Chemistry Letters Vol.34, No.11 (2005)

TCE Removal from Porous Media Using an Ozone-saturated Solvent

Martha Elena Alcántara-Garduño,* Tetsuji Okuda,† Wataru Nishijima,† and Mitsumasa Okada
Department of Material Science and Chemical System Engineering, Hiroshima University, Higashi-Hiroshima 739-8527
†*Environmental Research Management Center, Hiroshima University, 1-5-3 Kagamiyama, Higashi-Hiroshima 739-8513*

(Received July 7, 2005; CL-050882)

A new technique for rapid and complete removal of trichloroethylene (TCE) from porous media was developed on the basis of chemical decomposition by ozone added to flushing solvent. The rate of TCE removal by the combination process of ozone with acetic acid flushing was from 1.2 to 2.5 times as high as the flushing process without ozone due to the chemical decomposition of TCE not only dissolved in the solution but also adsorbed on the porous media.

Chlorinated volatile organic compounds (CVOCs) such as TCE (trichloroethylene) and PCE (tetrachloroethylene) are the most common groundwater contaminants. The contamination of groundwater by CVOCs is typically caused by the accumulation of DNAPLs (dense non-aqueous phase liquids) in subsurface soils. Several methods and technologies have been proposed to remove DNAPLs from soil. The flushing method, which uses co-solvents and/or surfactants to increase the mass transfer of DNAPLs into aqueous phase is in practical use.[1–3] However, it still takes long time to remove DNAPLs and complete removal is also difficult.[4,5] We propose to combine chemical oxidation with flushing method to shorten the remediation time and to achieve the complete removal of DNAPLs.

Ozone is a powerful oxidizing agent and is known to oxidize chlorinated organic contaminants like TCE and PCE.[6–8] If ozone is used as an oxidant, the solvent chosen for the combination system should be required to dissolve ozone in high concentration without consumption of ozone by the solvent itself and high extraction capacity for DNAPLs. Acetic acid is one of suitable solvents for the proposed combination system because of nonreactivity with ozone and a high capacity to dissolve ozone.[9] Ozone and acetic acid would be favorable for on-site remediation because residual ozone could be naturally decomposed and remained acetic acid could be easily biodegraded by indigenous bacteria after the flushing.[10,11]

The objective of this study is to investigate the enhancement of DNAPLs removal by the combination of ozone and acetic acid. TCE was chosen as a typical DNAPLs contaminant.

Organic-free sand was prepared as a porous media; all the organics were removed to evaluate specifically the effect of acetic acid and ozone during TCE decomposition. The sand (320 ± 2 g) was sieved through a 500 µm sieve, washed with water, and baked at 650 °C for 6 h to eliminate soil organic matters. The sand was packed in a glass column (i.d. = 3.1 cm, L = 35 cm, Pyrex glass with Teflon cock). Ultrapure water was filled into the column and then TCE was injected using a microsyringe into the sand layer 1 cm below the top of the sand bed to create a high TCE saturation area. The column was sealed with a Teflon cap to prevent TCE loss by evaporation. The total mass of injected TCE was around 64 mg.

Acetic acid solutions with and without ozone were prepared as flushing media. Ozone gas was generated from dried oxygen (99.99%) using an ozone generator (Fuji Electric, POX-1). Ozone gas was supplied continuously into the acetic acid solutions at 20.8 mg O_3/min to make the solutions saturated with ozone. All the experiments were performed at room temperature (20 ± 2 °C).

Each acetic acid solution with or without ozone was pumped into the column in a downflow mode at 1.65 ± 0.20 mL/min. The pore volume, the volume of pores in the soil column, was used to show experimental period in this study, and one pore volume represented 75 ± 2 mL. The effluent from the column was periodically collected to determine ozone, TCE, chloride ion (Cl^-), and acetic acid concentrations. The amount of TCE decomposed was calculated from the concentration of Cl^-.

TCE concentration was determined according to the headspace method[12] using a GC-ECD (Shimadzu, GC-14B). The concentration of Cl^- was determined by titration with 0.005 M AgCl using a chloride electrode.[13] The iodometric method[14] was used to determine ozone concentration in the feed gas, in the initial acetic acid solution, and in the column effluent. Acetic acid concentration was determined by titration with 1.0 M NaOH.

