theoretical TCE Oxidized [g]	Theoretical TCE Remaining [g]	TCE mass removed by dissolution after chemical addition <sup>1</sup>
6	KMnO <sub>4</sub>	14.64	12.48	2.16	3.01
7	KMnO <sub>4</sub> /Sand B	14.64	12.48	2.16	0.24
8	KMnO <sub>4</sub> /CH <sub>3</sub> COOH	14.64	12.48	2.16	0.95
9	KMnO <sub>4</sub> /(NaPO <sub>3</sub> ) <sub>6</sub>	14.64	12.48	2.16	0.75

Note. 1. Estimated from effluent data to a cut-off level of 5 mg/L.

#### 5.0 DISCUSSION

The results from these experiments have shown that the addition of KMnO<sub>4</sub> to soil contaminated with TCE has a strong potential as a means of *in situ* remediation. The delivery of the oxidant to a zone of contamination is facilitated because of its aqueous form. It is likely that spilled chlorinated solvents would follow paths of greater permeability and would remain as residuals in areas of greater porosity. It is likely that applied oxidant solutions would follow similar paths. A similar case can be made for spills in fractured rock.

The extent of oxidation and the TCE remaining after treatment will influence subsequent groundwater quality. The amount of KMnO<sub>4</sub> applied in these experiments was limited so that a TCE residual would remain after treatment. This produced aqueous phase TCE concentrations in the effluent from the columns well in excess of the drinking water standard. It is expected that increased oxidant addition would reduce the TCE residual significantly beyond the levels shown

here. Experiments are in progress to study this. However, unacceptable aqueous phase concentrations might still exist for a period of time. None the less, it is reasonable to conclude that a procedure which may be able to destroy nearly all the TCE residual in soil and possibly fractured rock provides a significant improvement over present technologies.

The products of the oxidation of TCE by  $\text{KMnO}_4$  require further comment. The reaction produces  $\text{MnO}_2$  as a precipitate and concern existed whether or not clogging of the porous media would result. A deep brown colour, typical of  $\text{MnO}_2$  production, developed in the zone of residual saturation during oxidant application. However, the precipitate remained soft and mobile and in some cases, appeared in the effluent. No significant increase in head loss could be detected across those columns on which pressure measurements were made. There is reason, therefore, to believe the clogging in field applications will not be significant.

Manganese in solution from the treatment zone was also of concern. Measurements of Mn in the effluent from several columns receiving  $\text{KMnO}_4$  ranged from 0.171 mg/L to 0.279 mg/L. The drinking water standard for Mn is 0.05 mg/L and thus the samples measured exceeded this standard. However, this standard is based on aesthetics instead of toxicity, and impact of the Mn production is likely to be small, given the extent of the TCE destruction achieved.

Additional preliminary experiments showed that the procedure also works well for tetrachloroethylene (PCE).

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Note: Here is the reference if you would like to cite this work [Editor].

Gonullu, T., and G. Farquhar, 1989. Oxidation to remove TCE from soil, Department of Civil Engineering, University of Waterloo, unpublished manuscript, Available at: <http://www.civil.uwaterloo.ca/groundwater/oxlitrev.html>.