

# In-situ Chemical Oxidation of Residual TCE by Permanganate in Epikarst

Nihat Hakan Akyol, and Irfan Yolcubal

**Abstract**—In-situ chemical oxidation (ISCO) has been widely used for source zone remediation of Dense Nonaqueous Phase Liquids (DNAPLs) in subsurface environments. DNAPL source zones for karst aquifers are generally located in epikarst where the DNAPL mass is trapped either in karst soil or at the regolith contact with carbonate bedrock. This study aims to investigate the performance of oxidation of residual trichloroethylene found in such environments by potassium permanganate. Batch and flow cell experiments were conducted to determine the kinetics and the mass removal rate of TCE. pH change, Cl<sup>-</sup> production, TCE and MnO<sub>4</sub><sup>-</sup> destruction were monitored routinely during experiments. Non-reactive tracer tests were also conducted prior and after the oxidation process to determine the influence of oxidation on flow conditions. The results show that oxidant consumption rate of the calcareous epikarst soil was significant and the oxidant demand was determined to be 20 g KMnO<sub>4</sub>/kg soil. Oxidation rate of residual TCE ( $1.26 \times 10^{-3} \text{ s}^{-1}$ ) was faster than the oxidant consumption rate of the soil ( $2.54 - 2.92 \times 10^{-4} \text{ s}^{-1}$ ) at only high oxidant concentrations (> 40 mM KMnO<sub>4</sub>). Half life of TCE oxidation ranged from 7.9 to 10.7 min. Although highly significant fraction of residual TCE mass in the system was destroyed by permanganate oxidation, TCE concentration in the effluent remained above its MCL. Flow interruption tests indicate that efficiency of ISCO was limited by the rate of TCE dissolution and the rate-limited desorption of TCE. The residence time and the initial concentration of the oxidant in the source zone also controlled the efficiency of ISCO in epikarst.

**Keywords**—Epikarst, in-situ chemical oxidation, permanganate.

## I. INTRODUCTION

KARST aquifers possess major water resources with great potential, but due to their unique structure they are vulnerable to the contamination by dense non aqueous phase liquids (DNAPL). DNAPL sources zones are generally located in epikarst where the DNAPL mass is trapped either in karst soil or at the regolith contact with carbonate bedrock (Fig. 1). In-situ chemical oxidation by permanganate has been studied as an innovative technology for DNAPL remediation. Permanganate is a strong oxidant and capable of oxidizing a variety of organic compounds such as PAH, alkenes and BTEX over a wide pH range of 3 to 12. This remediation technology was also evaluated in detail by laboratory studies. Some of the researches demonstrated that TCE could be mineralized totally by KMnO<sub>4</sub> based on 100 % recovery of Cl

from TCE [11; 10; 3].

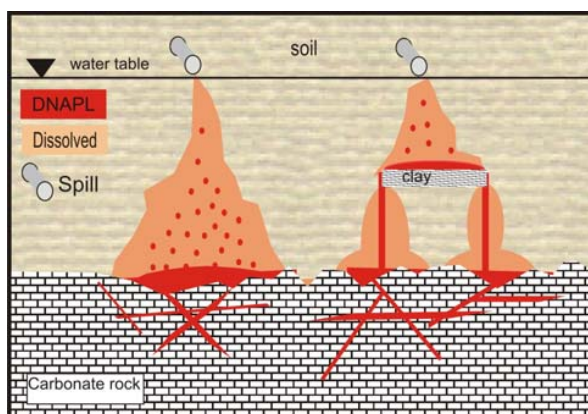


Fig. 1 Distribution of DNAPL accumulation in karst environment

The oxidation rate of TCE was mainly influenced by the oxidant concentration that is independent of both pH and ionic strength [13; 4]. Some studies revealed that TCE can be degraded rapidly by permanganate in various soils [2; 1; 7; 9; 8; 4]. For instance, [2] reported that TCE was completely destroyed in clay-sandy soil. [6] indicated that permanganate oxidation is effective in removing residual DNAPL in porous media. [7; 5] revealed that residual TCE was completely oxidized by KMnO<sub>4</sub> flushing. Although the performance of ISCO technology is well known in porous media, limited study exists in the literature regarding the efficiency of ISCO in bedrock aquifers. A work by [12] was the first application showing that the chlorinated solvent source areas in karst limestone aquifer can be effectively destroyed by hydrogen peroxide. The aim of this study was to investigate the performance of ISCO by potassium permanganate on destroying residual TCE mass located on the DNAPL source areas of karst aquifers (Fig. 1). Secondary objective was to find the optimal conditions for greater performance of ISCO in such environments. These objectives were achieved by performing some batch and flow-cell experiments.