Dissolved ozone concentrations in 0% (water), 10, 25, 50, and 100% acetic acid solutions were 9.3, 18.9, 21.2, 42.3, and 154.2 mg/L, respectively. Figure 1 shows the ratio of the amount of TCE removed to the amount of initial TCE ($[TCE]_r/[TCE]_0$) by flushing with the 10% acetic acid solution with and without ozone. TCE removal was significantly enhanced by the addition of ozone to the acetic acid solution. Removal rate with ozone (mg TCE/min) which was calculated by linear fitting after one pore volume until leveling off was found to be 2.5 times higher than that without ozone in the 10% acetic acid solution.

In Figure 1 the $[TCE]_r/[TCE]_0$ ratio exceeds 1; this was produced by experimental analysis error. The difference between the total initial TCE and TCE total recovered was 5%.

Figure 2 shows the eluted and decomposed fractions of TCE during flushing with the 10% acetic acid solution with ozone as

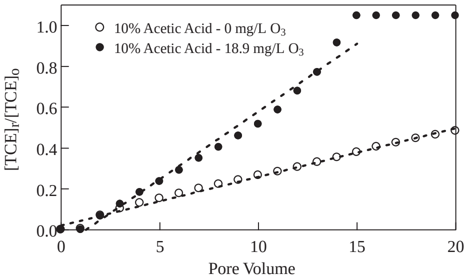

Figure 1. The ratio of the amount of TCE removed to the amount of initial TCE in 10% acetic acid solution with and without ozone. $[TCE]_r$: TCE removed, $[TCE]_0$: initial TCE.

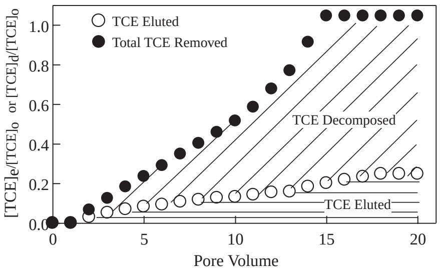

Figure 2. Eluted and decomposed fractions of TCE during flushing by 10% acetic acid solution with ozone. TCE Eluted: $[\mathrm{TCE}]_e/[\mathrm{TCE}]_0$; TCE decomposed: $[\mathrm{TCE}]_d/[\mathrm{TCE}]_0$; where $[\mathrm{TCE}]_e$: TCE eluted, $[\mathrm{TCE}]_d$: [TCE] decomposed; $[\mathrm{TCE}]_0$: initial TCE.

shown in Figure 1. The fraction of normalized TCE eluted, $[\mathrm{TCE}]_e/[\mathrm{TCE}]_0$, was calculated using the TCE in the effluent. On the other hand, the fraction of normalized TCE decomposed, $[\mathrm{TCE}]_d/[\mathrm{TCE}]_0$, was calculated from the amount of Cl^- ions in the effluent (3 mol Cl^- ions = 1 mol TCE). The removal of TCE from porous media by flushing with ozone was mainly achieved by the decomposition of TCE. At 15 pore volumes, the percent decomposition of TCE to the total removed TCE was 76%.

The rates of TCE removal by 0, 10, 25, 50, and 100% acetic acid solutions with and without ozone are summarized in Figure 3. The combination with ozone enhanced removal rates at all acetic acid solutions. Effects of ozone on TCE removal rate were more significant in the lower concentrations of acetic acid. It would be due to that TCE was mainly removed by chemical decomposition on porous media by ozone, because the TCE elution was small in the lower acetic acid solution. The percent decomposition to the total TCE removal in 15 pore volumes was high at 10 and 25% acetic acid solutions, and it was around 80% of total TCE removal. On the other hand, the percent decompositions were around 25 and 20% in 50 and 100% acetic acid solutions, respectively.

