

## ***In Situ* Chemical Oxidation of a Perchloroethene Source Area Using Potassium Permanganate**

Mark J. Salvetti, P.E.<sup>1</sup>, Barbara R. Nwokike<sup>2</sup>, Willard A. Murray, Ph.D., P.;E.<sup>3</sup>

**Abstract:** A solution of potassium permanganate (KMnO<sub>4</sub>) was flushed through a PCE source area at the Naval Training Center, Orlando, Florida. The KMnO<sub>4</sub> oxidized residual PCE and dramatically reduced PCE concentrations in groundwater. The pilot study was conducted at Operable Unit 4 at the Naval Training Center (NTC), Orlando, Florida. Operable Unit 4 consists of the former base dry cleaning facility. Groundwater PCE concentrations within the source area were measured at concentrations as high as 28,000 µg/L. The entire source area is estimated to be approximately 80 feet wide, 200 feet long, and 30 feet deep. Approximately two-thirds of the source area is located beneath the former laundry building. Three groundwater extraction/injection well pairs were used to create a 65-foot-long recirculation cell. Groundwater was extracted, dosed with KMnO<sub>4</sub>, retained in mixing tanks to allow the PCE in the extracted groundwater to oxidize, and then injected, while meeting strict Florida UIC regulations. A series of monitoring points were used to measure contaminant concentrations, KMnO<sub>4</sub> consumption, and changes in groundwater inorganic concentrations.

KMnO<sub>4</sub> has been shown to be an effective oxidant for PCE and TCE (Schnarr et al, 1997; Hood et al, 1998; West et al, 1997). In-situ oxidation is accomplished when an aqueous solution of KMnO<sub>4</sub> is injected or flushed through the source area. Byproducts of oxidation include carboxylic acids (CA), manganese dioxide solids (MnO<sub>2</sub>), and chloride when oxidizing chlorinated compounds. The basic stoichiometry for the oxidation of PCE is as follows:



Oxidation of chlorinated compounds to CA's occurs at pH's above 3. Carbon dioxide is formed instead at lower pH's (Huang et al, 2000). This reaction does not generate excess heat or vapor, and any excess KMnO<sub>4</sub> is stable, allowing it to be flushed through a source area by pumping to maximize contact with the contaminant zone.

Three injection wells were installed approximately 10 feet apart, oriented perpendicular to the direction of the natural groundwater flow. Each injection well was 4-inches inside diameter (ID) and a total depth of approximately 35 feet below land surface (bls). The wells were screened from 5 to 30 feet bls (across the entire treatment zone). Three extraction wells were also installed approximately 65 feet to the west (hydraulically downgradient) and directly opposite the injection wells. Each extraction well was 4-inches ID and screened from 10 to 30 feet bls.

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<sup>1</sup>Associate Engineer, Harding ESE, 107 Audubon Road, Wakefield, MA, 01906, USA, Ph (781)213-5652, Fax (781)246-5060, [mjsalvetti@mactec.com](mailto:mjsalvetti@mactec.com), (corresponding author).

<sup>2</sup>Engineering Manager, US Navy Southern Division, Naval Facilities Engineering Command, 2155 Eagle Drive, North Charleston, SC, 29406, USA, Ph (843)820-5566, Fax (843)820-5563, [brnwokike@efdsouth.navy.mil](mailto:brnwokike@efdsouth.navy.mil).

<sup>3</sup>Principal Consultant, Harding ESE, 107 Audubon Road, Wakefield, MA, 01906, USA, Ph (781)213-5654, Fax (781)246-5060, [wamurray@mactec.com](mailto:wamurray@mactec.com).

Eleven shallow and four deep wells were available across the treatment cell to monitor the progress of the injected  $\text{KMnO}_4$  front and to monitor groundwater VOC concentrations during the pilot study. The shallow wells were installed to a depth of approximately 18 feet bls. The deep wells were installed to a depth of approximately 35 feet bls. A 2-foot thick dense, cemented sand layer was located from approximately 18 to 20 feet bls. VOCs were detected above and below the cemented sand layer.

Florida strictly regulates underground injection to groundwater. Exceedance of primary drinking water standards in the injected  $\text{KMnO}_4$ -dosed groundwater was not permitted, even when conducting groundwater remediation. This constraint played a role in the design of the aboveground treatment system as well as the necessary  $\text{KMnO}_4$  dose.