## II. MATERIALS AND METHODS

### A. Materials

Carbonate soil and the travertine bedrock were collected from Antalya Travertine Plateau which is a well-characterized

Authors are with Kocaeli University, Department of Geological Engineering, Umuttepe Campus 41380-TR Kocaeli, Turkey (e-mails: hakan.akyol@kocaeli.edu.tr, yolcubal@kocaeli.edu.tr).

karst aquifer system. The soil material consists of 69 % sand, 27 % silt, and 4 % clay fractions. The soil is alkaline (pH=8.37) and contains high carbonate content and intermediate organic matter. The travertine is also highly permeable and contains secondary porosity.

### B. Methods

#### 1. Batch Experiments

Batch experiments were performed to determine the rate of oxidant consumption and the oxidation kinetics of residual TCE. Oxidant consumption experiments were performed by adding a known amount of soil and permanganate solutions at varying concentrations to the 50 ml of PE vials. The vials were put on shaker and sampled periodically for measuring permanganate concentration. TCE oxidation experiments were performed in headspace vials using the same procedure described. Samples were analyzed for measuring the rates of TCE and  $MnO_4$  destruction and Cl production. Some experiments were duplicated to check the reproducibility of the results.

#### 2. Flow-cell Experiments

The degradation of residual TCE located in the carbonate soil and at the regolith contact with travertine bedrock was examined by a set of flow-cell experiments. The oxidation of residual TCE in the carbonate soil was investigated by the 1-D column experiments. The column is glass made and has a dimension of 5 cm diameter and 15 cm in length (Fig. 2). The oxidation of residual TCE pooling at the regolith contact with travertine was investigated by a custom made stainless steel 2-D flow cell (12cm (H) x 27 cm (L) x 5 cm (W) (Fig. 3). Front side of the 2-D flow cell was covered by the Plexiglas material for visual examination of the oxidation reaction and the possible mobilization of TCE mass. A known amount of TCE mass was injected into the soil and the pools located above the travertine. After providing sufficient time for the dispersion of TCE, flow cell was flushed by potassium permanganate either as a pulse or continuous input. Non-reactive tracer tests were also conducted prior and after the oxidation process to determine the influence of oxidation on flow conditions. During experiments, effluent samples were collected periodically and analyzed for Cl, pH,  $MnO_4$  and TCE. Breakthrough curves obtained from the flow-cell experiments were analyzed using methods of moments for determining the amount of TCE mass destroyed.



Fig. 2 1-D flow-cell experimental setup



Fig. 3 2-D flow-cell experimental setup

### III. RESULTS

Oxidant consumption rate of the calcareous soil is significant. Oxidant demand was determined to be 20 g  $KMnO_4/kg$  soil. The oxidant consumption rate of the soil is between  $2.54 - 2.92 \times 10^{-4} s^{-1}$  depending on the initial oxidant concentrations (40-120 mM  $KMnO_4$ ). The half life of permanganate ranged from 30.5 to 47.8 min. The oxidation of the residual TCE in the calcareous soil is determined to be first order and the reaction rate is around  $1.26 \times 10^{-3} s^{-1}$ . Oxidation rate of residual TCE was faster than the oxidant consumption rate of the soil at only high oxidant concentrations ( $> 40$  mM  $KMnO_4$ ). The half life of TCE ranged from 7.9 to 10.7 min. Flow-cell experiments showed that TCE mass was removed completely from the systems. During the oxidation of TCE, chloride production and permanganate consumption were rapid. pH also dropped from 7.2 to 6.2 indicating that soil matrix buffered the acidity produced (Fig. 4). During the first flow interruption test, effluent TCE and Cl concentrations showed a rapid rise and then drop, indicating the remaining of DNAPL in the system. Following the second flow interruption, although Cl concentration of the effluent showed no detectable change, TCE concentration of the effluent showed similar response to the results of the first flow interruption test. At each flow

interruption test, an oxidant mass which is ten-fold greater than the initial TCE mass was injected in the source zone and resided in the system for four days before the initiation of the continuous water flush. The results of both flow interruption tests clearly indicate that TCE dissolution and desorption processes control the amount of TCE mass destroyed. Bromide tracer tests indicated that  $MnO_2$  precipitation occurred during TCE oxidation had no effect in flow conditions.