However, the TCE removal rate increased significantly between 25 and 50% for both with and without ozone, as shown in Figure 3. The role of decomposition did not increase (Figure 3) with the increase in ozone concentration. It indicates that the improvement of TCE removal from 25 to 50% was due to the increase in elution capacity, i.e. solubility for TCE. The elution capacity of the solvent with higher acetic acid concentration was very high and the maximum removal was achieved within 2 or 3 pore volume of solvent applied as shown in Figure 4 (50% acetic acid).

It was reported that complete removal of the NAPLs in soils by alcohol flushing was not possible due to the complex entrapment architecture of NAPLs such as residual, ganglia, blobs, and pools.[5,15] Figure 4 shows the comparison between with and without ozone. The complete removal could not be achieved without ozone even after 15 pore volumes. It was possible by the combination with ozone even at 4 pore volumes. It suggests that ozone in acetic acid solutions could decompose TCE not only dissolved in the solution but also TCE adsorbed strongly onto the porous media by direct decomposition of TCE.

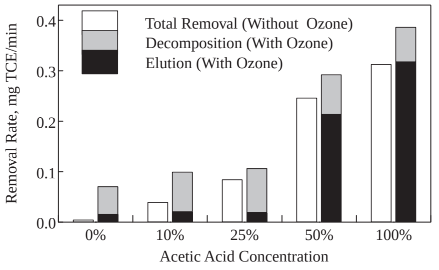

Figure 3. Removal rate for TCE at several acetic acid solutions with and without ozone.

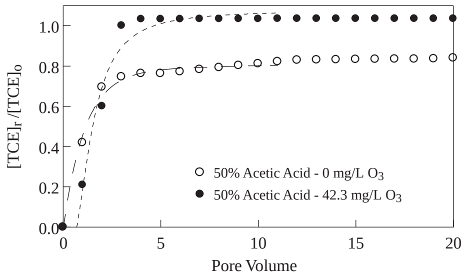

Figure 4. Total TCE removal from the porous media by 50% acetic acid solution with and without ozone.

The TCE removal from porous media was enhanced by the combination of ozone with flushing process with acetic acid solution. The enhancement of TCE removal by the combination process was from 1.2 to 2.5 times in comparison with the flushing process without ozone, and was caused by the chemical decomposition of TCE not only dissolved in the solution but also adsorbed on the porous media. The complete TCE removal from the porous media was achieved in the combination process.

References

1 Y. Ouyang, J. S. Cho, and R. Mansell, *Water Res.*, **36**, 33 (2000).
2 Y. Yortsos and A. K. Stubos, *J. Colloid Interface Sci.*, **6**, 208 (2001).
3 M. Delshad, G. A. Pope, and K. A Sepehrnoori, *J. Contam. Hydrol.*, **23**, 303 (1996).
4 C. N. Mulligan, R. N. Yong, and B. F. Gibbs, *Eng. Geol.*, **60**, 371 (2001).
5 K. Soga, J. W. E. Page, and T. H. Illangasekare, *J. Hazard. Mater.*, **110**, 13 (2004).
6 H. Choi, H. N. Lim, J. Kim, T. M. Hwang, and J. K. Kang, *J. Contam. Hydrol.*, **57**, 81 (2002).
7 W. T. Shin, X. Garanzuay, S. Yiacoumi, C. Tsouris, B. Gu, and G. Mahinthakumar, *J. Contam. Hydrol.*, **72**, 227 (2004).
8 S. J. Masten, *Ozone: Sci. Eng.*, **2**, 287 (1991).
9 Y. Nakano, K. Okawa, W. Nishijima, and M. Okada, *Water Res.*, **37**, 2595 (2003).
10 TOXNET system (http://toxnet.nlm.nih.gov). Acetic Acid.
11 P. Lundegard, R. Sweeney, and G. Ririe, *Environ. Forensics*, **1**, 3 (2000).
12 "Japan Industrial Standard" (1985), K0125.
13 A. L. Teel, C. R. Warberg, D. A. Atkinson, and R. J. Watts, *Water Res.*, **35**, 977 (2001).
14 "Standard Methods for the Examination of Water and Wastewater," 20th ed., APHA, AWWA, WEF (1998).
15 C. Hofstee, C. Gutiérrez Ziegler, O. Trötschler, and J. Braun, *J. Contam. Hydrol.*, **67**, 61 (2003).