The treatment system was rented from Carus Chemical (the sole domestic producer of  $\text{KMnO}_4$ ) and returned at the conclusion of the pilot study. The  $\text{KMnO}_4$  pilot study system consisted of two 1,600 gallon polyethylene tanks piped in series (Tank 1 and Tank 2), a  $\text{KMnO}_4$  feed system, extraction and injection pumps, cartridge filters used to filter the  $\text{KMnO}_4$  solution prior to injection, and a control system. Extracted groundwater was fed to Tank 1. Groundwater from Tank 1 was pumped to the  $\text{KMnO}_4$  feed system and then recycled back to the tank. Treated groundwater then flowed from Tank 1 and into the bottom of Tank 2 by gravity. The  $\text{KMnO}_4$  solution overflowed from near the top of Tank 2 through a standpipe (to maximize residence time) to an injection pump. The solution was filtered to remove  $\text{MnO}_2$  solids and then piped to the injection wells. The two-tank arrangement was used to provide adequate residence time to allow the VOCs in the extracted water to oxidize to below primary standards prior to injection. The treatment system extracted groundwater at a total flow of 3 to 4 gallons per minute (gpm) for the duration of the pilot study.

The  $\text{KMnO}_4$  powder was purchased from Carus Chemical in 330 pound drums. The  $\text{KMnO}_4$  was fed using two drum inverters, each emptying a 330-lb drum of  $\text{KMnO}_4$  into the hopper of a screw feeder. The screw feeders were fitted with level sensors; when one hopper was empty, the control system switched to the second feeder. Once the second feeder emptied, the system was shutdown unless a new drum of  $\text{KMnO}_4$  had been fitted to the first feeder. In this fashion, 660 lbs. of  $\text{KMnO}_4$  could be loaded at one time, allowing over three days of unattended operation before additional  $\text{KMnO}_4$  needed to be loaded.

Benchscale studies were used to develop rate constants for the oxidation of PCE by  $\text{KMnO}_4$ . The oxidation is a pseudo-first order reaction when an excess of  $\text{KMnO}_4$  is present. Standard kinetics equations were used to predict the ex-situ oxidation rate of PCE in the extracted groundwater. At an extracted groundwater flow of 4 gpm, a 4 gram/liter dose of  $\text{KMnO}_4$  was predicted to oxidize PCE from 5,000  $\mu\text{g/L}$  to less than 3  $\mu\text{g/L}$  in 8 hours. A field GC was used during startup to confirm this performance. The entire pilot study was conducted injecting  $\text{KMnO}_4$  at a concentration of 4 grams/liter and a flow of 3 to 4 gpm.

Groundwater samples were collected from within the treatment cell during system operation to evaluate performance. Sodium thiosulfate was added to each water sample

to consume any excess  $\text{KMnO}_4$ , and prevent further VOC oxidation within the sample vials after collection.

The progression of the injected  $\text{KMnO}_4$  across the treatment cell was best observed by measuring groundwater conductivity and color. Groundwater conductivity increases due to the increase in dissolved solids introduced by the  $\text{KMnO}_4$  solution. However, conductivity alone is not an adequate measure of permanganate strength, as the potassium in solution is enough to raise the conductivity, even if all of the permanganate ion is consumed. Color was also used as an indicator for the presence of permanganate.

The pilot study operated for approximately 5 months. VOC concentrations in the shallow zone decreased dramatically in most of the monitoring wells during the period of operation. PCE concentrations were reduced from concentrations as high as 24,300  $\mu\text{g/L}$  to concentrations near or below MCLs.

In the deep zone, the decreases in VOC concentrations during the pilot test were more modest. This was likely due to preferential flow of the injected  $\text{KMnO}_4$  into the shallow zone. Changes in groundwater color and conductivity were small, indicating the  $\text{KMnO}_4$  was not well distributed into this zone.

A full-scale conceptual design has been prepared. The full-scale system will consist of three extraction/injection cells operating at a total flow of approximately 15 gpm and a  $\text{KMnO}_4$  dose of just 1 gram/liter. Dedicated extraction and injection wells will be used to better focus the flushing of  $\text{KMnO}_4$  through the shallow and deep zones. Filtration of  $\text{MnO}_2$  from the dosed groundwater must also be improved using rotary drum, stacked discs, or membrane filters. The cartridge filters used in the pilot study required too frequent replacement to be practical for full-scale use.

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