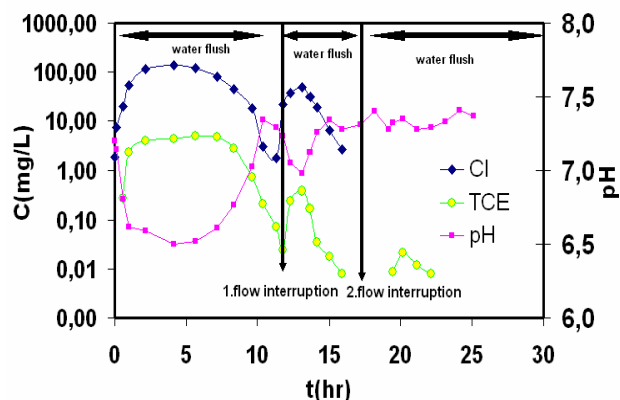


Fig. 4 TCE, pH and Cl changes during the oxidation of residual TCE by  $KMnO_4$  in 2-D flow cell experiment

#### IV. CONCLUSION

The results showed that although residual TCE mass injected into the epikarst soil and the pools on the travertine bedrock was recovered completely in all flow cell experiments, the effluent TCE concentration remained above its MCL ( $5 \mu\text{g/L}$ ) at the end of each initial oxidant injection. TCE degradation by permanganate was limited by the rate of TCE dissolution and the rate limited desorption of TCE as indicated by the flow interruption tests. Residence time of the oxidant in the source zone as well as the initial concentration of oxidant also controlled the performance of ISCO. In subsurface environments especially with high oxidant demand, it is critical to optimize initial oxidant concentration as well as residence time of oxidant in the source zone for greater destruction of DNAPL mass by permanganate per oxidant injection.

#### ACKNOWLEDGMENT

This research was supported by a grant 104Y063 provided by The Scientific and Technological Research Council of Turkey (TUBITAK).

#### REFERENCES

- [1] S.-R. Cline, O. R. West, Siegrist, S. R, W. L. Holden., 1997. Performance of in situ chemical oxidation field demonstration at DOS sites. *Proceedings of In Situ Remediation of the Geoenvironment Conference. Minneapolis, MI, USA.*
- [2] D. D. Gates, R.L Siegrist, S. R. Cline., 1995. "Chemical oxidation of contaminants in clay or sandy soil. *J. Environ. Eng.* 121, pp. 582-588.

- [3] K. C. Huang, G. E. Hoag, P. Chheda, B. A. Woody, G. M. Dobbs., 1999. Kinetic study of oxidation of trichloroethylene by potassium permanganate. *Environ. Eng. Sci.* 1116, 265-274.
- [4] K. C. Huang, G. E. Hoag, P. Chheda, B. A. Woody, G. M. Dobbs., 2000. A pilot scale study of oxidation of trichloroethylene by sodium permanganate. *Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds.* Monterey, CA, USA, pp. 145-152.
- [5] K. C. Huang, G. E. Hoag, P. Chheda, B. A. Woody, G. M. Dobbs., 2002. Chemical oxidation of trichloroethylene with potassium permanganate in a porous medium. *Advances in Environmental Research.* 7, 217-229.
- [6] X. D. Li, F. W. Schwartz, 2004. DNAPL mass transfer and permeability reduction during in situ chemical oxidation with permanganate. *Geophysical Research Letters.*,31.
- [7] M. Schnar, C. Truax, G. Farquhar, E. Hood, T. Gonulla, B. Stickney., 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and tetrachloroethylene DNAPLs in porous media. *J. Contam. Hydrol.* 29, 205-224.
- [8] R. L. Siegrist, K. S. Lowe, L. C. Murdoch, T. L. Case, D. A. Pickering., 1999. In situ oxidation by fracture emplaced reactive solids. *J. Environ. Eng.* 125, 429-440.
- [9] P. G. Tratnyek, T. M. Johnson, S. D. Warner., H. S. Clarke, J. A. Baker., 1998. In situ treatment of organics by sequential reduction and oxidation. . *Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds.* CI-5, pp. 371-376.
- [10] C. T. Truax., 1993. Investigation of the in-situ potassium permanganate oxidation of residual DNAPLs located below the groundwater table. *M.S. Thesis. University of Waterloo, Ontario, Canada.*
- [11] P. A. Vella, B. Veronda., 1992. Oxidation of trichloroethylene: a comparison of potassium permanganate and Fenton's reagent. *Chemical Oxidation: Technology for the Nineties in Proceedings of the Third International Symposium.* PA, USA, pp. 75-82.
- [12] R. F. Weston., 2000. Summary report for the In situ chemical oxidation remediation pilot study of the bedrock aquifer at the Southeastern (SE) disposal area. Letterkenny Army Depot, Chambersburg, PA.
- [13] Y. E. Yan, F. W. Schwartz, 1998. Oxidative degradation of chlorinated ethylenes by potassium permanganate. *Environ. Sci. Tcehnol.* 34, 2535-2541.